



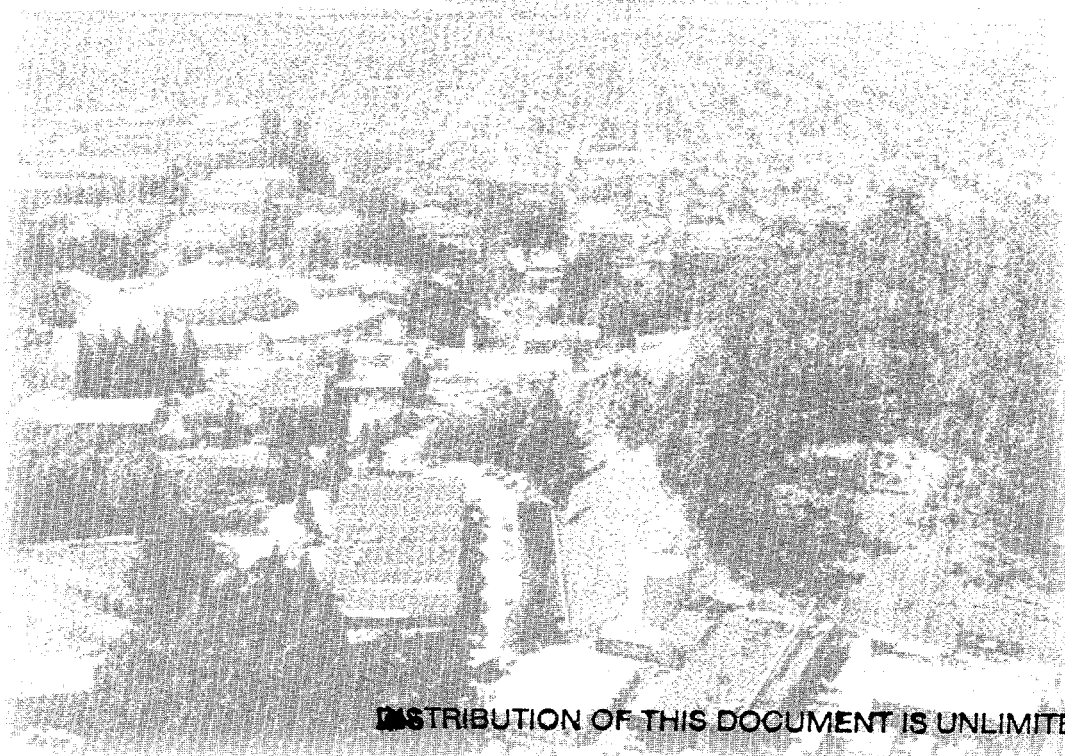
ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Fabrication and Electronic Transport Studies of Single Nanocrystal Systems

David L. Klein
Materials Sciences Division

May 1997
Ph.D. Thesis

RECEIVED
JUL 22 1997
OSTI



DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

STER

MASTER

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory
is an equal opportunity employer.

**Fabrication and Electronic Transport Studies
of Single Nanocrystal Systems**

David Louis Klein
Ph.D. Thesis

Department of Physics
University of California, Berkeley

and

Materials Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

May 1997

MASTER

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, the Office of Naval Research, Order No. N00014-95-F-0099, and the Packard Foundation.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED



DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Fabrication and Electronic Transport Studies
of Single Nanocrystal Systems

by

David Louis Klein

B. S. (University of Arizona, Tucson) 1992
M. A. (University of California, Berkeley) 1994

A dissertation submitted in partial satisfaction of the
requirements for the degree of

Doctor of Philosophy

in

Physics

in the

GRADUATE DIVISION

of the

UNIVERSITY OF CALIFORNIA, BERKELEY

Committee in charge:
Professor Paul L. McEuen, Chair
Professor Daniel Rokhsar
Professor A. Paul Alivisatos

Spring 1997

Fabrication and Electronic Transport Studies of Single Nanocrystal Systems

Copyright © 1997

by

David Louis Klein

The Government reserves for itself and others acting on its behalf a royalty free, nonexclusive, irrevocable, world-wide license for governmental purposes to publish, distribute, translate, duplicate, exhibit, and perform any such data copyrighted by the contractor.

The U.S. Department of Energy has the right to use this document for any purpose whatsoever including the right to reproduce all or any part thereof

Abstract

Fabrication and Electronic Transport Studies of Single Nanocrystal Systems

by

David Louis Klein

Doctor of Philosophy in Physics

University of California, Berkeley

Professor Paul L. McEuen, Chair

Semiconductor and metallic nanocrystals exhibit interesting electronic transport behavior as a result of electrostatic and quantum mechanical confinement effects. These effects can be studied to learn about the nature of electronic states in these systems.

This thesis describes several techniques for the electronic study of nanocrystals. The primary focus is the development of novel methods to attach leads to prefabricated nanocrystals. This is because, while nanocrystals can be readily synthesized from a variety of materials with excellent size control, means to make electrical contact to these nanocrystals are limited.

The first approach that will be described uses scanning probe microscopy to first image and then electrically probe surfaces. It is found that electronic investigations of nanocrystals by this technique are complicated by tip-sample interactions and environmental factors such as solvation and capillary forces.

Next, an atomic force microscope technique for the catalytic patterning of the surface of a self assembled monolayer is described. In principle, this nano-fabrication technique can be used to create electronic devices which are based upon complex arrangements of nanocrystals.

Finally, the fabrication and electrical characterization of a nanocrystal-based single electron transistor is presented. This device is fabricated using a hybrid scheme which combines electron beam lithography and wet chemistry to bind single nanocrystals in

tunneling contact between closely spaced metallic leads. In these devices, both Au and CdSe nanocrystals show Coulomb blockade effects with characteristic energies of several tens of meV. Additional structure is seen the transport behavior of CdSe nanocrystals as a result of its electronic structure.

A handwritten signature in black ink, appearing to read 'L. P. ME' followed by a long horizontal stroke.

To my grandparents:

Michael and Isabel Klein

I love and miss you both.

Table of Contents

Chapter 1: Introduction and Background	1
1.1 Introduction	1
1.2 Towards Zero-Dimensions	2
1.3 A Sense of Perspective	3
1.3.1 Temperature	4
1.3.2 The Charging Energy of a Nanocrystal	4
1.3.3 Quantum Levels in a Semiconductor Nanocrystal	5
1.3.4 Quantum Levels in a Metallic Nanocrystal	7
1.3.5 Putting it Together	8
1.4 A Reminder of Our Goal	8
 Chapter 2: The Basics of Transport Through a Dot	 12
2.1 Overview	12
2.2 Transport Through a Dot	12
2.2.1 Modeling the Dot	12
2.2.2 Tunnel Junctions	14
2.2.3 A Well Defined Dot	15
2.3 Coulomb Blockade - Classical Dots	17
2.3.1 General Features	17
2.3.2 Coulomb Oscillations	18
2.3.3 I- V_{sd} Curves - a Toy Model	21
2.3.4 I- V_{sd} Curves - A More Rigorous Model	27
2.4 Coulomb Blockade - Quantum Dots	29
2.4.1 General Features	29
2.4.2 $V_{sd} \approx 0$ - Equilibrium Transport	31

2.4.3 $V_{sd} \neq 0$ -Non-Equilibrium Transport	32
2.5 Summary	34
Chapter 3: History and the Work of Others	35
3.1 Overview	35
3.2 Early Work	36
3.3 Top-Down Devices	37
3.3.1 Introduction and some Theory	37
3.3.2 Metallic Dots	38
3.3.3 Semiconductor Dots	40
3.4 Bottom-Up Devices	46
3.4.1 Introduction	46
3.4.2 SPM Techniques	47
3.4.3 Other Techniques	47
3.5 Where We Stand	48
Chapter 4: The Nature of CdSe Nanocrystals	49
4.1 Introduction	49
4.2 Bulk CdSe	49
4.2.1 Physical Properties	49
4.2.2 Electronic Structure	49
4.3 CdSe Nanocrystals	52
4.3.1 Fabrication	52
4.3.2 Electronic Structure - Theory	53
4.3.3 Electronic and Physical Structure - Experiment	57

Chapter 5: Scanning Probe Studies of Surfaces	59
5.1 Motivation	59
5.2 STM Imaging of Nanocrystals	59
5.3 AFM Imaging of Nanocrystals	60
5.4 Conducting AFM and Solvation Phenomena	67
5.4.1 The Plan of Attack	67
5.4.2 Force vs. Distance Measurements on HOPG in Hexadecane	68
5.4.3 Conductance vs. Distance Measurements on HOPG in Hexadecane	70
5.4.4 Summary of Solvation Measurements on HOPG	71
5.4.5 Relevance of Solvation Forces to Spectroscopy Experiments	73
5.5 Summary and Consequences	76
 Chapter 6: Catalytic AFM	 77
6.1 Background	77
6.2 Introduction	79
6.3 Formation and Catalysis of the SAM	81
6.4 Derivatization of the SAM	82
6.5 Imaging and Results	84
6.6 Conclusions	86
 Chapter 7: Fabrication of Nanocrystal Devices	 89
7.1 Introduction	89
7.2 Optical Lithography	91
7.2.1 Overview	91
7.2.2 Step 1 - Oxide Growth and Patterning	91
7.2.3 Step 2 - Definition of Gate Bonding Pads	93
7.2.4 Step 3 - Definition of Source and Drain Leads	93

7.3 Electron Beam Lithography	94
7.4 Attachment of Nanocrystals	100
7.5 The Completed Device	101
Chapter 8: Measurements of Nanocrystal Devices	102
8.1 Overview	102
8.2 Au Nanoparticles	102
8.2.1 Overview	102
8.2.2 A 5.8 nm Au Nanoparticle Device	102
8.2.3 A 2 nm Au Nanoparticle Device	104
8.2.4 Discussion	107
8.3 CdSe Nanocrystals - Two Terminal Measurements	108
8.3.1 Introduction	108
8.3.2 Overview	108
8.3.3 Temperature Dependence	113
8.3.4 Random Telegraph Noise	113
8.3.5 The Death of a Device	115
8.3.6 Summary	117
8.4 CdSe Nanocrystals - Three Terminal Measurements	117
8.4.1 Introduction	117
8.4.2 Depletion of a Nanocrystal	121
8.4.3 LO Phonon Emission	123
8.4.4 Transport Via Excited States	125
8.4.5 On the Number of Nanocrystals in Our Device	125
8.5 Discussion	128

Chapter 9: Summary and Future Directions	131
9.1 Summary	131
9.2 Future Directions	132
 Appendix A: Coulomb Blockade Program	 134
A.1 Introduction	134
A.2 The Model	134
A.3 The Program	136
 Appendix B: Scanning Probe Microscopy	 137
B.1 Introduction	137
B.2 Scanning Tunneling Microscopy	137
B.3 Atomic Force Microscopy	139
B.4 Tip Convolution Effects in AFM	144
B.4.1 A Model	144
B.4.2 Experiments	147
 Appendix C: Chemistry Related to Nanocrystals	 149
C.1 Nanocrystal Synthesis	149
C.2 Attachment of Nanocrystals to Au	150
 Appendix D: Chemistry Related to Catalysis Experiments	 151
D.1 Formation of an Alkylbromide SAM	151
D.2 Displacement of Bromide With an Azide	152
E.3 Derivatization of Amino groups with Aldehyde-Modified Beads	153
E.4 Derivatization of Amino Groups with ATTO-TAG	153

Appendix E: Details of Device Fabrication	154
E.1 Introduction	154
E.2 Fabrication Overview	154
E.3 The Wafer	154
E.4 Formation of a Thick Wet Oxide	154
E.5 Definition of Gate Regions	155
E.6 Make Gate Contacts	156
E.7 Form Source and Drain Leads	156
E.8 Form Source and Drain Bonding Pads	157
E.9 Apply e-Beam Resist	157
E.10 e-Beam Lithography and Evaporation	157
E.11 Possible Improvements	158
 Appendix F: Summary of All Devices	 159
 Appendix H: Working Device Factoids	 166
 References	 170

List of Symbols

1-D	One dimensional
2-D	Two dimensional
2DEG	Two dimensional electron gas
α_{nl}	Product of r and k that correspond to a zero in the spherical Bessel function
AFM	Atomic force microscopy
β	$(kT)^{-1}$
C	Capacitance
C_d	Drain-dot capacitance
C_g	Gate-dot capacitance
C_s	Source-dot capacitance
C_{tot}	Total capacitance of a dot
CLSM	Confocal laser scanning microscope
CVD	Chemical vapor deposition
d	Distance between a nanocrystal and a lead
ΔE	Typical quantum energy level spacing
ΔE_N	Energy difference between the N^{th} and $(N-1)^{th}$ energy levels
ΔN	Number of excess electrons on a dot
$\Delta\mu$	Energetic difference between two leads
e	Charge of the electron (1.602×10^{-19} C)
ϵ	Dielectric constant
E	Energy
E_c	Charging energy of a dot
E_f	Fermi energy
E_i^N	Energy of the i^{th} state of a N electron dot
e-beam	Electron beam

F	Total angular momentum within a nanocrystal; $F = J + L$
ϕ	Azmuthal angle within a sphere
Φ	Electrostatic potential of the dot
Φ_0	Offset electrostatic potential of a dot
φ_{klm_l}	Envelope wavefunction in a spherical dot
FESEM	Field emission scanning electron microscope
G	Conductance
Γ point	$k=0$, high symmetry point in a crystal
Γ_{int}	Typical internal decay rate of excited states in a dot
$\bar{\Gamma}$	Tunneling rate going with a drop in electrochemical potential
$\bar{\Gamma}$	Tunneling rate going against a drop in electrochemical potential
$\bar{\Gamma}_s$	Dot-source tunneling rate
$\bar{\Gamma}_d$	Drain-dot tunneling rate
Γ_{tot}	Total decay rate of a state ($\Gamma_{\text{int}} + \langle \Gamma \rangle$)
$\langle \Gamma \rangle$	Typical tunneling rate through a quantum state
h	Plank's constant (4.14×10^{-15} eV-s)
$\hbar$	$h/2\pi$ (6.658×10^{-16} eV-s)
HOPG	Highly oriented pyrolytic graphite
I	Current
I_d	Dot-drain current
I_s	Source-dot current
IETS	Inelastic tunneling spectroscopy
IPA	Isopropyl alcohol
j_ℓ	Spherical Bessel function
J	L+S Total angular momentum of a bulk state
k	Wavevector of a state
k_f	Fermi wavevector

k	Boltzmann's constant ($86 \mu\text{eV/K}$)
κ	Decay length for tunneling
ℓ	Angular momentum quantum number of a state
L	Angular momentum quantum number of an envelope function
LED	Light emitting diode
m^*	Effective mass
m_e	Mass of the electron ($9.1 \times 10^{-28} \text{ gm}$)
m_ℓ	Projection of the angular momentum along a arbitrary axis
MBE	Molecular beam epitaxy
MIBK	Methyl isobutyl ketone
MIM	Metal-insulator-metal tunnel junction
μ	Electrochemical potential
μ_d	Electrochemical potential of the drain lead
μ_{dot}	Electrochemical potential of the dot
μ_N	$U(N) - U(N-1)$; the "electrochemical potential" of a N electron dot
μ_0	Offset electrochemical potential of the dot
μ_s	Electrochemical potential of the source lead
n	Primary quantum number of a state
N	Total number of conduction electrons in a dot
N_0	Number of conduction electrons in a dot when V_{sd} and V_g are equal to zero
OMCTS	Oxamethyltetrasiloxane
p	$\ell=1$ quantum state
P	$L=1$ quantum state
PMMA	Polymethylmethacrylate
P(MMAMAA)	Poly(methylmethacrylate-co-methacrylic acid)
PMT	Photo multiplier tube
θ	Polar angle within a sphere

Q	Charge on a dot
r	Radius of a nanocrystal
R	Resistance
R_{eff}	Effective resistance
R_s	Source-dot resistance
R_d	Dot-drain resistance
ρ_i	Probability that a dot has i electrons
RBS	Rutherford back scattering
RF	Radio frequency
s	$\ell=0$ quantum state
S	$L=0$ quantum state
S	Spin quantum number
sp^3	A hybridized molecular orbital
SAM	Self assembled monolayer
SEM	Scanning electron microscope
SET	Single electron transistor
SFA	Surface force apparatus
SIS	Superconductor-insulator-superconductor tunnel junction
SPM	Scanning probe microscopy
STM	Scanning tunneling microscopy
T	Temperature
TEM	Transmission electron microscope
TOPO	tri-n-octyl phosphine oxide
U	Energy of a dot
V	Volume of a dot
V	Voltage
V_g	Gate voltage

V_{sd}	Source-drain voltage
x	Radial ordinate within a sphere
XPS	X-ray photoelectron spectroscopy
$Y_{\ell}^{m_{\ell}}$	Spherical harmonic

Acknowledgments

The work described in this thesis would not have been possible without the help of numerous folks. My years at Berkeley have been fun, rewarding, and interesting; I value them highly.

I would first like to thank my advisor, Paul McEuen, whose guidance, assistance, and patience was invaluable to my research. Most advisors would have probably slapped me around a fair bit; he didn't and I'm thankful.

Then there's the McEugonots, quite an interesting bunch... Its been fun to watch the group grow from the nucleus of Keith, Geoff, Leo and Dave (#1) to the empire of Cobby (a.k.a. Dave #3), Kent, Mark, Mike, Raghu, Hongkun, Noah, and Andrew. The group is still young, but has had a truly impressive track record. I look forward to hearing about its future exploits.

I'd also like to thank the chemical fiends over in the Alivisatos lab. Without the help of Paul Alivisatos, Janet Bowen-Katari, Richard Roth, Kim Hamad, and all the others I would have never had the high quality nanocrystals to play with.

Next I'd like to thank the gaggle who took the time to help proof read parts of this monstrosity. Without the help of Paul McEuen, David Cobden, Hongkun Park, and Jen Glass you'd probably throw this book down before you got to the fun bits. I'd also like to thank Jorg Janssen, David Dixon, Uri Banin, and Paul Alivisatos for allowing me to present some of their measurements and calculations.

Then there are the third floor folks. Whose lunchtime banter and evening bloodlettings at Duke and Warcraft must have cost me at least a year or two; But they were a good year or two...

The various members of the Haller group have fed me *quite well* and let me use lots of their stuff, and I'm appreciative of both.

Outside the lab I'd like to thank my parents and family who have supported my rather long academic habit and given me the encouragement that I have needed to make it this far. I'd also like to thank Zoe for dealing with the time that this has kept us apart; too long.

And lets not forget all the friends I've made during my time here. I'd like to thank Kent, Dane, and the Marks for spending so much time with me. I'd also like to thank the assorted freaks from the Berkeley Hang Gliding Club. Flying has been one of the greatest discoveries of my time here, and this club has truly enhanced my life.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098; by the Office of Naval Research, Order No. N00014-95-F-0099, and by the Packard Foundation.

Chapter 1

Introduction and Background

1.1 INTRODUCTION

In the dissertation that follows, the reader can find a description of the efforts of others and myself to measure the electrical transport through nanometer sized chemically derived crystals (nanocrystals). Working with such particles gives us an opportunity to probe the electrical properties of materials as they transcend an individual atom's discrete energy levels and approach the continuum nature of bulk crystals.

After a brief introduction, I begin (chapter 2) with a quantitative discussion of the transport phenomena that one expects to see in nanocrystals. This discussion will address the effects of single electron charging, quantum confinement, and collective excitations on the electrical transport through nanocrystals. As many of these effects have been previously studied in micron and nanometer scale devices, I then follow (chapter 3) by discussing past experimental studies on mesoscopic systems. Then, in chapter 4, I review some of the characteristics of CdSe nanocrystals, the material we chose to study.

Following these reviews, I discuss the various avenues that we have explored in our attempts to electrically probe nanocrystals. This represents the keystone of this thesis. For, while well characterized nanocrystals of varying chemical nature can be readily fabricated, the problem of how to "wire up" a nanocrystal is not yet adequately solved. Traversing the path from macroscopic wires down to nanometer scale leads is a non-trivial problem and is the focus of many research efforts.

The first path I discuss (chapter 5) employs a scanning tunneling microscope (STM) and a conducting atomic force microscope (AFM) in an attempt to probe the electrical response of nanocrystals bound atop a conducting substrate.

Chapter 6 then describes the use of a platinum coated AFM cantilever to catalyze chemical reactions. This allows us to selectively modify the exposed end groups of linker

molecules and to pattern the functionality of a surface. As a result, we are able to control where subsequently introduced molecules or nanocrystals will bind. This then provides a path to create complex arrangements of nanocrystals for electrical studies.

Finally, in chapters 7 and 8, I will present the most successful path that we explored. Here, we fabricate leads by electron beam lithography and then deposit semiconductor (CdSe) or metallic (Au) nanocrystals. On some of these samples, a single nanocrystal bridges the gap between the leads and thus is accessible for electrical transport measurements. These transport measurements reveal electrostatic and quantum confinement effects such as Coulomb blockade.

1.2 TOWARDS ZERO-DIMENSIONS

In a typical treatment of transport through a solid, we assume that all properties of interest are intrinsic; a 2 cm length of wire has the same character as a 1 cm segment. The phonon energies, density of states, effective mass, resistivity, melting temperature, etc., are intrinsic properties that depend only upon the material's composition, not its size. This assumption is one of the first made in a solid state course [see for example Ashcroft and Mermin 1976, or Kittel 1996] and the basis of design for most commercial electronic devices. However, we know that this approximation must break down when we cut the wire small enough; ultimately we would end up with an atom. In this limit, the allowed energy levels are discrete and are spaced on the order of several eV.

This thesis will discuss objects whose size is between that of the discrete atom and that of bulk crystals. Such a small object (in our case 1 - 10 nm in diameter) is in general referred to as a *dot*. Here, many bulk crystal properties (such as crystal structure, band structure, phonons, etc.) remain. In addition we find atomic like structure reflecting the finite size of the system.

One type of confinement effect is electrostatic in nature. An isolated particle with a very small total capacitance, C_{tot} , will have a well defined number of electrons if it meets the criterion:

$$\frac{e^2}{C_{tot}} \gg kT. \quad (1-1)$$

In other words, if the electrostatic charging energy* associated with adding or removing a single quantum of charge is greater than kT , the number of charges resident on the object is well defined. As a result, until we provide enough energy to access other charge states, electron transport through the island is not possible. This effect is known as Coulomb blockade and was first reported by Gorter [1951]. The theory was first developed by Kulik and Shekhter [1975]. A detailed discussion of Coulomb blockade mediated transport is given in chapter 2.

Also of interest are the effects of quantum confinement energy levels. These *particle-in-a-box* energy levels are the result of localizing the electron's wavefunction to a small region in space. Depending on the material makeup of the nanocrystal, the spacing of these levels can vary from being degenerate to rivaling the particle's charging energy. If the quantum level spacing at the Fermi level, ΔE , is smaller than the levels' linewidth (set by kT or its natural linewidth[†], $\hbar\Gamma_{int}$) we will call the dot a *classical dot*. If they have non-trivial spacing ($\Delta E \gg kT$, $\hbar\Gamma_{int}$) we will call the dot a *quantum dot*.

1.3 A SENSE OF PERSPECTIVE

Before we start, it is interesting to look at how the different energy scales come into play as we approach zero dimensionality. In particular, we consider the Coulomb and quantum energies as they compare to the intrinsic energies (or at least approximately intrinsic until we must abandon the last remnants of bulk properties) of the system such as the band gap, phonon energies, work function, and temperature.

*Here expressed in terms of the total capacitance of the object.

†Here defined in terms of the intradot decay rate of the state, Γ_{int} .

1.3.1 Temperature

Let us first discuss the magnitude of thermal broadening, kT . At room temperature (~ 300 K), kT is ~ 25 meV. This means that the electrons in our system will occupy a ~ 25 meV distribution about the ground state configuration. This thereby limits our ability to resolve lower energy features. If we would like greater energy resolution, we need to use cryogenics. A liquid nitrogen bath cools our sample to 77 K ($kT = 6.6$ meV), while liquid helium gets us to 4.2 K ($kT = 0.36$ meV). We can use a flowing helium, variable temperature cryostat to fill in the full range of temperatures in-between. To get colder than 4.2 K, we must switch to pumped He systems. A pumped ^4He cryostat will get us down to ~ 1 K ($kT \sim 90$ μeV) and a pumped ^3He system will allow for measurements down to ~ 0.4 K ($kT \sim 30$ μeV). To get even lower in temperature, we can use a continuous flow dilution refrigerator and cool our sample to 10 mK ($kT \sim 1$ μeV)*. We can use the above numbers as a guideline for the temperature to which we must cool our sample to obtain a desired energy resolution. We note, however, that the effective broadening is often several times kT (see chapter 2) and the above numbers simply give a magnitude of the energy uncertainty.

1.3.2 The Charging Energy of a Nanocrystal

To get a sense of scale for the charging energy of a nanocrystal, we consider an isolated conducting sphere of radius r . The self capacitance of such an object is given as its radius. Hence, we can write

$$E_c = \frac{e^2}{r} = \frac{1.4}{r} \text{ eV} \cdot \text{nm}. \quad (1-2)$$

It is interesting to note that this is simply twice the ground state binding energy of a Bohr atom whose radius is that of the nanocrystal. In general, transport measurements require that we attach leads to the nanocrystal under measurement. Equation 1-2 does not account for the capacitive coupling of these leads to our dot. A simple model for calculating this

*Although, due to the lack of electron-phonon coupling at these temperatures, our electron temperature will typically bottom out at ~ 100 mK ($kT \sim 10$ μeV).

coupling comes by considering the potential distribution about a point charge placed above an infinite, grounded plane. This plane then represents a lead. Our dot is taken as a roughly spherical equal potential shell of radius $\sim r$ about the charge. We can then estimate the dot-lead capacitance* as:

$$C \cong \epsilon r \left(1 + \frac{r}{2d} \right). \quad (1-3)$$

Here, d is the distance between the edge of the sphere and the plane and ϵ has been introduced to allow for a dielectric media about the dot. The total capacitance of the dot will be approximately twice the capacitance between the dot and either lead. We thus roughly estimate the charging energy of a dot placed between two leads as:

$$E_c = \frac{e^2}{C} = \frac{0.7}{\epsilon r} \left(1 + \frac{r}{2d} \right)^{-1} eV \cdot nm. \quad (1-4)$$

For a $r = 3$ nm spherical dot bound 1 nm away from two leads in a $\epsilon = 2$ environment, we obtain a charging energy of ~ 50 meV. As we will see in later chapters, the above parameters are appropriate for the nanocrystal system that we study.

1.3.3 Quantum Levels in a Semiconductor Nanocrystal.

For a nanocrystal made from a semiconductor material (such as CdSe), transport often occurs near a band edge. We can estimate the quantum energy level spacing here by modeling the system as a spherical box of radius r . We then fill this box with non-interacting particles of effective mass, m^* . This is a familiar classroom quantum problem (a nice discussion appears in Cohen-Tannoudji [1977]) with the wavefunction in the box being described by spherical free waves of the form:

$$\varphi_{klm_\ell}(x, \theta, \phi) = \sqrt{\frac{2k^2}{\pi}} j_\ell(kx) Y_\ell^{m_\ell}(\theta, \phi). \quad (1-5)$$

Here, j_ℓ is the ℓ^{th} order spherical Bessel function and $Y_\ell^{m_\ell}$ is the spherical harmonic function. $\hbar \ell$ corresponds to the orbital angular momentum for the particle. The projection

* Specifically, we consider a line tangent to the ground plane that intercepts our point charge. On this line, we require the potential to be V (for a charge Q) at the point which is of distance r from the point charge and distance d from the ground plane (making the point charge be the distance $r+d$ above the ground plane).

of the orbital angular momentum along an arbitrary axis, $\hbar m_\ell$, ranges from $-\hbar\ell$ to $\hbar\ell$. The energy of a particle of effective mass m^* at a given wave vector k is

$$E = \frac{\hbar^2 k^2}{2m^*}. \quad (1-6)$$

For our assumption of a spherically symmetric quantum well, we find that the energy of a state is independent of m_ℓ and so an energy state of given ℓ is $2\ell + 1$ degenerate. With the further assumption that the well is infinite, we only retain k states whose wavefunction goes to zero at the periphery of the nanocrystal (at $x = r$). We are then left with 3 quantum numbers to define a given state; ℓ the angular momentum, n the order of the zero in the ℓ^{th} order spherical Bessel function, and m_ℓ the projection of the angular momentum. We can rewrite equation 1-6 as

$$E_{n\ell} = \frac{\hbar^2}{2m^* r^2} \alpha_{n\ell}^2, \quad (1-7)$$

where $\alpha_{n\ell}$ is the dimensionless product of k and r which corresponds to the n^{th} zero in the ℓ^{th} order spherical Bessel function. Noting that the $\alpha_{n\ell}$'s generally scale in units of π , we rewrite equation 1-7 as follows:

$$E_{n\ell} = \frac{\hbar^2 \pi^2}{2m^* r^2} \left(\frac{\alpha_{n\ell}}{\pi} \right)^2 = \frac{0.37}{r^2} \left(\frac{m_e}{m^*} \right) \left(\frac{\alpha_{n\ell}}{\pi} \right)^2 eV \cdot nm^2. \quad (1-8)$$

Each level is $2\ell + 1$ degenerate. For free electrons, we have two spin states and so gain a factor of two in degeneracy.

For a 3 nm semiconductor dot (with $m^* = 1$) $E_{1,0}$ is ~40 meV or just a bit smaller than e^2/C_{tot} . The next several energy levels will have varied spacing and degeneracy but in general will be spaced on order* of $E_{1,0}$ (see section 4.3.2).

We now have the quantum levels of a perfect spherical well with no inter-particle interactions. When we discuss a real system we must consider interacting electrons living in the band of a crystal which is finite in size and has significant surface effects. We can partially model this by starting with the band structure of a bulk crystal and describing the carriers with a quasi-particle effective mass and the spin of the band. This approach is quite

*Or a bit smaller than.

reasonable for the lowest lying levels of a reasonably large nanocrystal ($r > 1\text{nm}$). When we consider higher lying levels or smaller nanocrystals, the crystal levels mix and so we need a more detailed theory. One such theory for CdSe* is that of Ekimov *et al.* [1993] (see chapter 4). From this work, we find that an effective mass approximation is adequate for the lowest lying levels, but band mixing significantly mixes the higher lying levels of a nanocrystal.

1.3.4 Quantum Levels in a Metallic Nanocrystal.

For a metallic nanocrystal (such as Au) the number of conduction electrons approximates the number of nuclei. Nanocrystals considered here are 1 - 10 nm in size and so have thousands of conduction electrons. For transport, this means that we must consider the quantum energy spacing of levels that sit above thousands of lower energy occupied states. This spacing can be approximated by considering a Fermi sea of N electrons bound in a metal of volume V . Such a system has a Fermi energy of

$$E_f = \frac{\hbar^2 k_f^2}{2m^*} = \frac{\hbar^2}{2m^*} \left(\frac{3\pi^2 N}{V} \right)^{2/3}, \quad (1-9)$$

where k_f is the Fermi wavevector and m^* is the effective mass of the system. We can then estimate the quantum energy barrier to electron addition as

$$E_f(N+1) - E_f(N) \equiv \left. \frac{\partial E_f}{\partial N} \right|_V = \frac{\hbar^2}{3m^*} \left(\frac{3\pi^2}{V} \right)^{2/3} N^{-1/3}. \quad (1-10)$$

This can be re-expressed in terms of the Fermi wavevector, k_f , and the nanocrystal radius, thereby obtaining

$$\Delta E(k_f) = \frac{3\pi\hbar^2}{4m^* k_f} \frac{1}{r^3}. \quad (1-11)$$

This then gives us the quantum mechanical energy cost to add a single electron to a metallic quantum dot of radius r . Plugging in the appropriate values, we obtain:

$$\Delta E \approx \frac{0.2}{r^3 k_f} \left(\frac{m_e}{m^*} \right) eV \cdot \text{nm}^2. \quad (1-12)$$

* The semiconductor dot of choice in our work.

Typically k_F is $\sim 10 \text{ nm}^{-1}$ and so a 3 nm radius metallic dot would have a level spacing of only $\sim 0.7 \text{ meV}$.

1.3.5 Putting it Together.

So far we have only discussed how the finite size of a crystal affects its carriers. To be complete, we should look at other length and energy scales observed in a bulk solid and see how they compare to those of our nanocrystal. This is done in table 1-1 for a metal, Au, and a ionic semiconductor, CdSe. The larger energies ($> 1 \text{ eV}$) such as the Fermi energy and work function are much greater than the confinement energy scales that we will be discussing. As a result, they will only be minimally perturbed by the finite size of our crystal. On the other hand, the size and energy scales associated with melting, phonons, and excitons are much more comparable to the size and confinement energy scales present in the nanocrystals that we will discuss. As a result these properties can be size dependent [see, for example, Colvin *et al.* 1992; Goldstein *et al.* 1992; and Hoheisel *et al.* 1994]. Furthermore, these low energy excitations can influence electron transport experiments. For example, an electron passing through a CdSe quantum dot might absorb or emit a LO phonon thereby opening a new transport channel. We will consider these effects as we interpret our results later in this work.

Finally, to put it in perspective, we show summary figure 1-1. Here we present several of the above discussed energies and examine their relative magnitude as a function of dot size.

1.4 A REMINDER OF OUR GOAL

Having now made our way through an introduction to many of the concepts that will be used in this work, let's take a step back and remind ourselves of the goal - to

Property	Au	CdSe
Fermi Energy*	5.5 eV	N/A
Fermi Wavelength*	0.08 nm	N/A
Work Function ^{†,‡}	5.1 eV	6.6 eV
Band Gap [‡]	N/A	1.8 eV
Bond length [§]	0.28 nm	0.29 nm
Melting energy (kT_m) ^{§,‡}	115 meV	130 meV
Cohesive energy per atom [§]	3.81 eV	N/A
Debye Energy ^{§,‡}	14 meV	16 meV
Optical Phonon Energy [‡]	N/A	26 meV
Exciton Binding Energy	N/A	15 meV
Exciton Radius	N/A	5.9 nm

Table 1-1: Some salient energy scales for bulk CdSe and Au.

* Ashcroft and Mermin, 1976.

† CRC, 1992.

‡ Böer, 1990.

§ Kittel, 1996.

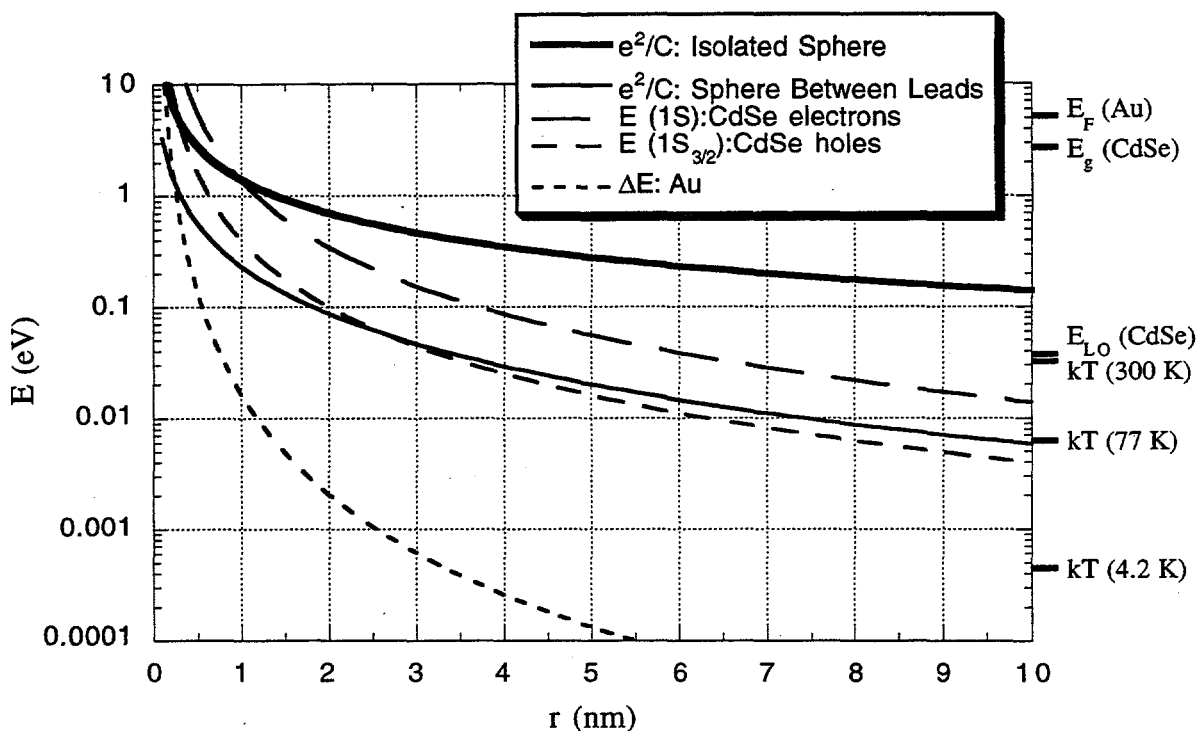


Figure 1-1: A comparison of some the energies found in our nanocrystals. In this plot, we show the dependence of Coulombic and quantum energy scales upon the radius of a spherical nanocrystal. For Coulombic effects we show the charging energy (e^2/C_{tot}) of an isolated conducting sphere (equation 1-2) and a conducting sphere that bridges two leads (equation 1-4). For a sense of scale for quantum energy levels, we show the ground state energy for the first electron and the first hole sitting in a CdSe nanocrystal (equation 1-8, $m_e^* = 0.13$, $m_h^* = 0.45$). We also show the mean level spacing at the Fermi level for a Au nanocrystal (equation 1-12, $k_F = 12 \text{ nm}^{-1}$).

measure the transport through a nanocrystal. In particular we will be considering CdSe and Au nanocrystals which are a few nanometers in radius. As we can see from figure 1-1, these should both have Coulomb energies which are quite significant at temperatures below 100 K. Au nanocrystals will have very closely spaced quantum levels and so can represent a classical dot. On the other hand, CdSe nanocrystals will have levels which should be observable at easily obtainable temperatures.

In the following chapter, we discuss the transport through a dot and will see how the above effects play out.

Chapter 2

The Basics of Transport Through a Dot

2.1 OVERVIEW

Having introduced some of the relevant energy scales, we now review the basics of electronic transport through a dot system. As we have discussed in the previous chapter, a variety of confinement effects can be relevant to the transport in such systems. First, the electrostatic cost of adding electrons to a small island of material leads to transport behavior referred to as Coulomb blockade. Added to this are quantum mechanical, particle-in-a-box energy levels. For systems in which the quantum levels are closely spaced we will call the dot a *classical dot*. If the spacing is discrete we will call the dot a *quantum dot*.

2.2 TRANSPORT THROUGH A DOT

2.2.1 Modeling the Dot

A model for the dot system that we use is shown in Figure 2-1. This system is often called a *single electron transistor*. Here we have 3 leads of relevance: a source, a drain, and a gate. Electrons can enter or exit the dot only via the source or drain. We depict this with resistors between the dot and these two leads. We model the electrostatic coupling between the leads and the dot with capacitors and assume that the entire dot is at a single potential. The dot is also weakly electrostatically coupled to a gate which otherwise does not figure into the transport. The total capacitance of the dot, C_{tot} , is given as:

$$C_{tot} = C_s + C_d + C_g \approx C_s + C_d. \quad (2-1)$$

The Fermi level of the drain will be taken as the definition of zero energy. The source's electrochemical potential, μ_s is then given as:

$$\mu_s = -eV_{sd}. \quad (2-2)$$

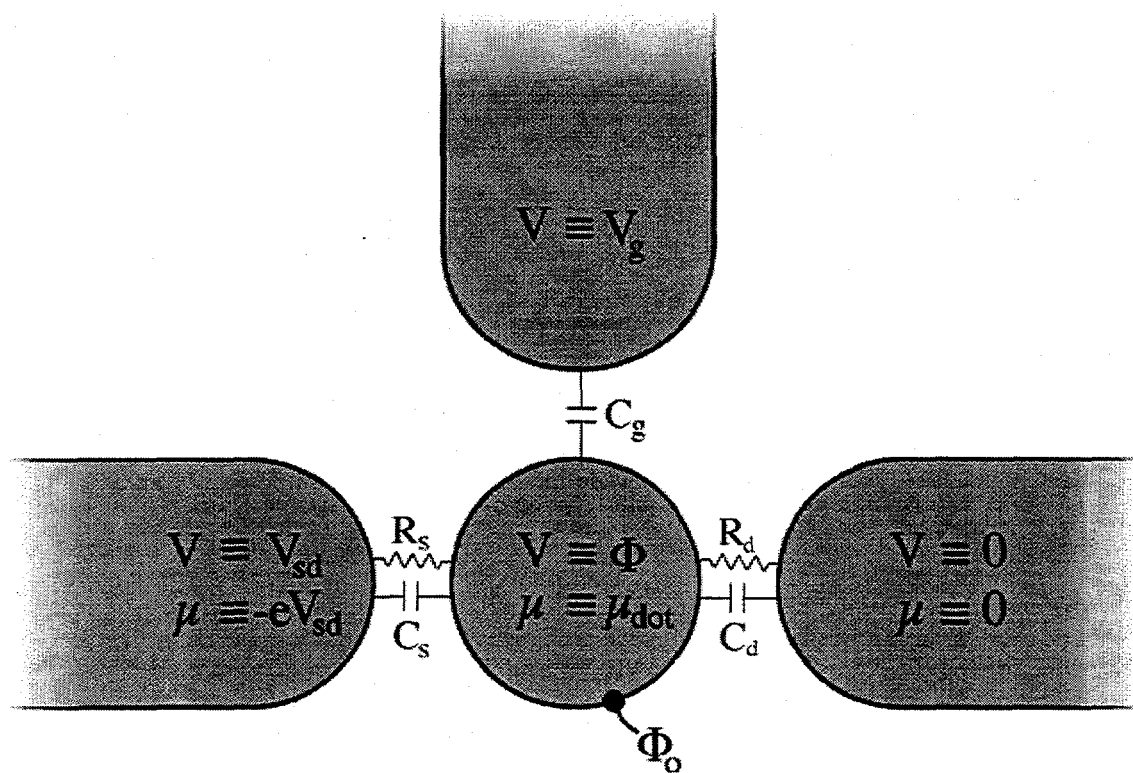


Figure 2-1: A schematic of a single dot device. The source is shown on the left of the figure, while the drain is on the right. We define the electrostatic potential of the drain to be zero, and denote the source bias as V_{sd} . Bridging the leads we have a dot which is in tunneling contact with both the source and drain (here depicted with resistors). The electrostatic coupling of the dot to the leads is modeled with capacitors. Above the dot we show a gate which is electrostatically coupled to the dot, but does not pass current. The potential of the dot when V_g and V_{sd} are zero is Φ_0 .

We call the electrostatic potential of the dot Φ and the electrochemical potential* of the dot μ_{dot} . When we do not apply any voltage to the leads, the dot would ideally have a total charge and electrostatic potential of zero. Here the number of electrons is exactly equal to the number of protons in the system. Most of the electrons will be tightly bound to their nuclei and unavailable for transport. N_0 of the electrons will be delocalized in the conduction band. We will call such a system a N_0 electron dot. If the band of interest is nearly filled, we can alternatively speak of a N_0 hole dot.

In addition to our leads, we must account for electrostatic coupling of the dot to nearby charges resident in our system. In general, the capacitance of this coupling is very small ($C \ll C_s, C_d, C_g$) and so the only effect will be the introduction of a small offset potential to the dot, Φ_0 .

2.2.2 Tunnel Junctions

We now address the nature of the particle exchange between the dot and the leads. This occurs through high impedance tunnel barriers. The impedance of a tunnel barrier depends upon its height and the level structure of the materials on either side. As a result, three broad classes for tunneling emerge.

1) If we have two deep, featureless Fermi seas with a small electrochemical potential difference, $\Delta\mu$, separated by a tunnel barrier, the tunneling rates between them [Simmons 1963, Beenakker 1991] are given by

$$\begin{aligned}\bar{\Gamma}(\Delta\mu) &= \frac{\Delta\mu}{e^2 R} \left(\frac{1}{1 - e^{-\Delta\mu \cdot \beta}} \right) \\ \bar{\Gamma}(\Delta\mu) &= \frac{\Delta\mu}{e^2 R} \left(\frac{1}{e^{\Delta\mu \cdot \beta} - 1} \right) = \bar{\Gamma}(-\Delta\mu)\end{aligned}\tag{2-3}$$

$\bar{\Gamma}$ and $\bar{\Gamma}$ are the tunneling rates going with and against the potential drop respectively, $\beta = (kT)^{-1}$, and R is the low bias *resistance* of the barrier. For macroscopic, metallic wires we

*We can not say that μ_{dot} is $-e\Phi$ though. The electrochemical potential will be discussed below.

can write $\Delta\mu = -e\Delta V$. The term in parenthesis approaches a Heavyside function as T goes to zero. The total current across a lone tunnel junction, given as the difference between $\bar{\Gamma}$ and $\bar{\Gamma}$, is ohmic and independent of temperature.

2) For tunneling from a Fermi sea to a well defined quantum level

($\hbar\Gamma_{\text{tot}} \ll kT \ll \Delta E$), where $\hbar\Gamma_{\text{tot}}$ is the total linewidth of the level* and ΔE is the energy level spacing. The tunneling rate onto and off of the state, $\bar{\Gamma}$ and $\bar{\Gamma}$ respectively, is given as:

$$\begin{aligned}\bar{\Gamma}_i &= \frac{\Gamma_i}{1 + e^{(E_i - \mu)/\beta}} (1 - \rho_i) \\ \bar{\Gamma}_i &= \frac{\Gamma_i}{1 + e^{-(E_i - \mu)/\beta}} \rho_i\end{aligned}\tag{2-4}$$

Here, Γ_i is the coupling constant of the state under consideration, E_i is the energy of the level, ρ_i is the probability that the level is occupied, and μ is the electrochemical potential of the Fermi sea.

3) We will not consider tunneling from a quantum level to a quantum level in this thesis. Suffice it to say that current will flow only when the levels are aligned in energy.

We are considering a single dot system (depicted in figure 2-1) and assume that our leads are metallic and well characterized by deep featureless Fermi seas. Thus the source-dot and dot-drain tunnel junctions can either be ohmic (equations 2-3) in nature if we are dealing with a classical dot; or Heavyside (equations 2-4) in nature if we have a quantum dot ($\Delta E \gg kT$). We will first discuss classical dots in section 2.3 and then address quantum dots in section 2.4.

2.2.3 A Well Defined Dot

If the leads shown in figure 2-1 were to be in intimate contact with the central dot, electrons would simply be flowing through a narrow wire, not an isolated dot. In order to have a well defined dot, we must isolate it from the rest of the world. This means that we must *pinch off* all electronic states that bridge the dot to either lead. In other words, the

* Γ_{tot} is given as the sum of the internal decay rate and the tunneling rate into and out of a given level.

source-dot and dot-drain junctions must be tunneling in nature with high enough barriers that the number of electrons on the dot is well defined.

For a classical dot, the transition from an ohmic to a tunneling junction occurs when the characteristic resistance of junction, R , becomes larger than the *quantum of resistance*, h/e^2 [Averin and Odintsov 1989, Geerligs *et al.* 1990a, Likharev 1988, and Averin and Likharev 1991, Averin and Nazarov 1992]. This translates to the requirement that for an isolated dot:

$$R \gg \frac{h}{e^2} = 25,813\Omega. \quad (2-5)$$

A proper derivation of this expression is non-trivial, but we note that h/e^2 is the simplest way to write a resistance in natural units. One could then make the claim that first order transport processes will occur with a rate proportional to $\frac{h}{e^2}R^{-1}$; that second order processes occur at rate $(\frac{h}{e^2}R^{-1})^2$; and so on. As a result, when comparing the first order process of an electron jumping from the source onto the dot and then from the dot to the drain to higher order processes, we could easily believe that for $R \gg h/e^2$ the first order term would dominate. This turns out to be roughly correct.

Let's now talk about quantum dots [following Beenakker 1991, Averin and Nazarov 1990, and Averin and Nazarov 1992]. We can make a comparable argument to that presented for classical dots by defining an effective tunneling resistance for quantum dots. Consider a quantum dot with mean level spacing of ΔE and a mean tunneling rate of $\langle\Gamma\rangle$ for each level. Over the energy range ΔE , a current of $e\langle\Gamma\rangle$ can flow through the dot. Ohm's law can then be used to define a quantum dot's effective radius as

$$R_{eff} = \frac{1}{e^2} \frac{\Delta E}{\langle\Gamma\rangle}. \quad (2-6)$$

We can now make the same argument as we did in the classical case and require equation 2-5 to hold. This leads to the requirement that

$$\Delta E \gg h\langle\Gamma\rangle. \quad (2-7)$$

For a quantum dot, (2-7) must be satisfied for the number of electrons on the dot to be discretized.

A second concern for quantum dots is that we want to make sure that the quantum levels on the dot remain well defined when coupled to the reservoirs in the leads. We write the average width of a quantum level as $\hbar\langle\Gamma_{\text{tot}}\rangle$, where $\langle\Gamma_{\text{tot}}\rangle$ is the total decay rate of a typical level,

$$\langle\Gamma_{\text{tot}}\rangle = \langle\Gamma_{\text{int}}\rangle + \langle\Gamma\rangle. \quad (2-8)$$

Here $\langle\Gamma_{\text{int}}\rangle$ is the internal decay rate and $\langle\Gamma\rangle$ is the tunneling rate of the average level. For the quantum levels of a system to be well defined, we require that $\hbar\langle\Gamma_{\text{tot}}\rangle \ll \Delta E$.

For a sense of scale; a 1 nA current passing through the dot, represents a tunneling rate of $\sim 10^{10}$ Hz, and a broadening of 25 μV .

2.3 COULOMB BLOCKADE - CLASSICAL DOTS

2.3.1 General Features

We consider Coulomb blockade in the device depicted in figure 2-1. For now, we will limit our discussion to a classical dot (quantum levels are considered below in section 2.4). The charge of the dot is the sum of that induced by each of the leads.

$$Q = -\Delta Ne = (\Phi - V_{sd})C_s + (\Phi)C_d + (\Phi - V_g)C_g - \Phi_o C_{\text{tot}}. \quad (2-9)$$

Here, ΔN is the number of excess electrons on the dot, $(N - N_o)$, and $\Phi_o C_{\text{tot}}$ is the charge induced by the local environment (see section 2.2.1). We can solve (2-9) for the potential of the dot to obtain:

$$\Phi = \frac{-\Delta Ne}{C_{\text{tot}}} + \Phi_o + \frac{V_{sd}C_s + V_gC_g}{C_{\text{tot}}}. \quad (2-10)$$

The total energy of the dot is then given as:

$$U(N) = \frac{1}{2}C_{\text{tot}}\Phi^2 = \frac{(-\Delta Ne + \Phi_o C_{\text{tot}} + V_{sd}C_s + V_gC_g)^2}{2C_{\text{tot}}}. \quad (2-11)$$

For transport, we are interested in the energy needed to add/remove the N^{th} electron to/from the dot. The energy required to add the N^{th} electron to a dot with $N-1$ electrons, is given as:

$$\begin{aligned}\mu_N &= U(N) - U(N-1) \\ &= \frac{e}{C_{\text{tot}}} \left[\left(\Delta N - \frac{1}{2} \right) e - \Phi_o C_{\text{tot}} - V_{sd} C_s - V_g C_g \right].\end{aligned}\quad (2-12)$$

We call μ_N the electrochemical potential of the dot for the N^{th} electron. For ease in upcoming analysis, we define $\mu_o = e(\Phi_o + e/2)$ thereby giving:

$$\mu_N = -\mu_o + \frac{e}{C_{\text{tot}}} \left[\Delta N e - V_{sd} C_s - V_g C_g \right]. \quad (2-13)$$

Now armed with an expression of the energy required to change the charge state of our quantum dot, we can analyze its transport.

2.3.2 Coulomb Oscillations

There are several ways we can study Coulomb blockade in the laboratory. The first that we will discuss is the measurement of Coulomb oscillations. Here, for the device shown in figure 2-1, we vary the gate voltage, V_g , while leaving the source-drain bias, V_{sd} , fixed at a value much smaller than the thermal bath energy, kT . The effect of the increasing gate is to lower the electrochemical potential of the dot past the point at which it is energetically favorable for it to gain an electron. As the dot makes the transition from N to $N+1$ electrons, the source-drain conductivity goes from zero (Coulomb blockade for N electrons), to a finite value (charge degeneracy between N and $N+1$ electrons), and then falls back to zero (Coulomb blockade for $N+1$ electrons). This process is called a Coulomb oscillation and was first described by Kulik and Shekhter [1975].

Figure 2-2 will help us understand this process. We are considering a classical dot at temperature kT and a small source-drain bias ($V_{sd} \ll kT$). In figure 2-2a we show the electrochemical potential for different charge states of a dot. We show the filled Fermi seas for the source and drain on either side. The source is at a bias slightly below zero and the

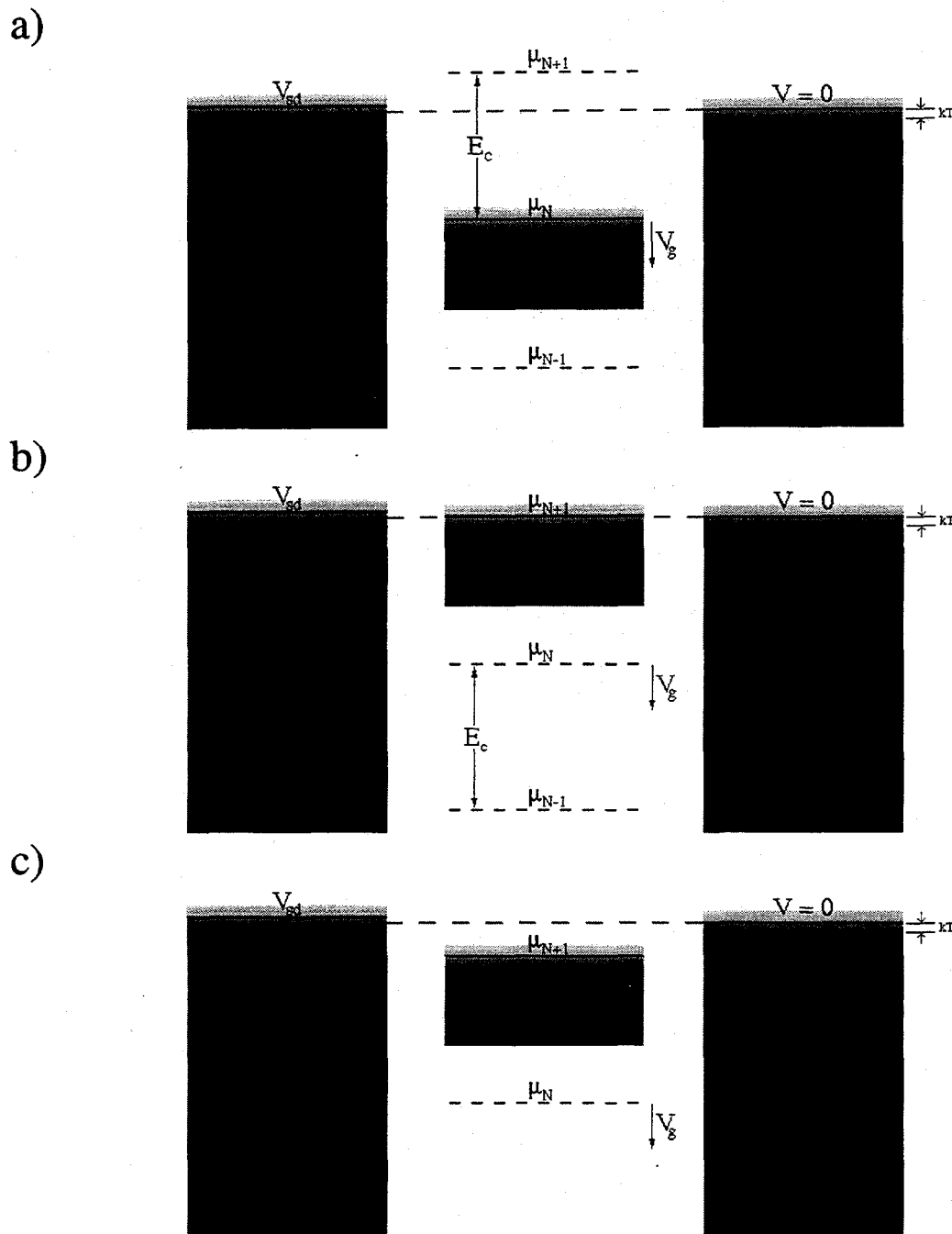


Figure 2-2: A schematic of some energy diagrams related to Coulomb oscillations. From left to right in each figure we depict the Fermi seas of the source, dot, and drain for the device shown in figure 2-1. We take energy as the vertical axis, and show electron density with shading (darker = more electrons). The lower density about the Fermi level reflects thermal broadening. With solid dashed lines we show what the electrochemical potential of the dot *would be* if we changed the number of resident electrons. With a gray dashed line we show the Fermi level of the drain which is defined as zero energy. a) Coulomb blockade for a N electron dot. b) The effect of increasing the gate voltage. Here, the electrochemical potential of the $N+1$ electron state lies within kT of leads' Fermi levels. As both the N and $N+1$ electrons states are now available for transport, state (b) is conducting. c) With a further increase in gate voltage, we have Coulomb blockade for $N+1$ electrons.

Fermi seas are thermally broadened. The electrochemical potential of the dot depends upon the number of electrons resident on it (equation 2-13). For the situation diagrammed here, the dot will have N electrons (the solid line). With dotted lines we show where the electrochemical potential of the dot would be if it held $N+1$ or $N-1$ electrons.

Let us now consider the transport through our dot. For the N electron dot, we have a continuum of filled levels up to the N -electron Fermi level, μ_N . Above that energy we have a continuum of empty states (alternatively, filled hole states). In short, we have a normal metal with N electrons. However, transport through the dot requires us to add or remove an electron. In figure 2-2a we see that the electrochemical potential of the $N+1$ electron system lies a charging energy above the electrochemical potential of the N electron system. As there are no electrons in the leads available for transport at this energy, a small source-drain bias will pass no current through the dot. This is referred to as the Coulomb blockade regime.

As we increase the gate voltage, we lower the electrochemical potential of the N electron dot until it reaches $-e^2/C$ (figure 2-2b). At this point, the electrochemical potential of the $N+1$ electron dot becomes negative (relative to the Fermi level of the drain). This results in the dot drawing an electron from a lead to have $N+1$ electrons. Thermal energy will broaden this transition so that the occupation probability of the $N+1$ state of the dot will smoothly transition between 0 and 100%. In other words, in figure 2-2b, the energy difference between the N and $N+1$ electron dot is smaller than kT . At this charge degeneracy point, electrons can jump onto and off of the dot and our source-drain conductivity will become finite.

Eventually (figure 2-2c) we will have increased the gate voltage to the point that the $N+1$ level is well below the Fermi level of the source and drain. This is the same situation depicted in figure 2-2a except that the dot now has $N+1$ electrons on it. Current cannot flow, because the $N+2$ electron state is still well above the Fermi level of either the source or drain, and there are no empty states in the leads for the $(N+1)^{\text{th}}$ electron to flow out.

We have now seen that as we increase the gate voltage we will only get a finite source drain conductivity in the event that the electrochemical potential of a particular charge state of our dot lies within order kT of the Fermi level of our leads. The dependence of the conductance on the gate voltage at a given temperature, when $kT \ll e^2/C$, is given as:

$$G = \frac{1}{2(R_s + R_d)} \frac{\frac{\mu_N}{kT}}{\sinh\left(\frac{\mu_N}{kT}\right)}. \quad (2-14)$$

Equation 2-14 can be readily derived by a combination of the tunneling rates of both tunnel junctions (equation 2-3) and a consideration of the probability of the dot having either N or $N+1$ electrons* [Beenakker 1991]. We can now summarize the transport through a quantum dot as we augment the gate voltage. This summary is shown in figure 2-3. We start on the left with a dot (for ease assumed to have $\Phi_0=0$) with N_0 resident electrons. The conductance here is zero. As the gate voltage increases, the total energy of the system rises and the electrochemical potential for the dot drops until μ_{N+1} passes zero; now we see a Coulomb oscillation in the source drain conductivity as the dot settles into the $N+1$ electron configuration. This process then repeats as the number of electrons accumulates to $N+2$, $N+3$, and so on. The graphs of the conductance and occupancy of the dot are derived from the program discussed in appendix A.

2.3.3 I- V_{sd} Curves - A Toy Model

We now consider the dependence of the current on the source drain bias for a fixed gate voltage. The effect of raising the source drain bias is to increase the range of energies in the dot that are available for transport. As this range envelops new charge states, we augment the source drain current, thereby producing a current-voltage characteristic referred to as a Coulomb staircase.

*Much like the model that will be discussed in 2.3.3

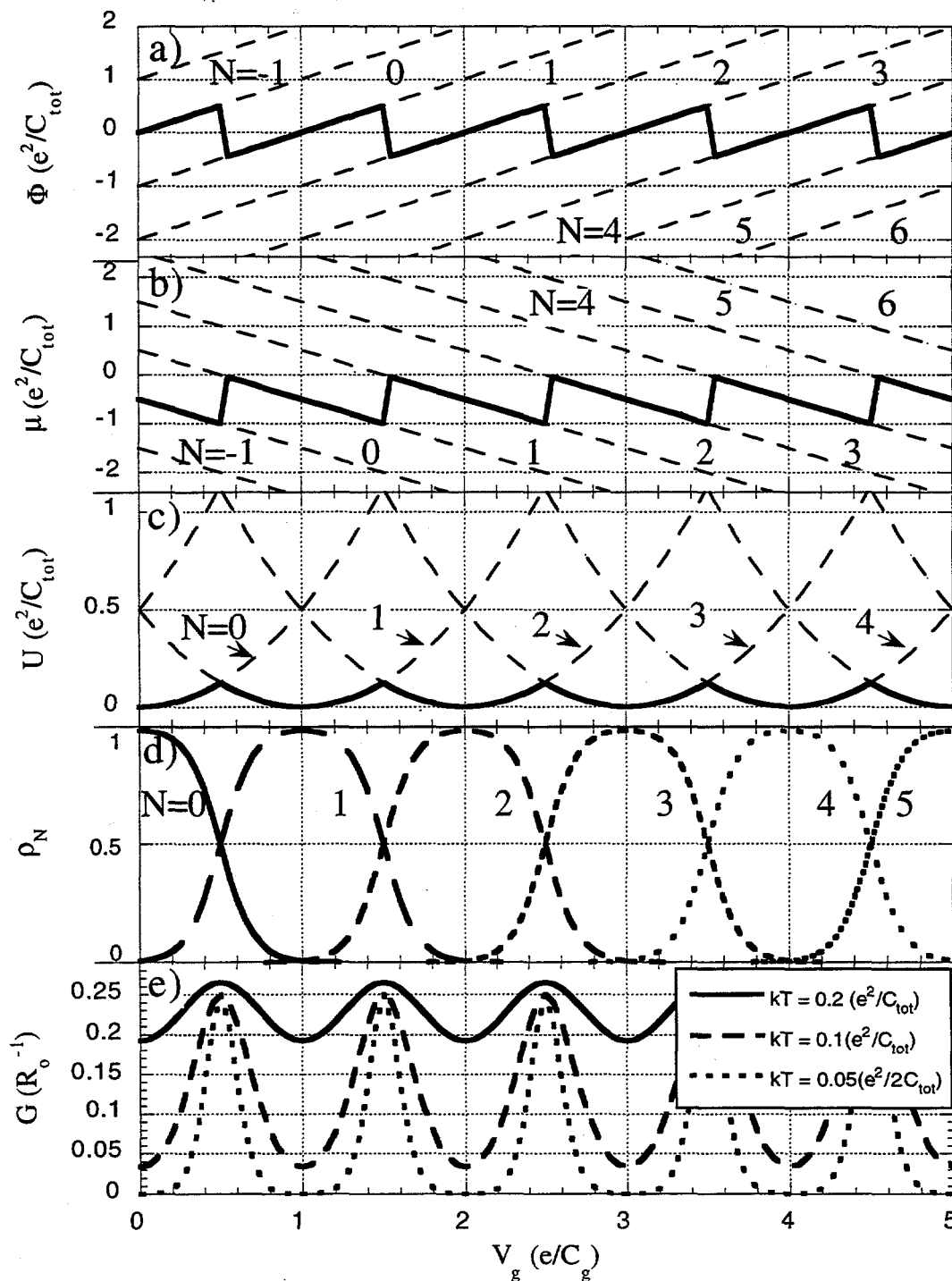


Figure 2-3: Aspects of Coulomb oscillations for electrons in a classical dot. The dot is symmetric with $R_s = R_d = R_0$, $C_s = C_d = C_{tot}/2$ and $\Phi_0 = 0$. a) Possible (dashed lines) electrostatic potentials, Φ , for differing electron numbers (N) on the dot. In solid we show the $T = 0$, ground state electrostatic potential. b) Possible (dashed) and chosen (solid) electrochemical potential, μ_N , for the dot. c) Possible (dashed) and chosen (solid) electrostatic energy for the dot. d) Calculated probability of each charge state, ΔN , of the dot for $kT = 0.1e^2/C$. e) Calculated device current as a function of temperature.

Our analysis will again be based upon the device depicted in figure 2-1. The gate voltage will remain fixed and so we will lump it in with the offset potential, Φ_0 . The contribution of the gate to the dot's total capacitance will again be neglected.

Let us now explicitly calculate the development of the first features we expect to see in the current-voltage characteristic. As we are neglecting quantum structure, we model the dot as a featureless Fermi sea. To obtain an initial simple understanding of the transport, we assume $T=0$; temperature will be addressed in section 2.3.4. For $T = 0$, the current flow from a given lead into/out of the dot will grow linearly with $\Delta\mu$ if the lead's Fermi level is above/below the dot's and is zero otherwise. To make things clear, we break the symmetry of our system and assume that the dot-drain junction is of much higher impedance than the source-dot junction.

The energy diagram for small V_{sd} is as shown in figure 2-4a. As the empty $N+1$ electron state is above both leads' Fermi levels and the filled N electron state is below both Fermi levels, the source-drain current is zero. As we increase the source-drain bias, the dot remains blockaded until the Fermi level of the source falls below μ_N , or μ_{N+1} falls below the drain's Fermi level*.

Let us assume that the first event is the source's Fermi level passing μ_N as diagrammed in figure 2-4b. In this case electrons will flow off the dot (current flows onto the dot) at a rate given as:

$$I_s = e\bar{\Gamma}_s \rho_N$$

$$\bar{\Gamma}_s = \frac{\frac{1}{e}\mu_N + V_{sd}}{eR_s} \cdot \Theta(eV_{sd} + \mu_N), \quad (2-15)$$

where ρ_N is the probability that the N electron state is filled, and $\bar{\Gamma}_s$ is the rate at which electrons flow from the N electron dot to the source. Equation 2-13 gives us:

$$\mu_N = -\mu_0 - eV_{sd} \frac{C_s}{C_{tot}}, \quad (2-16)$$

thereby allowing us to rewrite 2-15 as:

*Keep in mind that the dot-lead capacitive coupling results in a shift of the electrochemical potential of the dot as we change the source-drain bias.

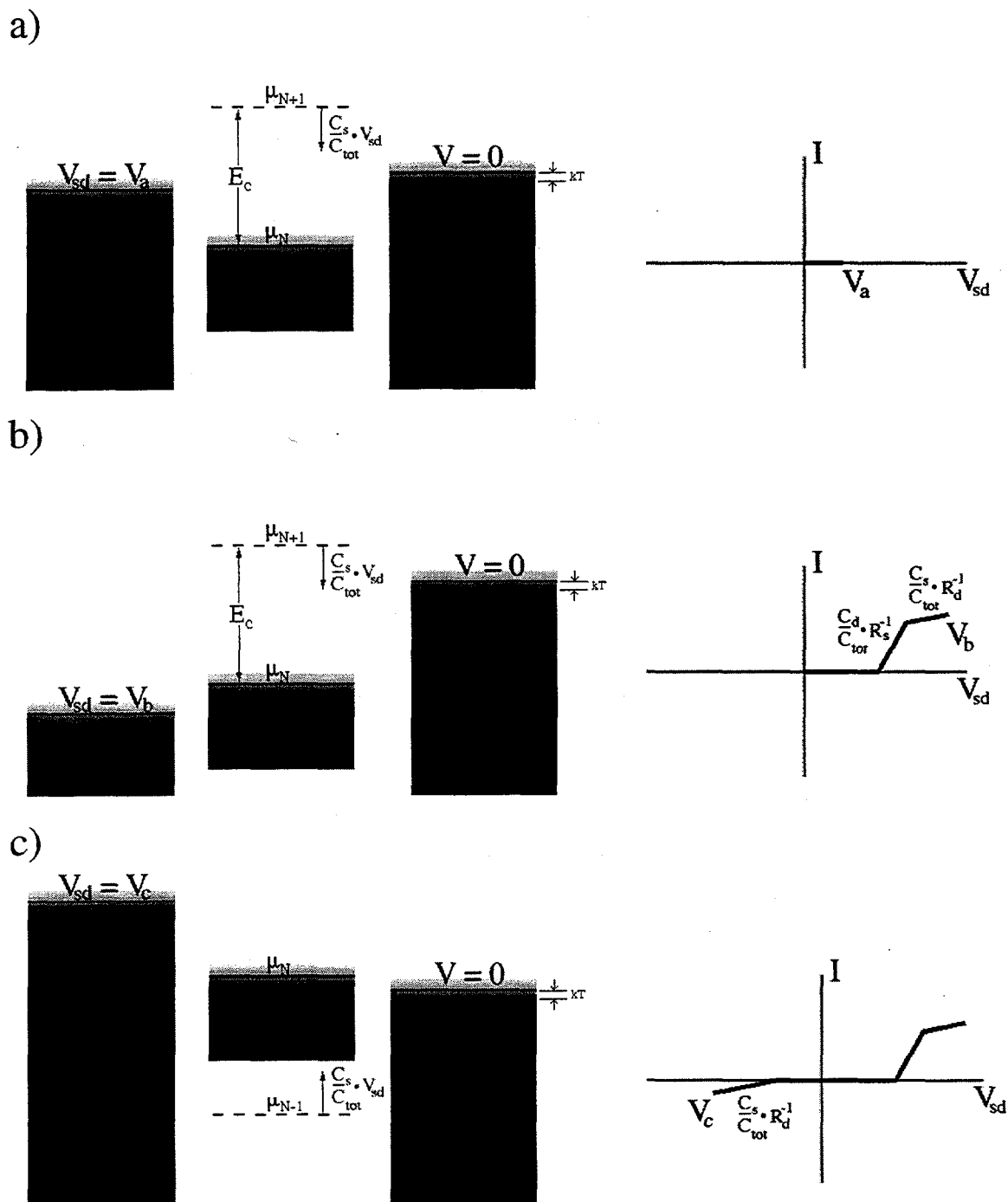


Figure 2-4: A schematic of some energy diagrams (see figure 2-2 for details) related to the Coulomb gap and staircase. a) For a small V_{sd} we have Coulomb blockade for a N electron dot, and no current flow (as shown on the right side of the figure). b) As we increase V_{sd} , we make the transition from a N to a $N-1$ electron dot. The corresponding I - V_{sd} characteristic is shown on the right, and described in the text. c) If we instead apply a negative V_{sd} , we can capacitively pull the dot's electrochemical potential until it passes the drain's Fermi level and thereby source current.

$$\bar{\Gamma}_s = \frac{1}{eR_s} \left(-\frac{\mu_o}{e} + \frac{C_d}{C_{tot}} V_{sd} \right) \cdot \Theta \left(eV_{sd} - \frac{C_{tot}}{C_d} \mu_o \right). \quad (2-17)$$

The electron flow onto the dot is

$$I_d = e\bar{\Gamma}_d \rho_{N-1} = e\bar{\Gamma}_d (1 - \rho_N)$$

$$\bar{\Gamma}_d = \frac{-\frac{1}{e}\mu_N}{eR_d} = \frac{1}{eR_d} \left(\frac{\mu_o}{e} + \frac{C_s}{C_{tot}} V_{sd} \right) \cdot \Theta \left(eV_{sd} + \frac{C_{tot}}{C_s} \mu_o \right). \quad (2-18)$$

In equilibrium, I_s must equal I_d . By combining equations 2-15 and 2-18 we obtain:

$$\rho_N = \frac{1}{\frac{\bar{\Gamma}_s}{\bar{\Gamma}_d} + 1}. \quad (2-19)$$

Which in turn gives us

$$I = e \left(\frac{1}{\bar{\Gamma}_s} + \frac{1}{\bar{\Gamma}_d} \right)^{-1}$$

$$= \left(\frac{R_s}{-\frac{\mu_o}{e} + \frac{C_d}{C_{tot}} V_{sd}} + \frac{R_d}{\frac{\mu_o}{e} + \frac{C_s}{C_{tot}} V_{sd}} \right)^{-1} \cdot \Theta \left(eV_{sd} - \frac{C_{tot}}{C_d} \mu_o \right) \cdot \Theta \left(eV_{sd} + \frac{C_{tot}}{C_s} \mu_o \right). \quad (2-20)$$

We can understand equation 2-20 by looking at figure 2-4b. The dot starts blockaded until the Fermi level of the source ($-eV_{sd}$) passes that of the N electron dot (μ_N). When this happens, current starts to flow. Because potential drop across the source-dot junction is much smaller than that of the dot-drain junction, $\bar{\Gamma}_d \gg \bar{\Gamma}_s$ and $\rho_N \cong 1$. In this situation the bottleneck to conduction is the rate at which electrons can get from the dot to the source and so the current is given as that which flows through the dot-drain barrier,

$$I \approx I_s = \frac{1}{R_s} \left(-\frac{\mu_o}{e} + \frac{C_d}{C_{tot}} V_{sd} \right) \cdot \Theta \left(eV_{sd} - \frac{C_{tot}}{C_d} \mu_o \right). \quad (2-21)$$

The current grows with a slope given as $1/R_s$ times a capacitive lever arm factor of $\sim 1/2$.

However, we recall that we have defined $R_s > R_d$. Thus the ability of dot to shed electrons to the source will soon exceed its ability to replenish electrons from the drain. Once this happens we will make the transition to a current which is regulated by the drain-dot barrier.

In this regime, the dot will tend to be in the N-1 electron state and the current will be given as:

$$I \approx I_d = \frac{1}{R_d} \left(\frac{\mu_o}{e} + \frac{C_s}{C_{tot}} V_{sd} \right). \quad (2-22)$$

The result of this back of the envelope calculation is shown on the right hand side of figure 2-4b. Such a feature is often referred to as a Coulomb step. As we further increase V_{sd} the current will linearly grow until either the source drops below μ_{N-1} , or μ_{N+1} drops below the drain. In either case, we will now have two accessible levels for transport. The effect is roughly similar to the above discussion, but we must now consider a 3x3 density matrix. This will be addressed in section 2.3.4.

To see how far we can push the toy model, we now apply a negative V_{sd} . The dot will again start out blockaded. Current will begin to flow when either μ_N rises about the drain, or μ_{N+1} is surpassed by the source. If the latter happens we will again have a Coulomb step identical to that discussed just above, but instead of $-\mu_o$, we use $-\mu_o + e^2/C_{tot}$. We note that the spacing of these two features is e^2/C_d and is independent of μ_o . Let us instead consider μ_N passing the drain (defined to be at 0 energy) as shown in figure 2-4c. The transport is now given as

$$I = e \left(\frac{1}{\bar{\Gamma}_{N-1}^s} + \frac{1}{\bar{\Gamma}_N^d} \right)^{-1} = \left(\frac{R_s}{-\frac{\mu_o}{e} + \frac{C_d}{C_{tot}} V_{sd}} + \frac{R_d}{\frac{\mu_o}{e} + \frac{C_s}{C_{tot}} V_{sd}} \right)^{-1} \cdot \Theta \left(-eV_{sd} + \frac{C_{tot}}{C_d} \mu_o \right) \cdot \Theta \left(-eV_{sd} - \frac{C_{tot}}{C_s} \mu_o \right). \quad (2-23)$$

This is the same as equation 2-20, except the arguments of the Heavyside functions are now of opposite sign. Now, instead of starting with the rather compliant source-dot junction limiting the current, we have the more restrictive dot-drain junction running the show. Here the current grows according to:

$$I \approx I_d = \frac{1}{R_d} \left(\frac{\mu_o}{e} + \frac{C_s}{C_{tot}} V_{sd} \right) \cdot \Theta \left(-eV_{sd} - \frac{C_{tot}}{C_s} \mu_o \right). \quad (2-24)$$

Because electrons from the source can always replenish the dot faster than they can drain into the drain, the dot will mostly stay in the N electron state and the current will continue to grow linearly as shown on the right hand side of figure 2-4c.

As V_{sd} grows, μ_{N+1} will eventually fall below the source's Fermi level or μ_{N-1} will rise above the drain's. This is again a situation which requires a 3×3 density matrix, which we discuss below.

To conclude this rather math intensive section, we offer a summary discussion of the salient points in the nature of a Coulomb gap. First, the gap is generally asymmetric, reflecting differences in the source-dot and dot-drain tunnel junctions. For the dot considered above, with $R_s > R_d$, Coulomb steps will occur each time the dot's electrochemical potential passes the source's. When the dot's electrochemical potential passes the drain's, a linear rise in current is seen, not a step.

2.3.4 I- V_{sd} Curves - A More Rigorous Model.

We would like to be able to consider conduction through multiple charge states of the dot as well as temperature effects. Here our toy model comes up short. We now turn to a slightly more thorough treatment of Coulomb blockade. Such a treatment remains analytical, but the expressions are complex enough that we confine them to a computer. We will again neglect quantum levels (but you only have to wait one more section to see their effect).

A description of our calculation appears in appendix A. Briefly we consider n possible charge states of a dot. For each possible charge state we calculate the tunneling rate of electrons onto and off of the dot from both the left and right lead using equations 2-3 and 2-13. We then use detailed balance to calculate the probability of the dot to be in each possible charge state and sum over charge states to get the current for a given voltage. Figure 2-5a shows a $T = 0$ Coulomb staircase for a representative set of junction parameters. In figure 2-5b we show the corresponding occupancy probability for each

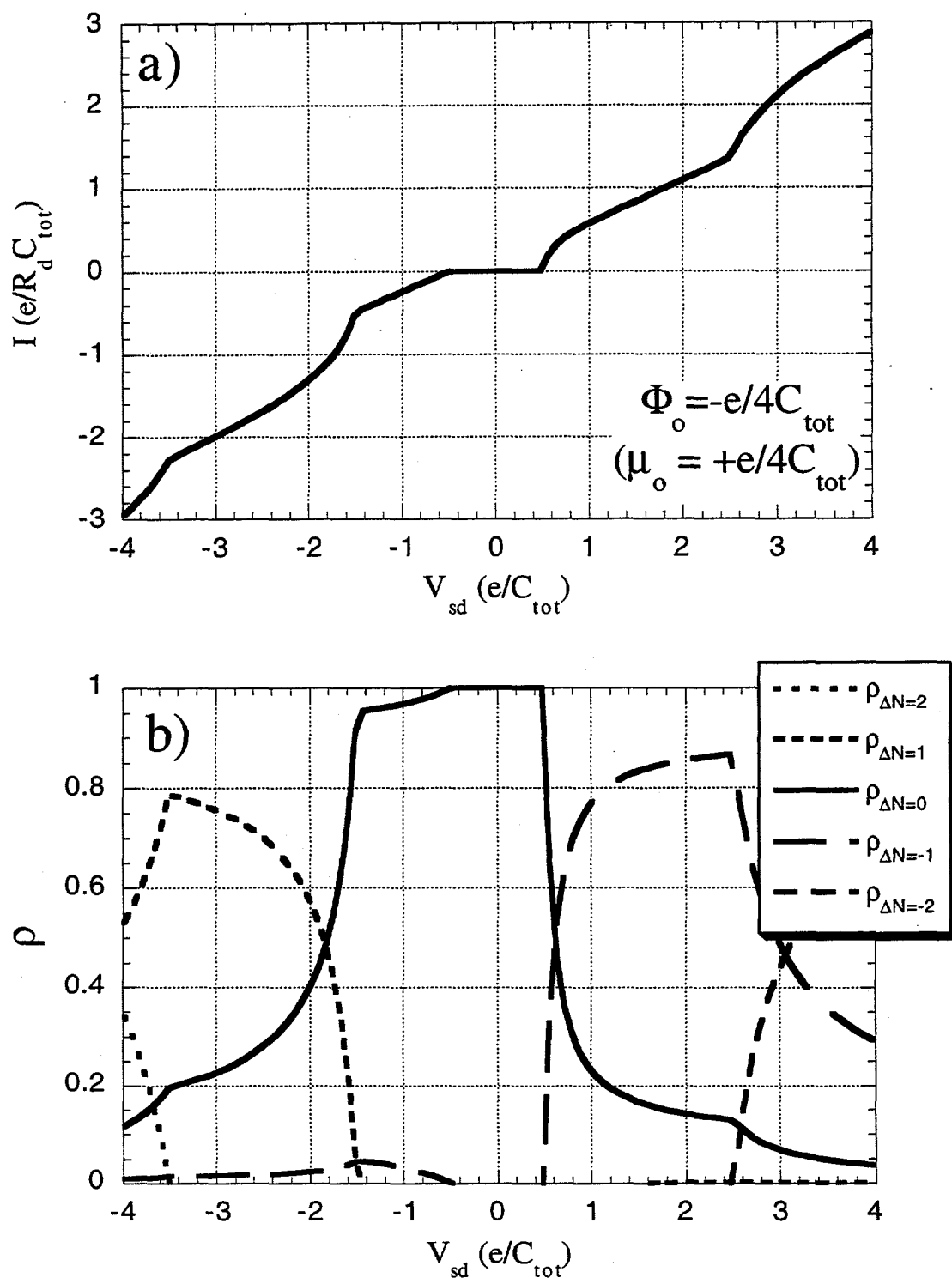


Figure 2-5: Calculated Coulomb staircase for electrons in a classical dot. The dot is asymmetric with $R_s = R_d/10$, $C_s = C_d = C_{tot}/2$, $\Phi_o = -e/4C_{tot}$, and $T = 0$. a) The I - V_{sd} characteristic of this system. b) The probability that the dot will have a given charge state as a function of V_{sd} .

charge state. The low bias development of the $I-V_{sd}$ curve is quite comparable to that calculated in section 2.3.3, with the main difference being that the Coulomb steps are now smooth*. This is a reflection of the smooth transition in charge state that occurs as we raise V_{sd} . In figure 2-6, we show a variety of curves to examine how various parameters effect the $I-V_{sd}$ characteristic. Figure 2-6a shows the effect of the offset potential on $I-V_{sd}$. One could change the offset potential with a gate or by letting it change as a result of variations in the local charge environment about the dot. As the offset potential changes, the Coulomb gap oscillates between e/C_{tot} and zero†. Figure 2-6b shows the same device, now at a variety of temperatures. Here, we see that the Coulomb staircase disappears when the temperature becomes comparable to the charging energy of the dot. Figure 2-6c shows the effect of changing one of the resistors to make the dot more symmetric. We note that, while the Coulomb gap remains well defined, the Coulomb staircase becomes poorly-defined when the two tunnel junction are made to be symmetric.

2.4 COULOMB BLOCKADE - QUANTUM DOTS

2.4.1 General Features

We now consider how quantum levels will be witnessed in the transport through a quantum dot. Now, when we write our electrochemical potential, we must consider the energy levels of the $N-1$ and N electron configurations, E_i^{N-1} and E_i^N . We thus rewrite equation 2-12 as

$$\begin{aligned}\mu_N &= U(N) - U(N-1) \\ &= -\mu_o + \frac{e}{C_{tot}} [\Delta Ne - V_{sd}C_s - V_gC_g] + \sum_{i=1}^N E_i^N - \sum_{i=1}^{N-1} E_i^{N-1}.\end{aligned}\quad (2-25)$$

In the energy levels of the N electron configuration is similar to those of the $N-1$ configuration, we can rewrite 2-25 as

$$\mu_N = -\mu_o + \frac{e}{C_{tot}} [\Delta Ne - V_{sd}C_s - V_gC_g] + E_N. \quad (2-26)$$

*Even though $T = 0$.

†When the Coulomb is zero, we have a Coulomb oscillation.

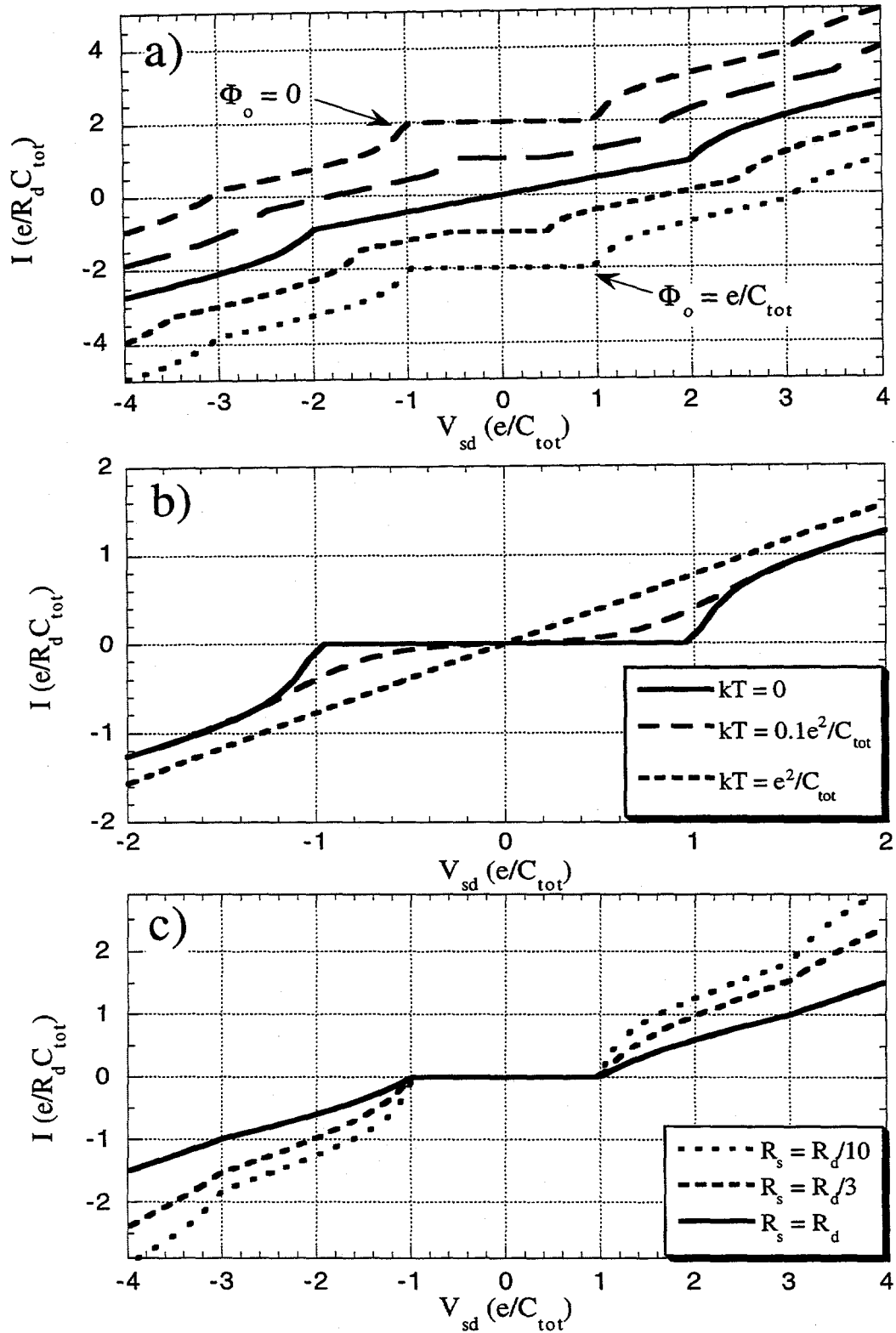


Figure 2-6: Calculated Coulomb staircases for electrons in a classical dot. a) The effect of changing Φ_o for a dot with $R_s = R_d/10$ and $C_s = C_d = C_{tot}/2$ at $T = 0$. b) The effect of changing the T for a dot with $R_s = R_d/10$ and $C_s = C_d = C_{tot}/2$ and $\Phi_o = 0$. c) The effect of changing the resistive asymmetry of a dot with $C_s = C_d = C_{tot}/2$ and $\Phi_o = 0$ at $T = 0$.

It is with these electrochemical potentials that we calculate the transport through a quantum dot.

In general this is more difficult than the classical dot case. This is because each level will couple to the leads with its own tunneling rates. Add to this the fact that the quantum energy levels of the N electron dot may bear little resemblance to those of the $N-1$ electron dot, internal decay rates can compare to tunneling rate, and the loss of a well defined dot capacitance (for the dot no longer has the same charge distribution for differing numbers of electrons). In the end, we can not put forward a simple model to fully describe the dot as we did above. However, we can still understand the behavior of the dot and use measurements to learn about the quantum level structure of the dot. This is most easily done for the case in which the mean level spacing, ΔE , is much smaller than the charging energy, E_c .

2.4.2 $V_{sd} \approx 0$ - Equilibrium Transport

Let us first consider the nature of Coulomb oscillations in a quantum dot. They will be very similar to those of the classical dot, with three differences:

- 1) The spacing between oscillations is not constant.
- 2) The heights of the oscillations are variable.
- 3) The oscillations have a different temperature dependence.

The first effect is a result of our new chemical potential (equations 2-25, 26). Before, we always had a constant spacing between oscillations of e^2/C_g . Now, we also have to bridge a quantum energy gap of ΔE_N . ΔE_N , defined as $E_N - E_{N+1}$, will vary from level to level and so will the spacing. In general the capacitive coupling of the dot to the leads will change, but this effect is often small and hard to separate from quantum energies and so will be neglected. The second effect is a result of differing tunneling rates for each quantum level. The third effect is a reflection of the different nature of the tunneling process in

dots (see section 2.2). We calculate the shape of a Coulomb oscillation in the regime $\hbar\Gamma_{\text{tot}}, V_{\text{sd}} \ll kT \ll \Delta E$ to be [Beenakker 1991]

$$G = \left(\frac{e^2}{\Gamma_s^{-1} + \Gamma_d^{-1}} \right) \frac{1}{4kT \cosh^2 \left(\frac{\mu_N}{2kT} \right)}. \quad (2-27)$$

This line shape is very similar to that of a classical quantum dot (equation 2-14). Figure 2-7 compares lineshapes for quantum and classical Coulomb oscillations. We see that we can differentiate the two by their temperature dependence. A classical dot will exhibit oscillations whose width, but not height depend upon temperature. A quantum dot's oscillation will grow in amplitude as the temperature is decreased so long as $\hbar\Gamma_{\text{tot}} \ll kT \ll \Delta E$; for $kT \ll \hbar\Gamma_{\text{tot}}$, the transport will be temperature independent; and for $\Delta E \ll kT$ we have a classical dot.

2.4.3 $V_{\text{sd}} \neq 0$ - Non-Equilibrium Transport

One can also consider Coulomb oscillations for a finite V_{sd} . With $V_{\text{sd}} > \Delta E > kT$, the Coulomb oscillations will deform into complex peak structure resultant from the occupancy of different quantum levels. Alternatively, we can fix the gate voltage, and sweep V_{sd} to study the Coulomb staircase (like we did in section 2.2.2). Here again, the non-continuous density of states will complicate the transport. These two studies differ from simple Coulomb oscillation studies in that the finite source-drain bias allows for the occupation of excited quantum states in the dot. This then allows us to look at the excited state energy spectrum of different charge states of the dot. Ultimately such studies are best done by sweeping both V_{sd} and V_g . Because the complications of self-consistently calculating the transport through multiple states of a dot is beyond the scope of this thesis we refer the reader to other works [such as Macucci *et al.* 1995 and Tanaka and Akera 1996,1997]. The reader can find experimental work on quantum dots by others in chapter 3, and by us in chapter 8.

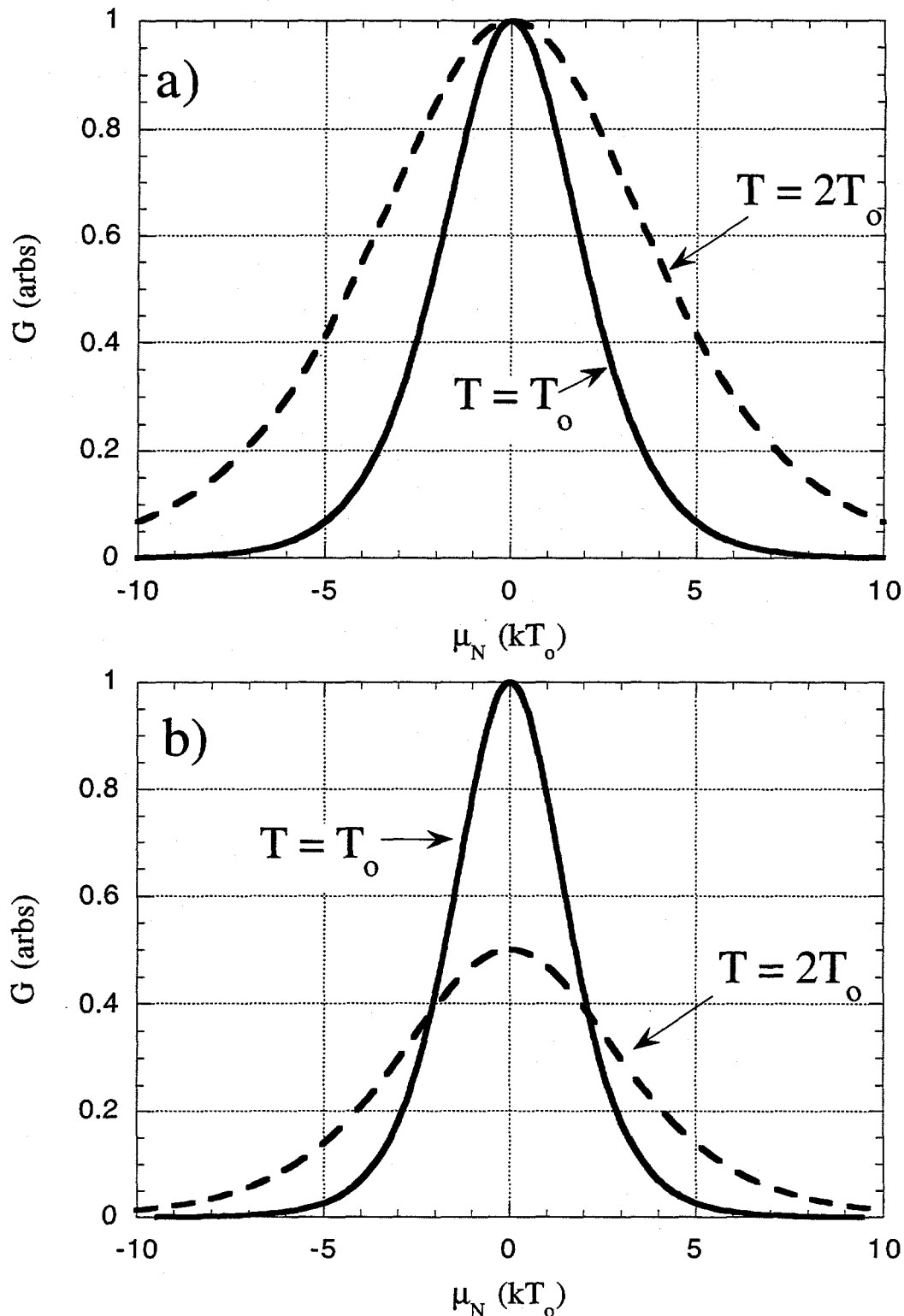


Figure 2-7: The effect of temperature on a (a) classical dot's and a (b) quantum dot's Coulomb oscillation. For both, we assume $kT \ll e^2/C_{\text{tot}}$ and for the quantum dot, we further assume that $\hbar\Gamma \ll kT \ll \Delta E$. We see that for a given temperature, a classical dot's oscillation is nearly identical to a quantum dot's, but as we double the temperature, the height of the quantum dot's oscillation changes, whereas a classical dot's only broadens.

2.5 SUMMARY

We have now discussed the effects of electrostatic and quantum confinement on the transport through a quantum dot. We have found that Coulomb blockade has a strong effect on the transport and results in phenomena such as Coulomb oscillations and the Coulomb staircase. By studying the detailed nature of these effects we will be able to learn about the nature of the electronic level structure in our nanocrystals.

Before we start a discussion regarding our efforts, we will first explore some of what has been learned in the experimental efforts of others in the field of meso-scopic physics. Much of the theory described above has been studied in the context of lithographically defined semiconductor heterostructures. A solid understanding of the results of these studies as well as optical and electrical response of nanocrystals will help us understand what we can expect to find in our system.

Chapter 3

History and the Work of Others

3.1 OVERVIEW

The field of nanometer scale fabrication is synonymous with chemistry, a field whose history is long and whose scope is beyond the reach of this work. However, the field whose concern is the electrical measurement of nanometer scale objects, nanoelectronics, is much younger. This is because the ability to electrically probe nanostructures requires that one be able to bridge the gulf between macroscopic leads* and nanoscopic objects†. Making this transition in scale is the keystone of nanoelectronics.

Since the mid-1980's physicists have attacked this problem by using lithography to pattern a thin film into desired geometries. This is sometimes called the *top-down* approach and has been used to fabricate mesoscopic transistors which show confinement effects such as Coulomb blockade and particle-in-a-box states. Because of materials and lithography limitations, these structures are usually made in the 20-500 nm size regime. As a result, the energy scale for confinement effects is typically < 1 mV and the studies have to be made at very low temperatures (< 100 mK). To raise the energy scale, many have focused on novel lithography methodologies to shrink the size of the fabricated objects. Of course, the finer the features one desires do define in this manner, the more difficult the task.

To overcome limitations in lithography, one can attack the problem in reverse. In a *bottom-up* approach, one grows structures to the desired size, rather than try to whittle a larger structure down. By this approach, one can easily fabricate structures whose size is less than 10 nm and thereby raise the energy scale of confinement effects. The difficulty is in finding ways to attach leads to these structures.

*The inner conductor of a BNC is 1 mm in diameter.

†The typical object that we will be discussing is 5 nm in diameter.

Below I will briefly outline some of the progress that has been made in the study of dots. I will start by discussing some early electrical measurements made on planar tunnel junctions which contain metallic inclusions. Following this, I will review systems made by the top-down lithographic approach. I will then discuss some of the newer systems fabricated with a bottom-up approach.

Several thorough reviews exist on Coulomb blockade, to which the reader is directed for further information [Beenakker 1991, *Single Charge Tunneling* ed. by Grabert and Devoret 1992, Kouwenhoven and McEuen 1997, Kouwenhoven *et al.* 1997].

3.2 EARLY WORK

Tunneling through a metal-insulator-metal (MIM) junction was first studied in the 1930s [Frenkel 1930, Holm and Meißner 1992,1993]. MIM and superconductor-insulator-superconductor (SIS) tunneling experiments became very popular again in the sixties. The systems typically studied were planar oxide barriers separating two metals. Aluminum and tin were popular metals for these experiments, for a uniform, high barrier oxide naturally grows on their surfaces. Furthermore, both will become superconducting at low temperatures*. Seminal papers from this period include work on Josephson tunneling in superconductors [Josephson 1962, Anderson and Rowell 1963], on Inelastic Tunneling Spectroscopy (IETS) [Jaklevic and Lambe 1966], and on point contact tunneling [Levinstein and Kunzler 1966]. Zeller and Giaever [Giaever and Zeller 1968, Zeller and Giaever 1969] extended this work by including small Sn particles in the oxide barrier. Their experiments effectively probed the response of two MIM junctions in series where the central metal was $< 100 \text{ \AA}$ in size. As discussed in chapters 1 and 2, such a system will exhibit Coulomb blockade phenomena. Further experiments fleshed out the transport behavior in other comparable systems [Yanson and Vlasenko 1969,1971; Galkin and Ignat'ev 1970, Lambe and Jaklevic 1969]. At the time, no easy to use Coulomb blockade

*1.175 K for Al and 3.722 K for Sn [CRC, 73rd ed.].

model existed and several models were used to explain the work of Zeller and Giaever and others. The model from which much of the current theory is derived is that of Kulik and Shekhter [1975].

In this early work, a basic understanding of Coulomb blockade was derived. In fact the energy scale for charging was quite high, allowing for remnants of Coulomb blockade to persist up to > 100 K [Giaever and Zeller, 1969]. The limitation was that measurements were made over numerous grains that conducted in parallel. As a result, detailed transport measurements were not possible. Little new progress was made until the mid-1980's, a time at which new lithography and thin film deposition techniques made possible the top-down fabrication of single island Coulomb blockade devices.

3.3 TOP-DOWN DEVICES

3.3.1 Introduction and some Theory

In the mid-1980's new processing techniques spawned a renewed effort on the study of Coulomb blockade devices. The theory was reworked [Likharev 1987, 1988; Mullen, Ben-Jacob, Jaklevic, and Schuss 1988; and Amman, Mullen, Ben-Jacob 1989] and offered insights for new experiments. A start to modern Coulomb blockade research can be set as the gated Coulomb blockade device of Fulton and Dolan [1987]. From this point, an explosion of research efforts followed and a variety of phenomena have been explored.

Among top-down devices, research can be broadly grouped into two classes: semiconductor and metallic devices. Semiconductor systems are typically made by a combination of etching and gates on a MBE grown heterostructure, while metallic systems are most often made from evaporated Al. I will cover these two topics separately, for, while they have developed in parallel, the methodologies and techniques used differ.

3.3.2 Metallic Dots

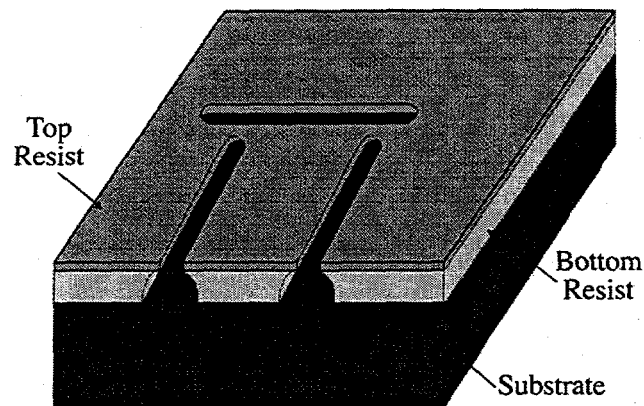
Metallic dots provide a good basis for the understanding of Coulomb blockade. This is because they have minimal quantum structure (see chapter 1) and typically have well defined oxide tunnel barriers. The first lithographically produced metallic dot was fabricated by Fulton and Dolan [1987]. Their dot has a source, drain, and a gate; is made of Al with oxide Al_2O_3 tunnel barriers; and is fabricated by a combination of e-beam lithography and a multi-angle evaporation process [Dolan 1977, Dolan *et al.* 1981, Bishop *et al.* 1985]. Their basic approach has been used in a majority of the metallic devices fabricated since and in figure 3-1 is shown in schematic. First, e-beam lithography is used to draw a pattern in a bilayer resist. The bottom layer of resist is chosen to be more sensitive to the electron beam than the upper layer. As a result the bottom layer is developed away, leaving the top layer as a suspended mask a couple hundred nanometers above the substrate (figure 3-1a). This mask is used in two separate evaporations, each done with the sample tilted at a different angle relative to the evaporation source. Because evaporation is directional* each of these evaporations will reproduce the mask at a different position on the underlying substrate (figure 3-1b,c). Between the evaporations, a bit of O_2 is let into the evaporation chamber to form an oxide barrier. This multiple angle technique is used in the majority of metallic dot systems†. Fulton and Dolan [1987] deposited a Cr-Au film on the back side of the Si substrate for use as a *back* gate, though more recently many have made Al *side* gates alongside their devices instead.

With this device Fulton and Dolan were able to see Coulomb oscillations and the Coulomb gap. Since then, several investigations have improved upon the system and used it to explore novel physics. Of particular interest has been studies on the effect of superconductivity in mesoscopic systems [Lafarge *et al.* 1991, Fulton *et al.* 1989]. Also of note has been the creation of electron turnstiles and pumps. These are 1-D arrays of dots which are driven with a RF waveform to pass a single electron per cycle [Delsing *et al.*

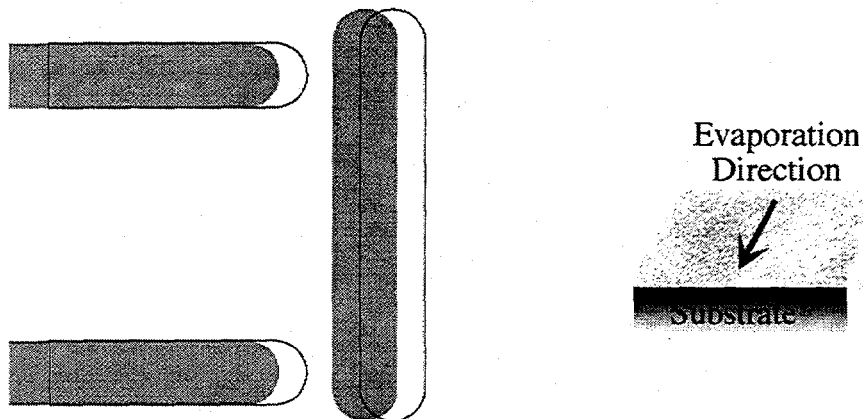
*Like a flashlight

†This technique is also used by us in the formation of our devices and further discussed in chapter 7.

a)



b)



c)

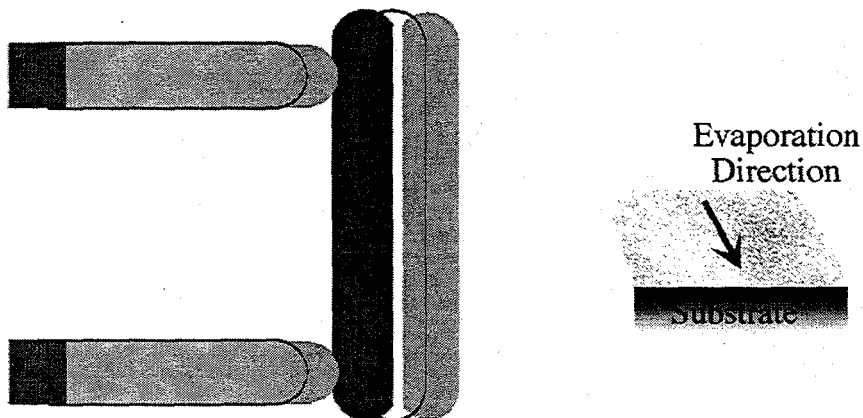


Figure 3-1: Use of the Dolan bridge technique to make an Al dot. a) e-beam patterning is done on a bilayer resist. The bottom layer is more electron sensitive and parts of the upper layer are left suspended. b) Angled evaporation is done on the patterned resist from (a). As a result, the pattern in the top resist (shown with a dark line) is shifted a bit to the left on the substrate (the deposited Al is shown in light gray). This layer is oxidized (now shown with dark gray) and the process is repeated (c) with the opposite angle evaporation (light gray). A oxide tunnel barrier now separates the two Al leads on left from an small Al island.

1989; Geerligs *et al.* 1990b; Pothier *et al.* 1991,1992; for a review, see Esteve 1992]. 2-D arrays have also proven interesting [for a review, see Mooij and Schön 1992].

As previously discussed, these metallic devices typically have charging energies on the order of 1 mV and thus will only exhibit Coulomb blockade phenomena* below 1 K. This is largely a result of limitations in lithography†. Recently, some novel techniques have been used to shrink the island size in the devices and so raise their charging energy. Nakamura *et al.* [1996a, 1996b] have made modifications to the Dolan approach which has allowed for Coulomb effects at temperatures approaching 100 K. Others have used novel lithographic techniques such as scanning probe microscopy (SPM) to locally modify thin films in the hopes of fabricating new metallic devices [Matsumoto *et al.* 1996]. Such approaches offer hope of new devices which probe ever smaller size scales.

3.3.3 Semiconductor Dots

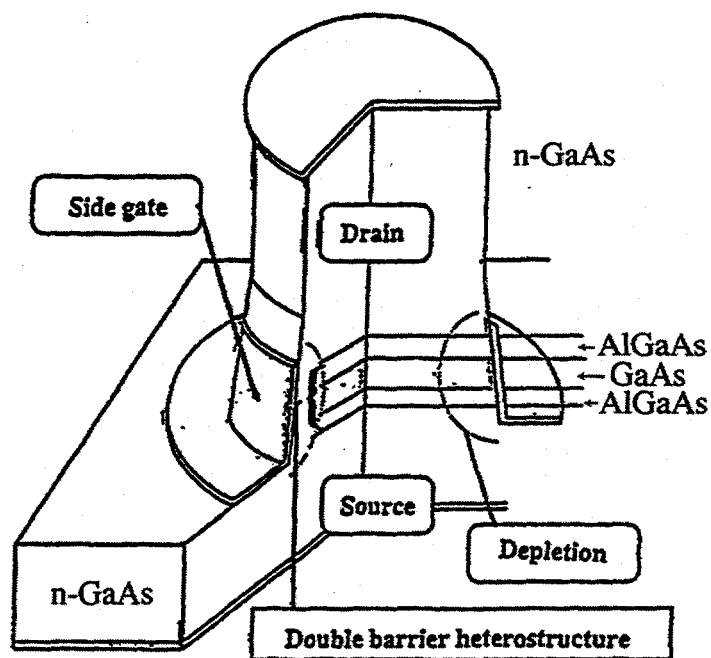
Mesoscopic semiconductor systems offer a wealth of interesting physics as a result of their low carrier densities and long mean-free paths. The majority of semiconductor systems are made from MBE grown GaAs/AlGaAs heterostructures. MBE allows for the deposition of high purity films with monolayer precision. This offers excellent control in the vertical confinement of carriers. Lateral confinement comes as a result of etching and/or gates.

One approach to the study of these heterostructures has been to construct a *vertical dot*. Here a GaAs/AlGaAs heterostructure is etched into sub-micron diameter columns. In figure 3-2a, we show a diagram of a vertical dot fabricated by Tarucha *et al.* [1996]. A dot is formed in a GaAs layer which is sandwiched between two AlGaAs barriers. Transport along the length of the column then probes the nature of the dot formed in the GaAs layer. A gate is deposited on the side of the column to control the electrochemical potential of the

* As discussed in chapter 1, because of the large electron density in metals, single particle states are not visible at obtainable temperatures.

† The best lithography approaches have a resolution limit of ~10 nm.

a)



b)

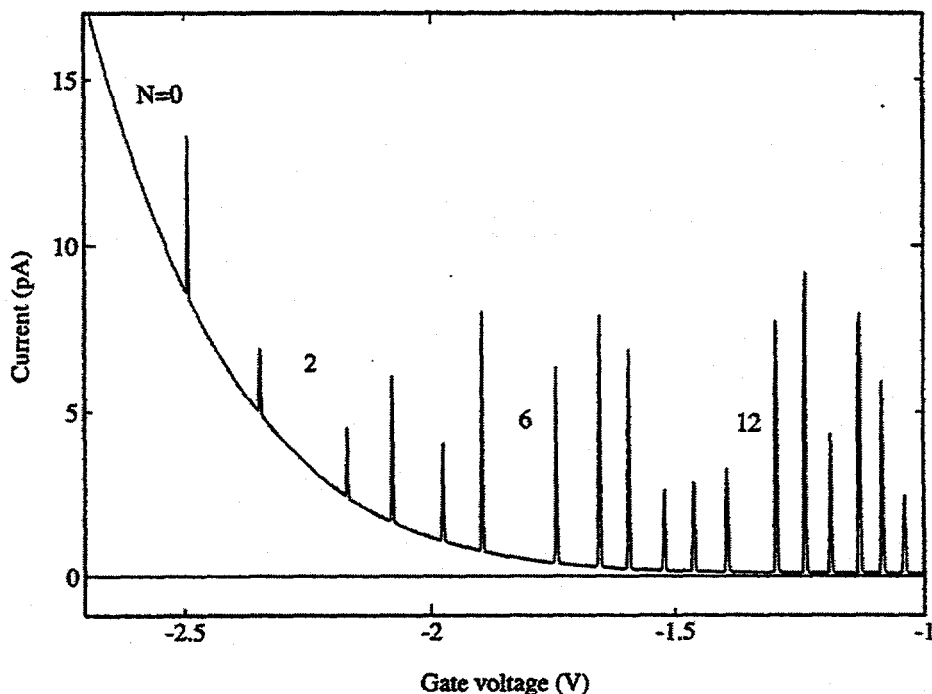


Figure 3-2: (a) Schematic of a vertical quantum dot fabricated by Tarucha *et al* [1996]. Current flows the length of the column and transport studies probe the nature of the dot formed in the GaAs well sandwiched between the two AlGaAs barriers. (b) Linear response of the dot as a function of the gate voltage applied. The gradual rise in current is a result of gate leakage current. Superimposed on this are several Coulomb oscillations. (From Jorg W. Janssen).

dot. In a vertical dot structure, one can completely deplete the dot and then probe its properties as the first few electrons are added. Studies of vertical dots were first performed by Reed *et al.* [1988]. More recently others have expanded upon this work [Su *et al.* 1991, 1992a, 1992b, 1994; Ashoori 1992, 1993, Tarucha *et al.* 1996]. In figure 3-2b we show the response of a vertical dot made by Tarucha *et al.*. Here we see that a -2 V gate bias is sufficient to deplete the dot of electrons. As the gate bias is made more positive, a series of Coulomb oscillations are seen as the first few electrons are added to the dot. The quality of the system is high enough that the quantum shell structure is preserved and a large barrier is seen as the 3rd, 7th, and 13th electrons are added*.

A significant amount of work has also been done on planar systems. Here a heterostructure is grown that confines the carriers to a plane. This sheet of electrons is then patterned into a 2-D device through a combination of gates and etches. The heterostructure typically used is called a two dimensional electron gas (2DEG). A schematic of a particular 2DEG heterostructure is shown in figure 3-3. Here electrons ionize from donors in a AlGaAs layer and fall into an underlying GaAs layer. The electrons are pinned against the GaAs-AlGaAs interface by Coulombic attraction to the now positively charged donor ions. Typically the vertical breadth of the electron wavefunction is < 100 Å and the sheet density is $1-5 \times 10^{11} \text{ cm}^{-2}$. Because the donor ions are separated from the conducting region† and as a result of the high quality of MBE films, electrons traveling in a 2DEG sheet can have mobilities of $> 10^6 \frac{\text{cm}^2}{\text{V}\cdot\text{s}}$.

Because of the low electron density in 2DEG, it can easily be depleted with moderate gate voltages. As a result, metallic leads deposited on the surface can be used to pattern the 2DEG into interesting structures. Figure 3-4a shows a typical 2DEG device [discussed in Dixon *et al.* 1996 and Kouwenhoven *et al.* 1994b]. A plateau of 2DEG runs from the upper left to the lower right of this figure. Bisecting this, lies 5 gates which can be

*These large barriers are the result of filled $l=0, 1$, and 2 shells.

†This is called modulation doping.

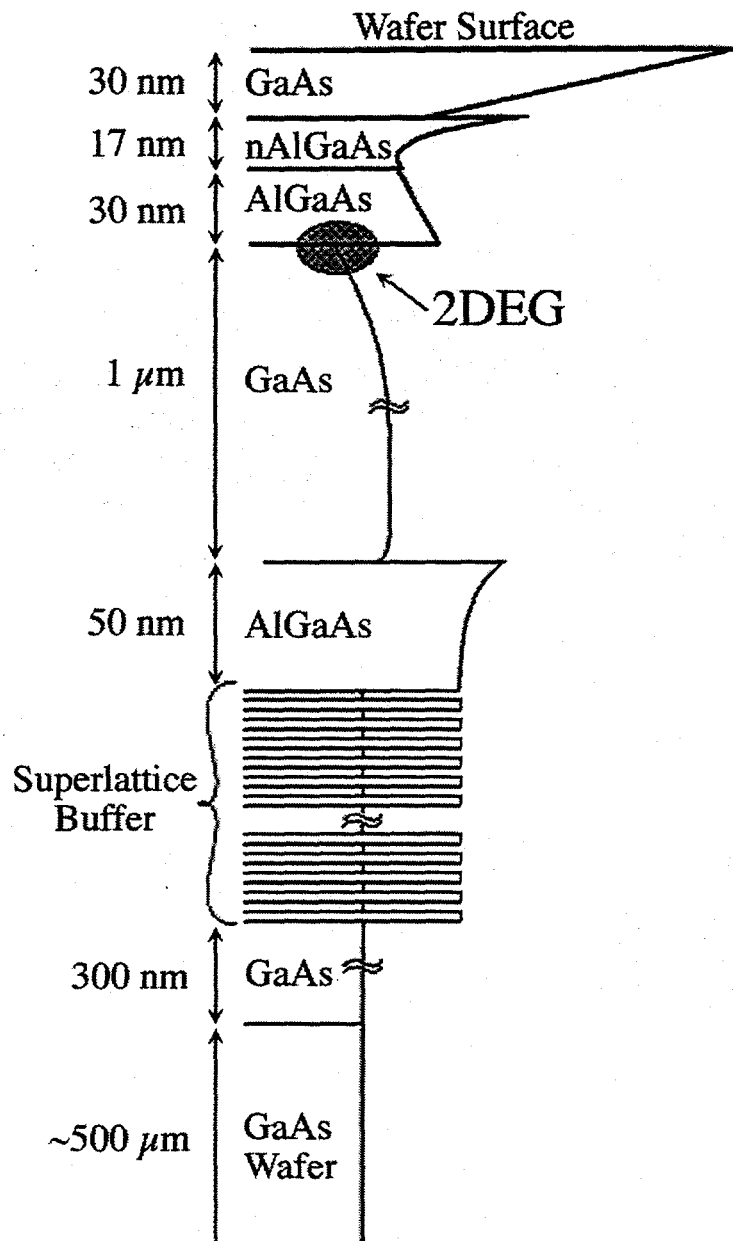
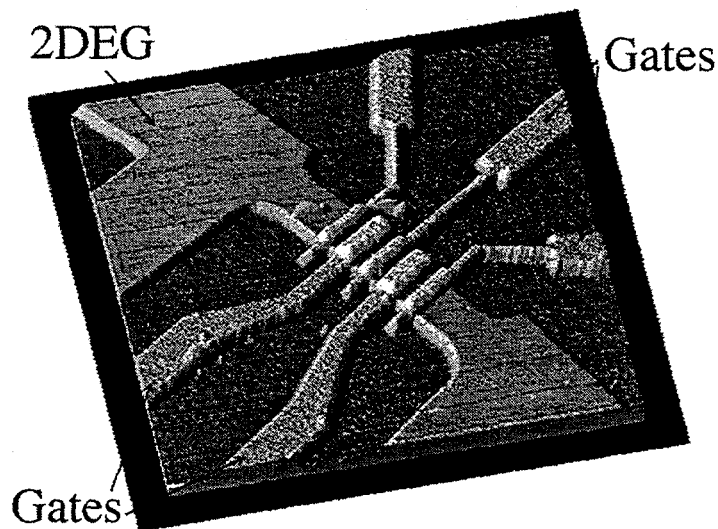


Figure 3-3: Schematic of a typical modulation doped heterostructure used to form a 2DEG. The line on the right sketches how the conduction band varies with depth into the wafer. The 2DEG is formed via the ionization of dopants in the 17 nm thick nAlGaAs layer.

a)



b)

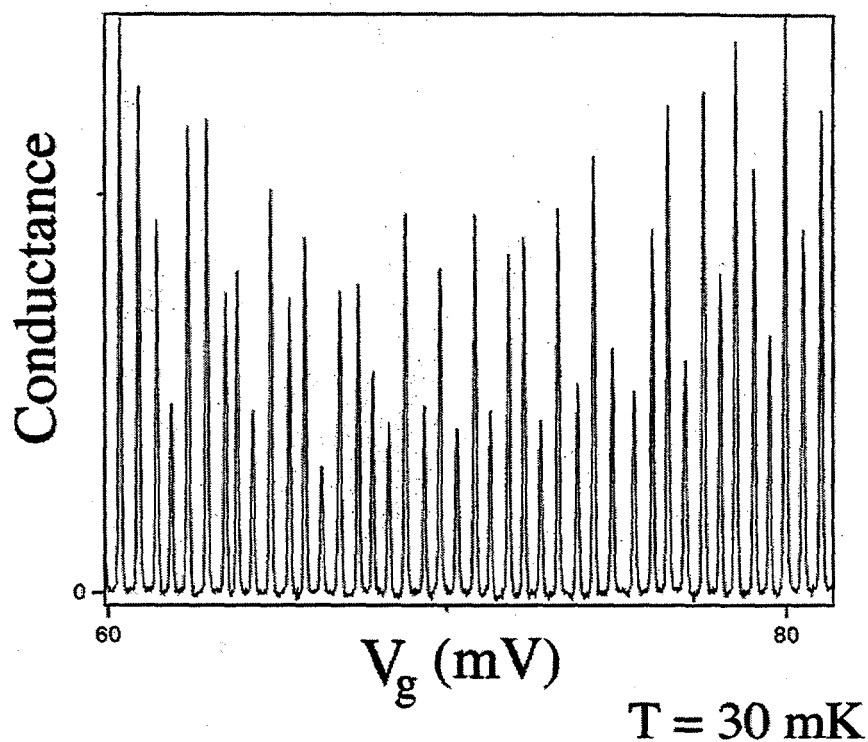


Figure 3-4: (a) AFM micrograph of a representative lateral quantum dot fabricated in 2DEG. Current flows the plateau of unetched 2DEG running from the upper left to the bottom right of this figure. Bisecting this are 5 gate leads which can be used to form either a single or multiple dots. (b) Linear response of a dot formed in this device a function of the gate voltage applied to a central gate. Several Coulomb oscillations of varying peak height and spacing are seen. (From David Dixon).

used to crease a variety of series dot configurations. Figure 3-4b shows Coulomb oscillations, representative of the transport through this system.

Similar 2DEG devices have been used to explore a variety of phenomena. The low electron density allows for the observation of quantum levels in these systems [Foxman *et al.* 1992, Johnson *et al.* 1992, Meirav *et al.* 1991, McEuen *et al.* 1991]. The long mean free path allows for the study of chaos [Baranger and Westervelt 1997]. Coupled quantum dots can be looked at as a laboratory for the study of "artificial molecules" [Livermore *et al.* 1996, Dixon *et al.* 1996, van der Vaart *et al.* 1995, Hofmann *et al.*, 1995]. Magnetic fields also cause interesting effects in the quantum Hall regime wherein a quantum Hall state and Landau levels form [McEuen *et al.* 1991, 1992, 1993, van der Vaart 1994]. AC fields have been used to study these systems as well; RF fields have been used to pass a current through an electron turnstile [Kouwenhoven *et al.* 1991a, 1991b, Odinstov 1991] and higher frequencies have been used to study photon assisted tunneling processes [Kouwenhoven *et al.* 1994a, 1994b, Oosterkamp *et al.* 1997].

Other semiconductor materials have also been used to make dots. In fact the first semiconductor dots were made accidentally in Si [Scott-Thomas *et al.* 1989]. More recent work have expanded the scope of investigations into Si dots [Guo *et al.* 1997 and Matsuoka *et al.* 1994, 1995]. While the complex band structure and low mean free path make Si a more complicated system to explore, its technological worth makes these efforts quite valuable.

Techniques to shrink the size of lithographically defined semiconductor dots are quite limited. This is because, in addition to lithographic limitations*, materials concerns are also a significant factor in these systems. Etching leaves behind a surface with many traps and impurities which will tend to deplete carriers that lie within 100 nm of an etched feature. Gates are no better, for the active region of semiconductor dots often lies ~100 nm below the surface. As a result, the voltage applied to a gate sitting atop the wafer will tend

*Which make sub-10 nm patterning very difficult.

to effect changes on a ~ 100 nm lateral scale in the underlying heterostructure. In the end, headway in the fabrication of sub-100 nm features in lithographically defined semiconductor dots has been slow.

3.4 BOTTOM-UP DEVICES

3.4.1 Introduction

As previously discussed, the fabrication of nanometer scale objects is often more easily done by using growth mechanisms rather than lithographic techniques. This bottom-up approach has a long history and has been exploited to fabricate everything from colored glass to high surface area catalysts. To take an example, nanometer sized Au colloidal particles have been used to form ruby glass and as a pigment (purple of Cassius) since the middle ages [Schmid 1992]. The size related reason for the color was first explained 140 years ago by Faraday [1847] and the modern chemical synthesis of colloidal Au particles was developed almost 50 years ago [Turkevich, 1951].

In the nanometer size regime, Coulombic energies are 10-100 meV and quantum energy spacings range from 0.1 - 10 meV. These energies are a full order of magnitude more than the smallest lithographically defined top-down devices. The first Coulomb blockade devices used a bottom up approach and were fabricated from 2-10 nm diameter grains of Sn grown on a substrate [Giaever and Zeller 1968, Zeller and Giaever 1969]. However these studies looked at numerous grains in parallel and the detailed nature of individual grains could not be seen. More recently, several approaches have been developed to look at one or a few nm-scale particles fabricated with bottom-up growth processes. I will overview some of the routes that have been used to fabricate and measure bottom-up devices below.

3.4.2 SPM Techniques

One approach to the study of nm sized particles has been scanning probe microscopy (SPM) (see appendix B for details). Here one scatters particles about a substrate and then brings a SPM tip above individual particles to perform electrical investigations. By this technique room temperature Coulomb blockade has been seen in metallic grains and clusters. [Schönenberger *et al.* 1992, van Benthum *et al.* 1988, Andres *et al.* 1996]. More recently this approach has been used to look at semiconductor nanocrystals [Alpers *et al.* 1995], large molecules [Soldatov *et al.* 1996,1997], and even single atoms [Yazdani *et al.* 1996]. SPM techniques are limited, however, by the need for mechanical feedback to create and maintain the tip-nanostructure tunnel junction, thus making long term, variable environment, or low temperature measurements difficult.

3.4.3 Other Techniques

To avoid the difficulties and uncertainties inherent to SPM spectroscopy, many novel approaches have been developed for the study of nanometer scale objects

One approach has been to use a break junction [Muller *et al.* 1992]. This is essentially a STM without any lateral motion and can easily be used to make a very stable tunnel junction. Zhou *et al.* [1995] have made a micromachined break junction which can be batch processed and has recently been used to study the transport through an aromatic molecule [Reed 1997].

Another approach has been to find specialized systems which readily form stable nanoscale devices. Ralph, Black, and Tinkham [Ralph, Black, and Tinkham 1995,1997; Black, Ralph, and Tinkham 1996] have studied superconductivity, level structure, and Coulomb blockade in Al grains grown over nanometer sized apertures. Chen and coworkers [1995] have studied Coulomb blockade in several AuPd nanocrystals deposited by ion beam between Au leads. Bockrath *et al.* [1997] and Tans *et al.* [1997] have observed Coulomb blockade in the transport through a carbon nanotube. Drexler *et al.*

[1994] have studied self assembled GaInAs dots in GaAs. These systems have been exploited to form fascinating devices, however they are not readily generalized.

The desire to be able to measure the host of nanometer scale materials currently being chemically synthesized has led many* to find general approaches for the study of nanometer scale objects. One class of approaches has been the use a SPM to position or fabricate nanoparticles in desired locales [McCord and Awschalom 1990, Montelius *et al.* 1997, Junno *et al.* 1995, Müller *et al.* 1995, and chapter 6 of this thesis]. Another has been to fabricate closely spaced leads and hope that a nanocrystal falls in the gap [Bezryadin and Dekker 1997, Klein *et al.* 1996a, and chapters 7 and 8 of this thesis]. Such work holds promise of providing a generalized fabrication scheme, but to date no technique has proven simple or reliable enough for broad application.

3.5 WHERE WE STAND

Having now reviewed some of the relevant literature it is a good idea to review our plans and put them in perspective. Our plan is to measure the transport through Au and CdSe nanocrystals. As we discussed above, Coulomb blockade is a well understood phenomena and has been extensively studied in top-down lithographic devices that operate at sub-Kelvin temperatures. Several groups have made specialized bottom-up Coulomb blockade devices that work at higher temperatures, but are not generalizeable to chemically derived nanocrystals such as CdSe. It is interesting to look at these materials for they can be well controlled by the chemists and have exhibited interesting behavior in various experimental measurements (section 4.3). By formulating a technique to make transport measurements through a CdSe nanocrystals, we can bridge the gap between chemically derived nanocrystals and the physics of single electron transistors; and with a little luck, learn something in the process.

*Including myself.

Chapter 4

The Nature of CdSe Nanocrystals

4.1 INTRODUCTION

Since much of this thesis focuses on electrical investigations of CdSe nanocrystals, we now review their salient characteristics and history. We have chosen to investigate this material because highly monodisperse single crystal CdSe nanocrystals can be readily made over a size regime of 2 to 6 nm. As discussed in chapter 1, for particles in this size range, Coulombic as well as quantum effects are important.

All of the bulk CdSe data discussed below comes from *Landolt-Börnstein Group III, Volume 17b: Semiconductors; Physics of II-VI and I-VII Compounds* [ed. Madelung 1982]. Reviews of CdSe (and other) nanocrystals include Alivisatos [1996a, 1996b] and Brus [1991].

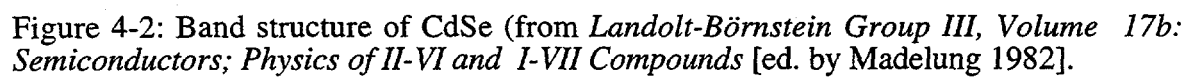
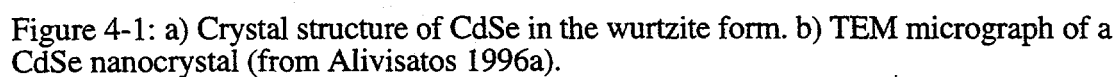
4.2 BULK CDSE

4.2.1 Physical Properties

In ambient conditions, there exist two stable phases of CdSe: wurtzite and zincblende. At high pressures a NaCl cubic phase also exists. The wurtzite phase (diagrammed in figure 4-1a) is the most common and is the phase of our nanocrystals. Table 4-1 lists of some of the physical properties of CdSe in the wurtzite form.

4.2.2 Electronic Structure

The CdSe bonding occurs between Cadmium's $5s^2$ ($L = 0$) atomic orbital and Selenium's $4p^4$ ($L = 1$) atomic orbital. These two atomic orbitals hybridize to form an sp^3 orbital in the crystal. In this hybrid orbital, the six bonding electrons lie in three p-like



Property	CdSe
Room temperature crystal structure	wurtzite and zincblende
Melting temperature	1514 °C
Density	5.81 g/cc ³
Bulk modulus	5.5 x 10 ¹⁰ Pa
Thermal conductivity	0.09 $\frac{\text{W}}{\text{cm}\cdot\text{K}}$
Heat capacity	13 x 10 ⁻³ $\frac{\text{cal}}{\text{mol}\cdot\text{K}}$
Magnetic susceptibility	-6 x 10 ⁻⁵ cm ³ /mol
Debye Temperature	180 K
LO phonon energy	26 meV
TO phonon energy	21 meV
Near IR refractive index ($\lambda = 1 \mu\text{m}$)	2.547
Near IR birefringence ($\lambda = 1 \mu\text{m}$)	0.019
Dielectric constant (DC)	~10
Band gap	1.8 eV
Ionization Energy	6.62 eV
Spin-orbit splitting energy	0.429 eV
Crystal field splitting energy (at the valance band edge)	26 meV
Electron g-factor	0.6
Hole g-factor	1.4
Electron mobility (room temperature)	~500 $\frac{\text{cm}^2}{\text{V}\cdot\text{s}}$
Hole mobility (room temperature)	~50 $\frac{\text{cm}^2}{\text{V}\cdot\text{s}}$
Exciton binding energy	15 meV
Exciton radius	5.9 nm

Table 4-1: Some salient properties of bulk CdSe in the wurtzite form.

states that form the valence band of the crystal. Above these states lies an empty s-like level which forms the conduction band of the crystal.

Figure 4-2 shows the calculated band structure of CdSe in the wurtzite phase. CdSe is a direct bandgap semiconductor, with a bandgap of 1.75 eV (at 300 K). The energy required to ionize an electron from the valence band of CdSe (to vacuum) is 6.62 eV.

Ideally, all three p-like bands of CdSe would be of equal energy at the high symmetry Γ point. In reality, spin-orbit and crystal field effects split these bands. Near the Γ point, the best way to label the crystal bands is by their total spin, J . Here, the $L = 1$ p-like crystal state couples strongly to the electron spin, resulting in a 4-fold degenerate $J = 3/2$ state and a 2-fold degenerate $J = 1/2$ state. Spin-orbit coupling lowers the $J = 1/2$ band 0.429 eV below the $J = 3/2$ band. There is also a small crystal field splitting of the $J = 3/2$ band into two doubly degenerate bands separated by 26 meV. Away from the Γ point, $k \cdot p$ splitting further separates the $J = 3/2$ states.

The effective mass of electrons in the conduction band is $0.11 m_e$ (m_e is the bare mass of the electron). The effective mass of holes in the valence band is $0.45 m_e$ perpendicular to the c axis and $\sim 1.0 m_e$ parallel to the c axis.

4.3 CDSE NANOCRYSTALS

4.3.1 Fabrication

Many methods exist for the preparation of CdSe nanocrystals. Our nanocrystals are made in solution by a prompt nucleation technique [Murray *et al.* 1993, Bowen-Katari *et al.* 1994, and see appendix C]. In this fabrication route, a solution containing Se and Cd is injected into heated (350°C) tri-*n*-octyl phosphine oxide (TOPO) resulting in the prompt nucleation of CdSe nanocrystals. Growth is then limited by the rapid depletion of starting materials in the solution and the resultant nanocrystals are highly monodisperse ($< 5\%$ size variations). The TOPO then ligates to the nanocrystals' surfaces, stabilizing the

nanocrystals and preventing agglomeration. In figure 4-1b we show a TEM micrograph of a CdSe nanocrystal fabricated by the above process

Similar techniques can be used in the fabrication of other II-VI (including CdS, ZnS, and HgS) and I-VII (including AgI and CuCl) nanocrystals. Synthesis routes for III-V (such as InP and GaAs) and group IV (such as Si and Ge) nanocrystals have also been demonstrated. These syntheses are more difficult owing to the higher degree of covalence of these materials and the associated difficulties in annealing them.

Other fabrication techniques for CdSe (and other) nanocrystals include growth within an inverse micelle [Steigerwald *et al.* 1988 and Kortan *et al.* 1990], electrodeposition [Golan *et al.* 1992,1994; Alpers *et al.* 1995], electrospray organometallic CVD [Denek *et al.* 1994], and nucleation within in a glass matrix* [Borelli *et al.* 1987 and Tanaka *et al.* 1992].

4.3.2 Electronic Structure - Theory

As discussed in chapter 1, one would expect both electrostatic and quantum confinement energies to be quite significant in CdSe nanocrystals. The simplest way to calculate these energies is to consider the electrostatic and quantum effects separately. The electrostatic (or charging) energy can then be calculated in the same way as was done for metallic particles (section 1.3.2). To this energy the system's quantum confinement energy levels are then added.

Several approaches have been taken to calculate the quantum confinement energy levels of a CdSe nanocrystal. In the simplest, the nanocrystal is treated as an infinite spherical well. The energy levels of a spherical well were introduced in chapter 1 (equation 1-8) as:

$$E_{nl} = \frac{0.37}{r^2} \left(\frac{m_e}{m^*} \right) \left(\frac{\alpha_{nl}}{\pi} \right)^2 eV \cdot nm^2. \quad (4-1)$$

*This technique is used to make several commercial color filters.

Here n and ℓ are the quantum numbers for each state and $\alpha_{n\ell}$ is the n^{th} zero of the ℓ^{th} order spherical Bessel function. Each state is $2\ell+1$ degenerate and has orbital angular momentum $\ell\hbar$. Figure 4-3 shows the energy spectrum resulting from equation 4-1. In this figure, we labeled each energy state as $n\ell$ (with $\ell=0$ labeled as "S", $\ell=1$ labeled as "P", and so on). Near the Γ point of CdSe, one can then use the electron effective mass ($0.11 m_e$) to estimate the energy levels of the conduction band and the hole effective mass ($\sim 1.0 m_e$) to estimate the energy levels of the valence band.

This model does not account for any band-band interactions. This is generally not a problem for conduction band calculations, as the conduction band is an isolated, doubly degenerate band. The valence band, however, is comprised of three separate bands (the heavy-hole, light-hole, and spin-orbit bands). Ekimov *et al.* [1993] considered band-band interactions and non-parabolicity effects in their calculations of the level structure of a CdSe nanocrystal. A plot of the single-particle energy states that they calculate as a function of nanocrystal size is shown in figure 4-4*. In their results, the conduction band states are similar in nature to those calculated above (see inset to figure 4-4), while in the valence band, the situation is more complicated. The three valence bands mix with the various angular momentum states of the nanocrystal's envelope function. The resultant states are best expressed in terms of the total hole angular momentum, $\bar{F} = \bar{J} + \bar{\ell}$, and ℓ^* , the new orbital quantum number. ℓ^* is formed from a combination of the $\ell = \ell^*$ and $\ell = \ell^* + 2$ spherical harmonics, an effect referred to as *S-D mixing*. The hole states of a nanocrystal are denoted by $n\ell^*_F$. The $1S_{3/2}$ level then is a linear combination of the ($\ell=0, J = 3/2$), ($\ell=2, J=3/2$) and ($\ell=2, J=1/2$) states of the unperturbed system. The energies of these states as calculated by Ekimov *et al.* compare favorably with experimental studies on the overall structure of the energy levels of a CdSe nanocrystal [Norris and Bawendi 1995a, Norris *et al.* 1995b].

*This calculation was originally performed for comparison to optical experiments on nanocrystals. As a result, only the hole states which contribute to optically allowed transitions are shown.

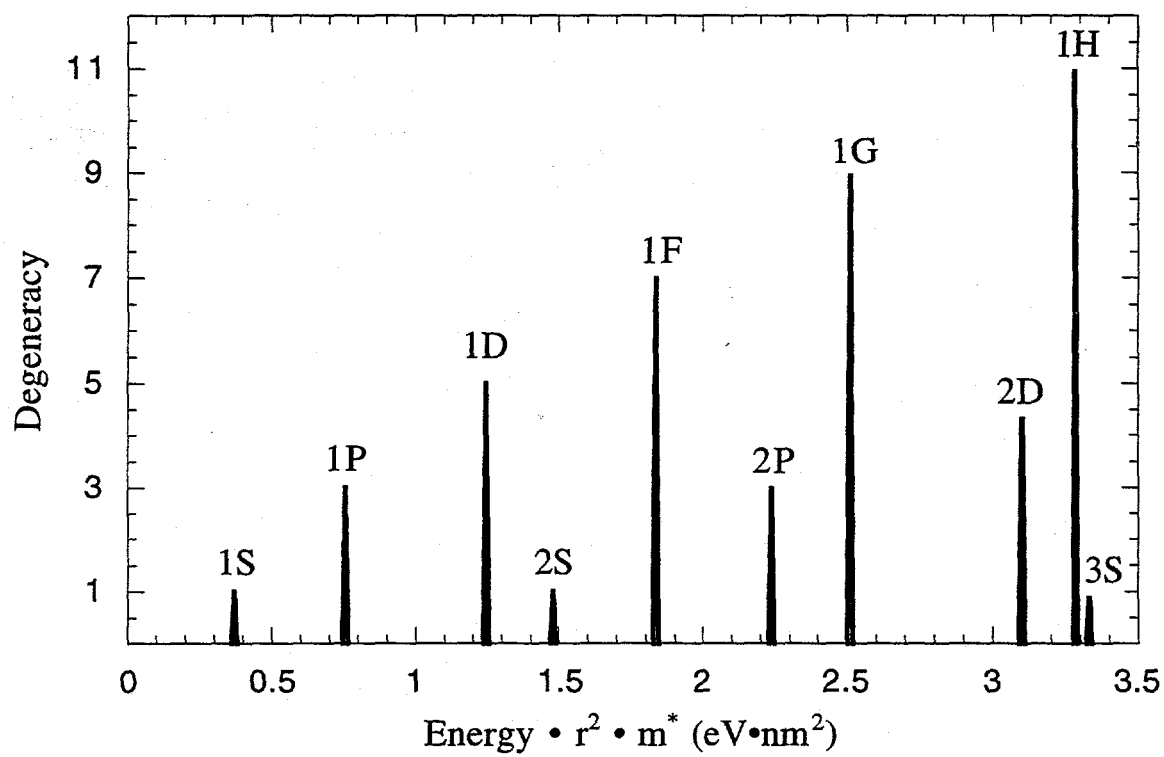


Figure 4-3: The first ten energy states of an infinite spherical well of radius r .

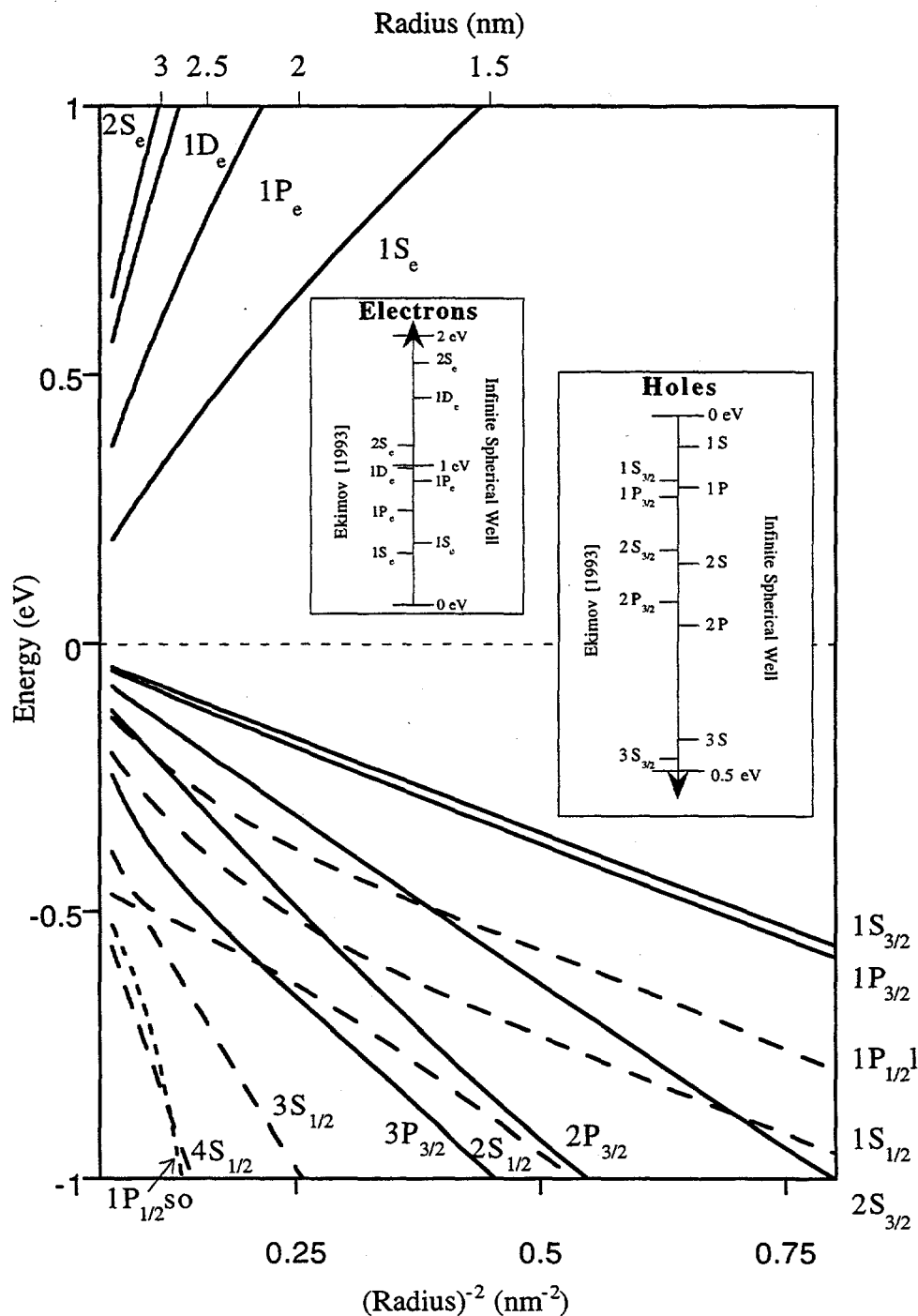


Figure 4-4: The electron and hole energy spectra as modeled by Ekimov *et al.* [1993] and calculated by Uri Banin. As this calculation was originally performed for comparison with optical spectroscopy experiments, only states which have optically allowed transitions are shown. For clarity we have drawn the $F = 3/2$ states with solid lines and the $F = 1/2$ states with dashed lines. In insets to this figure we compare this calculation of the electron and $F = 3/2$ hole spectra with the infinite spherical well model discussed in the text. This comparison is done for a 5.5 nm diameter nanocrystal (this is the size that we study in chapter 8). Only those levels which exist in both models are compared in these insets.

The calculation of figure 4-4 does not account for crystal field splittings, a significant effect (26 meV for bulk CdSe) on the level structure of CdSe. It also does not account for surface effects such as dangling bonds [Wang and Duke 1987], non-spherical nanocrystals [Efros and Rodina 1993], or a permanent nanocrystal electric dipole moment [Schmidt *et al.* 1997, Blanton *et al.* 1997]. Such effects can induce level splittings and shifts of order 10 meV and a full calculation of the energy states of a CdSe nanocrystal must take them into account. For example, recent experimental results have inferred significant interactions between even and odd parity states of the nanocrystal envelope function [Sacara *et al.* 1995, Schmidt *et al.* 1997]. This effect, which is likely associated with a dipole moment in the nanocrystal, causes significant deviations from the energy levels described in the above theory. Recent theoretical efforts have addressed some of these issues [Nirmal *et al.* 1995, Efros *et al.* 1996]. However, further experiments and calculations will be needed to fully understand the quantum confinement energy levels of nanocrystals.

We end this section by noting that the above discussion has neglected the consequences of electron-electron interactions on the energy levels. For a few electron (or hole) system, exchange and correlation energies have important effects on the level structure. In electron transport experiments*, one measures the energy required to add (or remove) an electron to (from) a nanocrystal. As the number of electrons on the nanocrystal is changed, its level structure and effective capacitance can also change [Tarucha *et al.* 1996 and Iafrante *et al.* 1995]. A full calculation of the addition energies present in a CdSe nanocrystal has yet to be performed.

4.3.3 Electronic and Physical Structure - Experiment

A variety of techniques have been used to study size dependent effects in CdSe nanocrystals. Their structure has been investigated by transmission electron microscopy

*Such as Coulomb oscillation experiments (see sections 2.3.2 and 2.4).

(TEM) [Shiang 1995], XPS has been used to study their surface [Bowen Katari *et al.* 1994], and X-ray diffraction has been used to study phase transitions [Tolbert and Alivisatos 1994].

Optical techniques such as optical absorption [Mittleman *et al.* 1994, Bawendi *et al.* 1990a], luminescence [Bawendi *et al.* 1990b], and hole burning [Bawendi *et al.* 1990b] have been used to measure quantum confinement energies. A recent extension to these optical measurements has been single nanocrystal spectroscopy [Empedocles *et al.* 1996]. The dipole moment of CdSe nanocrystals has been studied by two-photon spectroscopy and by dielectric dispersion measurements [Schmidt *et al.* 1997, Blanton *et al.* 1997]. Femtosecond spectroscopy has been performed to learn about carrier dynamics [Mittleman *et al.* 1994] and the phonons have been studied by resonant Raman spectroscopy [Shiang *et al.* 1995].

Recently, more complicated nanocrystals geometries have been created and studied. These include core-shell structures [Hines and Guyot-Sionnest 1996], dimers [Alivisatos *et al.* 1996], and superlattices [Murray *et al.* 1995]. Also of interest has been the fabrication of novel nanocrystal devices such as LEDs and photovoltaics [Colvin *et al.* 1994, Dabbousi *et al.* 1995, and Greenham *et al.* 1996].

Chapter 5

Scanning Probe Studies of Surfaces

5.1 MOTIVATION

As discussed in chapter 3, scanning probe microscopy, SPM (for an introduction to SPM please see appendix B), can be a good platform for nanometer scale electrical characterization of surfaces. This is because one can first use a SPM to image a surface and then use the same probe to electrically characterize structures of interest. An example of this approach is the use of a STM to electrically investigate isolated metal grains deposited on a substrate. Such STM studies reveal transport phenomena such as Coulomb blockade at room temperature [Schönenberger *et al.* 1992, van Benthum *et al.* 1988].

Encouraged by this work, we initiated SPM studies of CdSe and Au nanocrystals bound to a substrate by a monolayer of bifunctional linker molecules (appendix C). In this chapter, I will first discuss our efforts to image nanocrystals bound in such a fashion. I will then follow with a study in which we used the tunneling current from a metallic AFM stylus to explore solvation phenomena. These conducting AFM studies helped us to understand the influence of the environment on the imaging and electrically probing of a submerged surface. Further discussion of this work can be found in two published reports [Klein *et al.* 1995, Klein *et al.* 1997a].

5.2 STM IMAGING OF NANOCRYSTALS

Our first SPM goal was to image nanocrystals bound to a substrate by hexane dithiol linker molecules (for an overview of nanocrystal synthesis and bonding, please see appendix C). This obvious, yet non-trivial, first step towards electrical studies proved my bane for nearly a year. My problems were in common with others' anecdotal and published reports [e.g. Dorogi *et al.* 1996, Womelsdorf *et al.* 1991, Schleicher *et al.* 1993, and Ogawa *et al.* 1995].

For a substrate we chose a ~ 1000 Å thick Au film deposited on freshly cleaved mica. Because Au tends to have a grain size of a few nm (see Figure 5-1) we annealed the film overnight at ~ 350 °C to promote grain growth. The resultant substrate is shown in figure 5-2. Its large grains allow for the easy identification of nanometer scale particles. We then plasma cleaned this surface, and deposited the bifunctional layer followed by either Au or CdSe nanocrystals. By bringing a SPM tip within tunneling contact of nanocrystals deposited in the above fashion, one can expect to see Coulomb blockade phenomena at room temperature.

Figure 5-3 shows STM images of surfaces coated with 30 nm Au particles [made by British BioCell International]. These particles appear with bloated and distorted shapes and have heights ranging from 15 to 30 nm. As we change the operating conditions of the STM, we have observed that the particles are swept away and occasionally permanently distorted. Such tip-sample interactions are very similar to those seen by others trying to measure colloidal particles [for e.g. Schleicher *et al.* 1993 and Dorogi *et al.* 1995] and indicate that the STM tip perturbs our sample's morphology. Despite this damage, we made several attempts to take electrical spectra of nanocrystals using the STM. Unfortunately none of these spectra could be reproduced with sufficient consistency for interpretation.

The surface modification seen in figure 5-3 is likely the result of high forces applied by the STM's tip on the substrate [of a discussion, see Salmeron *et al.* 1991]. This is because the STM only uses tunneling current for feedback. The presence of a thin insulating layer atop the substrate can thus result in the application of large forces as the tip attempts to broach this barrier in an effort to source a current. This issue led us to force feedback (AFM) imaging of nanocrystals.

5.3 AFM IMAGING OF NANOCRYSTALS.

Figure 5-4 shows an attempt to image 28 Å diameter CdSe nanocrystals using contact AFM in ambient conditions and is typical of our attempts to image nanocrystals

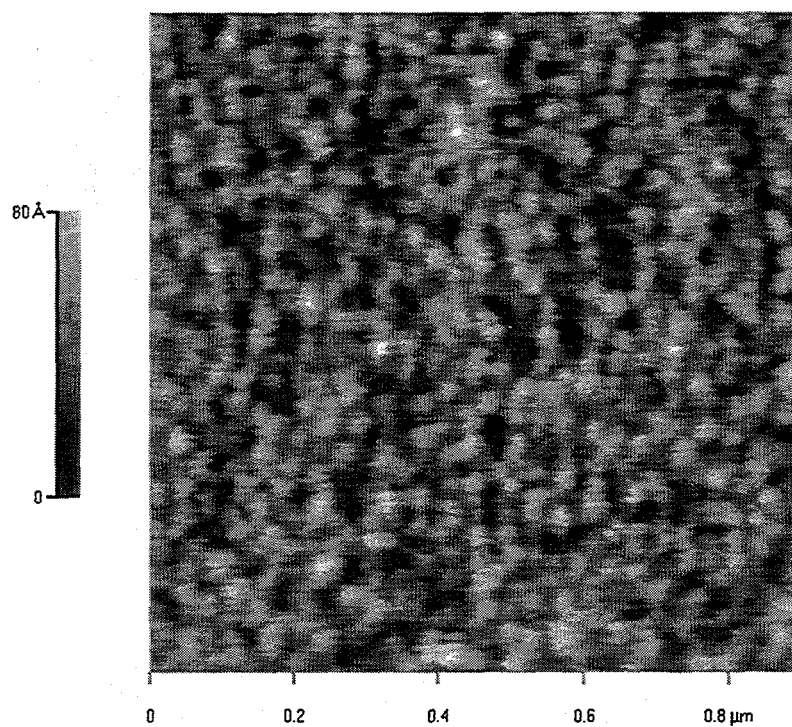


Figure 5-1: AFM micrograph of the morphology of a ~100 nm thick Au film on mica.

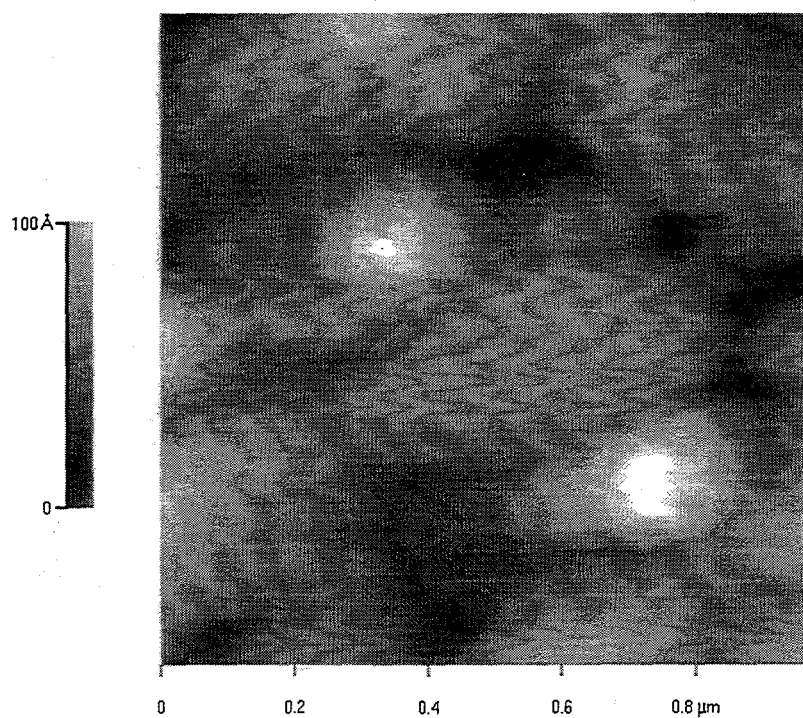
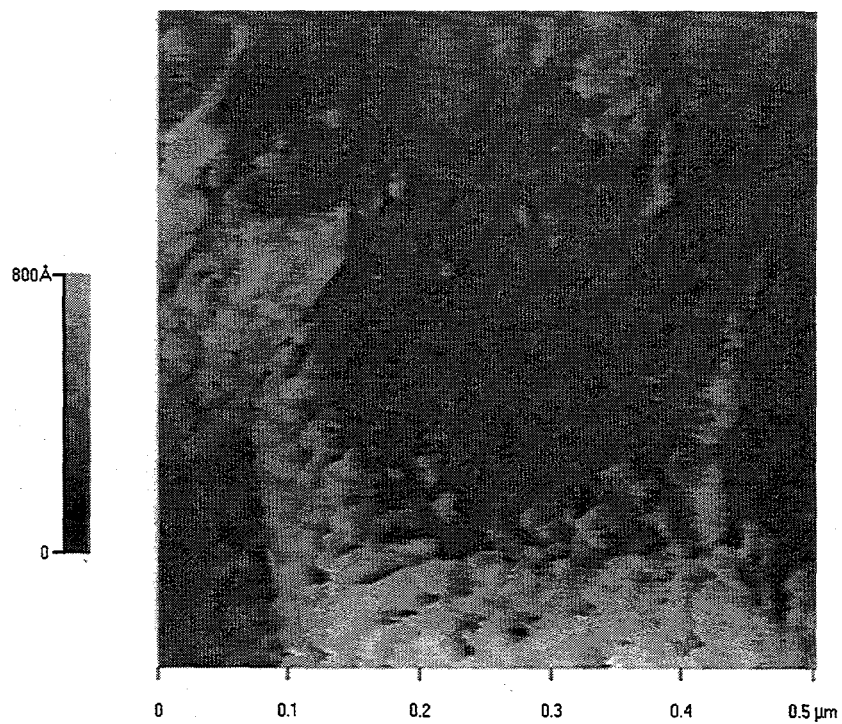


Figure 5-2: AFM micrograph of the morphology of a ~100 nm Au film on mica which has been annealed at 350 °C overnight.

a)



b)

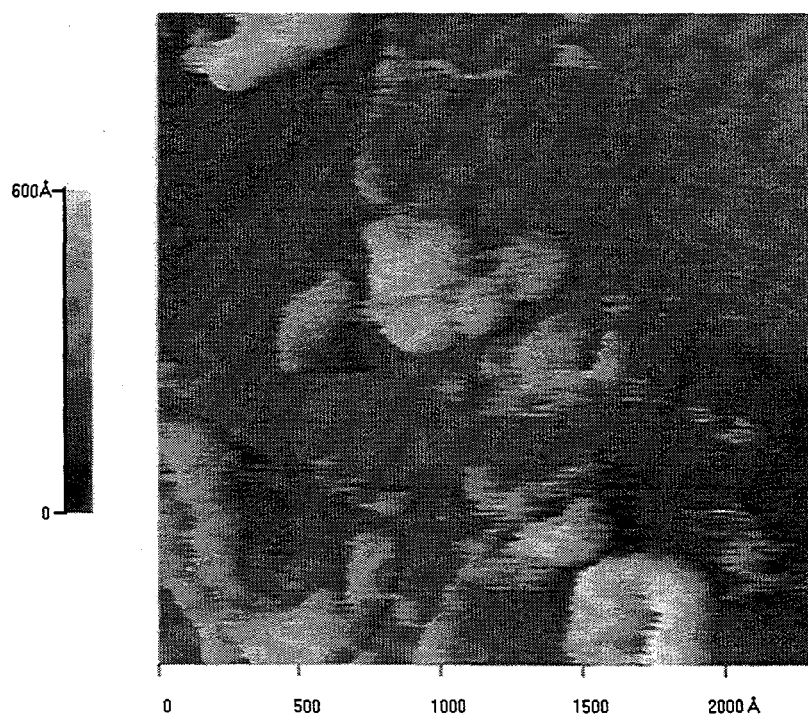


Figure 5-3. a) STM view of 30 nm colloidal Au particles deposited on annealed Au. b) STM image of the region just below the center of (a).

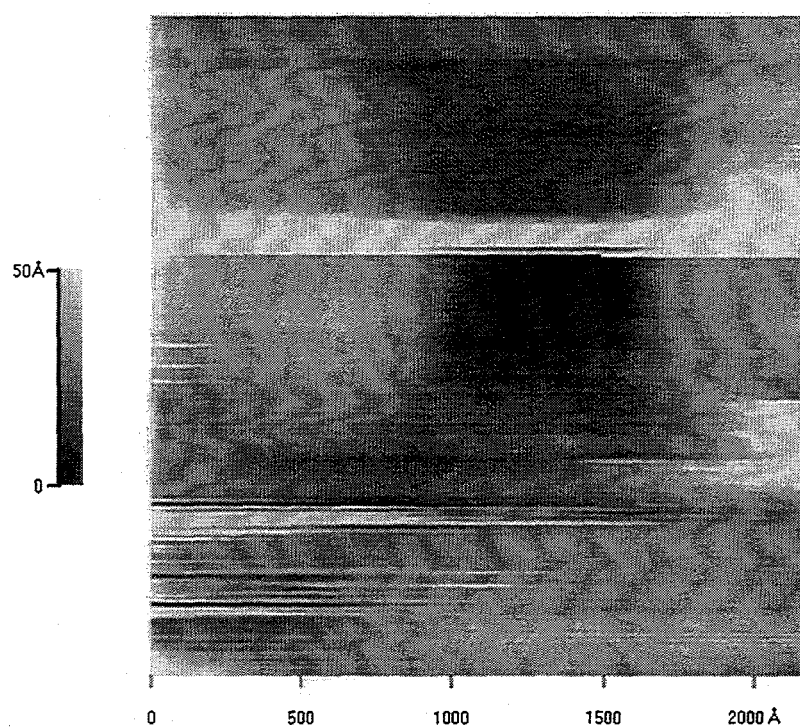


Figure 5-4. Attempt at an contact AFM image in ambient conditions of 28 Å CdSe nanocrystals. The reproducible features are the annealed Au substrate, while the nanocrystals appear as non-reproducible streaks as they are pushed about by the stylus.

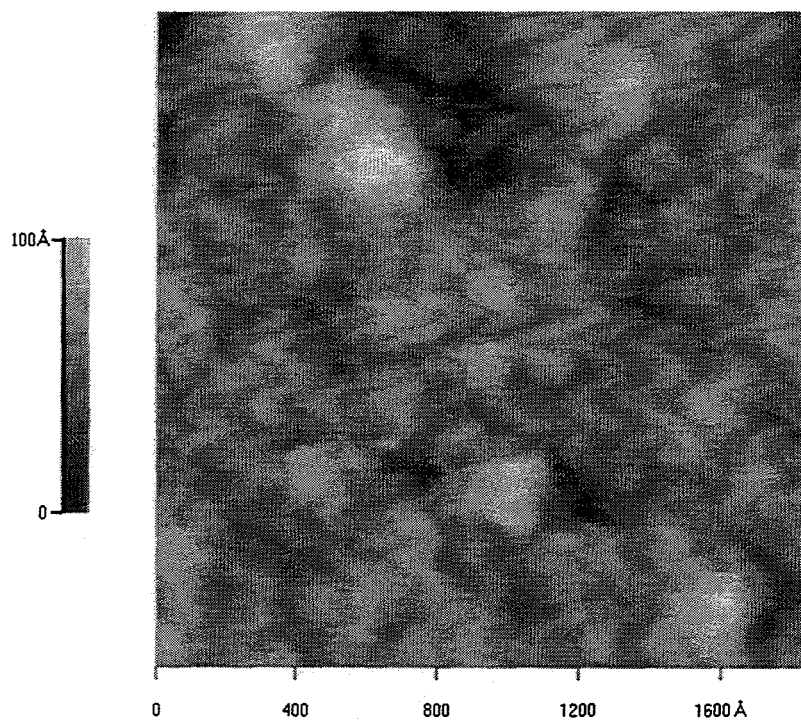
under these conditions. In general, as the stylus traverses the surface, it displays long, non-repeatable "streaks". These features are consistent with the notion of the tip knocking clusters from their binding site and then surfing them along the sample. At the point one is able to achieve a stable image, the sample is observed to be barren.

The inability to image these particles in ambient conditions arises from the capillary forces associated with water that condenses onto surfaces from the atmosphere. When the stylus is in contact with the sample, the wetting nature of the water induces an attractive tip-substrate interaction [M. Binggeli and C. M. Nate 1994, J. N. Isrealachvili 1992]. This effect can be measured by noting how much force is required to pull the tip away from the substrate. For our system, we typically measure such a force to be on the order of 30 nN. A sense of this can be obtained by noting that a nN is approximately an eV per Å, the order of the deformation and energy required to break a single covalent bond. Hence, 30 nN is more than sufficient to tear nanocrystals from their mooring to the substrate, thereby inhibiting the imaging of nanocrystals bound with hexanedithiols in ambient conditions. To avoid such capillary forces, we must use either non-contact imaging, or perform the AFM in a liquid environment or desiccated environment. We chose to explore contact imaging in a liquid environment.

In liquid we are able to image both CdSe and Au nanocrystals attached to a Au film via hexane dithiol. An image of a field of 28 Å diameter CdSe nanocrystals in isopropanol appears in Figure 5-5a. This image was obtained with a Si stylus and an imaging force of 0.5 nN. Notably, this is the same sample we could not image in air in figure 5-4. Figure 5-5b shows the same region after the stylus was rastered over a 50 nm square region with a normal force of over 20 nN. This was sufficient to remove the nanocrystals from the substrate and consistent with the problems we have when imaging in air.

In figure 5-6, we show a histogram of the measured heights of 28 Å CdSe nanocrystals. The mean measured height of these particles is 38 ± 15 Å. While within experimental error, this discrepancy can be the result of undersampling of small

a)



b)

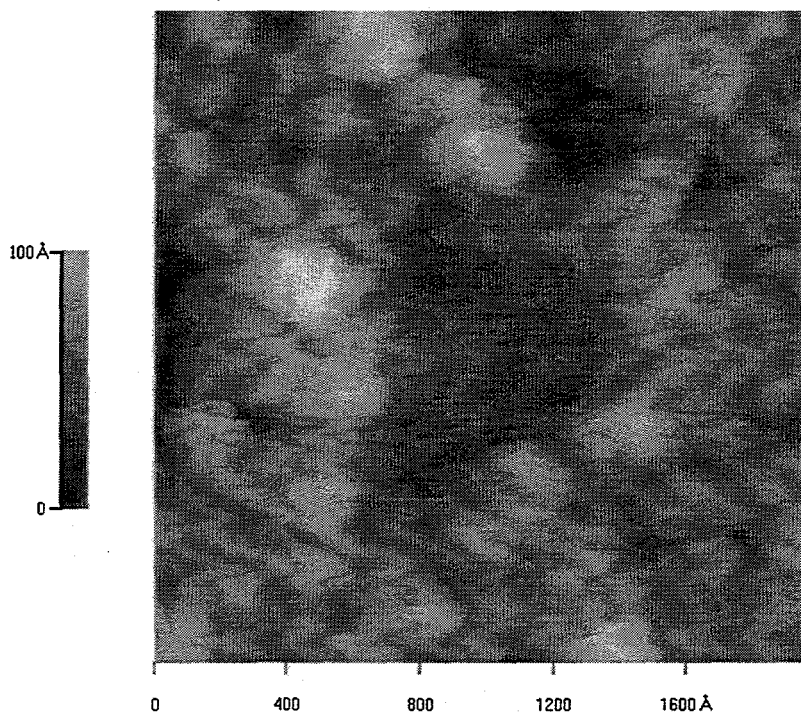


Figure 5-5: a) Topography of 28 Å CdSe nanocrystals measured by AFM in isopropanol. The mean measured height was 40 Å while the diameters are enlarged by the stylus. b) An image of the same area after a 50 nm square region in the center was scanned for several minutes with ~20 nN of force.

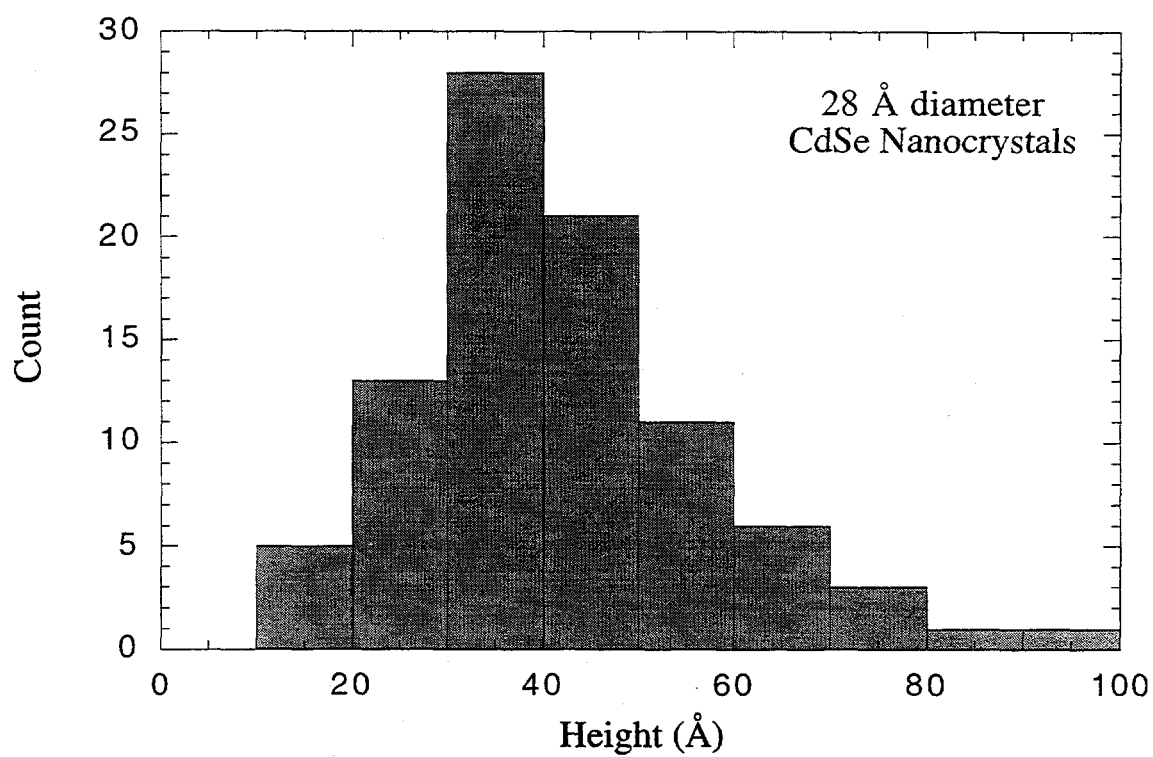


Figure 5-6: AFM measurements of the height of a variety of 28 Å diameter CdSe nanocrystals using a tip with a 100 Å nominal radius of curvature. The mean measured height is 38 ± 15 Å.

nanocrystals. It can also be the result of the TOPO layer that coats the nanocrystals (appendix C). The measured diameters of the particles are greatly expanded owing to the finite radius of curvature of the stylus (appendix B). By comparing the height and diameter of the nearly spherical [Shiang *et al.* 1995] nanocrystals, we can geometrically estimate the tip radius to be $\sim 110 \text{ \AA}$, in good agreement with the nominal tip curvature (appendix B). It should be noted that this artificial increase in the particle's diameter induced by the tip causes nanocrystals to appear to touch even when they are separated by several nanocrystal diameters.

Now armed with an approach to image our nanocrystals with an AFM, we needed to learn how to pass a current through the nanocrystals. The difficulties surrounding this issue are addressed in the next section.

5.4 CONDUCTING AFM AND SOLVATION PHENOMENA

5.4.1 The Plan of Attack

To make electrical measurements with an AFM, we first have to make the AFM stylus conduct. This was done by RF sputtering a 3 nm thick Cr adhesion layer followed by 15 nm of either Au or Pt onto the bottom of the AFM cantilever. RF sputtering was used (rather than evaporation) for deposition because it is not directional and therefore will uniformly coat the high aspect ratio AFM tip. Electrical contact to this film is then made with silver paint at the base of the cantilever.

We next have to learn how to interpret electrical measurements made with an AFM in a liquid. This is a non-trivial issue because liquids do not represent a completely innocuous environment. While liquids lack long range order, molecular interactions lead to correlations over several molecular diameters [Israelachvili 1992a, Israelachvili 1992b]. These correlations lead to solvation forces between closely spaced solid surfaces. These forces can be either repulsive or attractive and either monotonic or oscillatory. When the forces are oscillatory, the liquid is effectively layering onto the immersed surfaces as quasi-

crystalline boundary layers. Many measurements of such layering has been performed on macroscopic regions of mica using a surface force apparatus (SFA) [Horn *et al.* 1981]. More recently, others have extended these measurements by measuring oscillatory forces between an AFM tip and a substrate due to the presence of molecular layers [O'Shea *et al.* 1992, Lantz *et al.* 1994].

5.4.2 Force vs. Distance Measurements on HOPG in Hexadecane

As a test system to learn about solvation and AFM electrical investigations in a liquid, we examined the tunneling current between a metallized AFM tip and a highly oriented pyrolytic graphite (HOPG) substrate. HOPG was chosen as a substrate for electrical AFM measurements because it conducts and is easily cleaved to reveal a clean crystalline surface.

Measurements were made on freshly cleaved HOPG immersed in 99% pure hexadecane. Hexadecane is a highly non-polar liquid and as a result has low ionic conduction. This system has been shown to exhibit particularly strong solvation effects due to the near epitaxial match between the C-C bonds of the hexadecane and the underlying HOPG lattice [McGonigal *et al.* 1991, Elbel *et al.* 1994]. This lattice matching enhances the physisorption of an alkane monolayer to the substrate. Onto this well ordered layer, subsequent molecular layers are formed. Each additional layer is less crystalline, leading to a gradual transition to the isotropic liquid state.

We first measured the separation between the tip and the sample as a function of the normal force inferred from the deflection of the AFM cantilever as a function of z-piezo extension. Figure 5-7 depicts a force versus distance characteristic measured with a Si cantilever. Periodic jumps are seen in the tip-sample separation as the force is increased or decreased. As the normal force increases above 20 nN, the opposing solvation forces become large and repulsive; steps are difficult to ascertain in this region. Note that the inferred tip-sample distance is relative, hence the absolute position of the substrate's

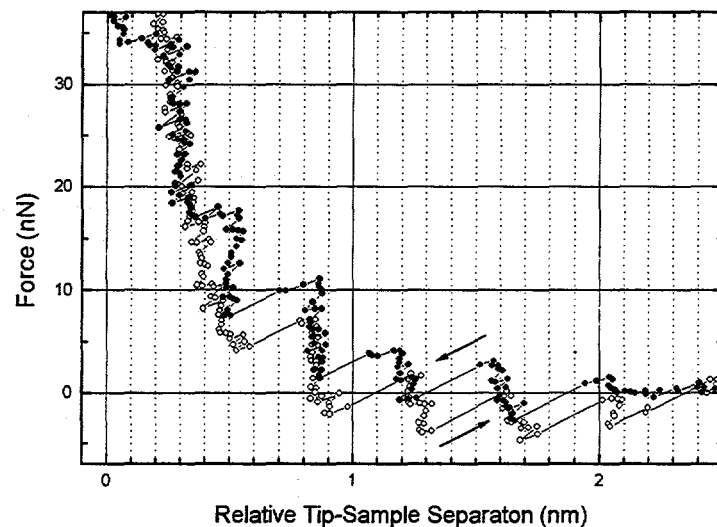


Figure 5-7. Tip-sample normal force measured against tip-sample relative separation for a Pt coated tip and HOPG in hexadecane. The filled (open) circles are measured as the force increases (decreases). The zero on the x-axis is arbitrary. The mean period of the observed force oscillations is 4.0 ± 0.4 Å.

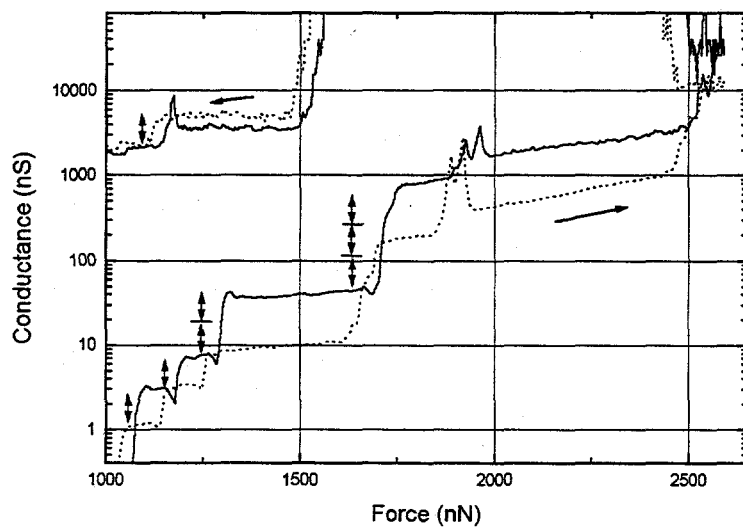


Figure 5-8. Tip-sample conductance measured against tip-sample normal force for a Au coated Si_3N_4 tip impinging on HOPG in hexadecane. The dotted line represents a measurement taken immediately after the solid line. Each measurement was taken over a period of 100 seconds.

surface is unknown. As the tip-sample conductance is immeasurably small in this region (<100 pS) the separation must be at least several nm.

The jumps in the tip-sample separation seen in figure 5-7 are a consequence of a solvation induced oscillatory force law between the tip and substrate [Israelachvili 1992a, O'Shea 1992]. Each jump represents the displacement of a single molecular layer from underneath the tip. The mean period of oscillation is 4.0 ± 0.2 Å. This is in good agreement with the effective diameter of alkanes (~ 4 Å). Such layering of alkanes on HOPG has also been observed with a SFA and by STM imaging [Horn 1981, Magonov 1994].

5.4.3 Conductance vs. Distance Measurements on HOPG in Hexadecane

As the tip-sample force exceeds tens of nN for sharp Si tips, or hundreds of nN for blunter Si_3N_4 tips (see appendix B), the tip-sample conductance becomes measurable. Figure 5-8 depicts the logarithm of the tip-sample conductance, G , versus the applied force for a Si_3N_4 tip, measured during two successive approaches and retractions. As the force is increased, the conductance is observed to increase in a series of jumps. At smaller forces (< 1300 nN), the steps are roughly equal in height (on a logarithmic scale) and represent ~ 2.2 fold increases in the conductance. At higher forces, the jumps are typically larger. As the force exceeds 2500 nN, the conductance jumps to an immeasurably large value (> 100 μS). As the force applied to the tip is diminished, the conductance remains relatively high until the force drops below zero, at which point the tip completely separates from the substrate. On the second measurement (dotted line), the sequence is somewhat different, but many of the conductance plateau values coincide.

The conductance jumps of figure 5-8 are interpreted as a result of the penetration of successive molecular layers by the AFM tip. For low bias tunneling through a square barrier, the tunneling conductance is expected to vary as [Simmons 1963]:

$$G \propto e^{-\kappa z}, \quad (5-1)$$

where $1/\kappa$ is the decay length associated with the barrier between the tunneling electrodes and z is the separation between the electrodes. To determine κ , we simultaneously measured the conductance change and the change in the tip-sample distance at a conductance jump (in the limited parameter region where both could be simultaneously obtained) for a number of coated Si tips. The value of the decay length, for $G < 1 \mu\text{S}$, was found to be $1/\kappa = 5 \pm 2 \text{ \AA}$. This decay length is significantly longer than that given by simple models based on the barrier height of hexadecane ($1/\kappa \sim 1 \text{ \AA}$ for a 1 eV barrier). Such deviations are often found in STM measurements and remain ill-understood. This value is the same for both Au and Pt coated tips, within experimental error.

This value of κ yields an expected single-monolayer ($4 \text{ \AA}$) conductance change of $G_{n-1}/G_n \sim 2.2$, where G_n is the conductance for n hexadecane layers between the tip and sample. This is in excellent agreement with the sizes of the smaller conductance steps shown in figure 5-8, indicating that these jumps correspond to monolayer changes. The larger steps represent multiple-layer jumps. For example, the solid line in figure 5-8 shows a single-layer jump, followed by a double-layer jump, and then a triple-layer jump. At high forces, the conductance is observed to exceed the conductance of a single atomic sized point contact, $(\frac{2e^2}{h}) = 77 \mu\text{S}$. We interpret this as the penetration of the last liquid monolayer. As the force is reduced, the AFM tip remains within a couple of solvation layers of the substrate. This hysteresis is a result of the large amplitude of the oscillatory forces near the substrate [Israelachvili 1992a].

5.4.4 Summary of Solvation Measurements on HOPG

Through the combination of the electrical and the deflection measurements above, we find that the solvation forces for hexadecane on HOPG persist for approximately twenty layers. The steps of figure 5-7 correspond roughly to layers 15-20, while the steps in the electrical measurements of figure 5-8 are due to layers ~ 1 -10. We note that either technique alone cannot be used to span this entire range. At large layer numbers, the

conductance is immeasurably small. At small layer numbers, or, equivalently very high forces, the tip-sample separation cannot be accurately determined. This is due to distortions in the cantilever-sample system [Sarid 1991].

It should be noted that the forces used for the penetration of the inner hexadecane layers are significantly larger than those typically encountered in solvation force experiments [Israelachvili 1992a, O'Shea *et al.* 1992]. This is likely due to two particularities of our system. First, the crystalline order imposed on the inner hexadecane layers by the HOPG [McGonigal *et al.* 1991, Elbel *et al.* 1994] hinders the hexadecane movement in the tip interaction region. Second, the hexadecane molecules can become entangled [Christenson *et al.* 1987]. This also leads to difficulty in the transport of molecules from beneath the AFM tip. These lateral restrictions of the hexadecane motion result in a metastable elevation of the solvation maxima [Christenson *et al.* 1987]. We have measured other systems with a conducting AFM, such as octamethyltetrasiloxane (OMCTS) on HOPG and hexadecane on gold, and found that the tip contacts the substrate (as witnessed by high tip-sample conductance) at much lower forces.

Another notable feature of the conductance measurements (figure 5-8) is the presence of dips in the conductance on the low force edge of the jumps and peaks on the high force edge. Detailed measurements of such features reveal that the conductance can change by a factor of two to four over the range of several nN. The equilibration times for these features are on the order of ten seconds. Such features are interpreted as changes in the electrical nature of the tip-sample junction. One possible change is in the local molecular density in the region through which tunneling occurs. This effects a change in the local dielectric constant, and hence the tunneling current. Such molecular rearrangements have been observed about the oscillatory force maxima in molecular dynamics simulations [Gelb *et al.* 1994].

5.4.5 Relevance of Solvation Forces to Spectroscopy Experiments

We note that solvation forces can be utilized to create very stable tunneling barriers between two surfaces. For a weak cantilever, the AFM tip can be more strongly bound to the sample than to the cantilever mount. As a result, mechanical noise does not effect the tip-sample gap and thus the conductance measurement. Figure 5-9 depicts the tip-sample conductance of the above system measured over ~40 minutes. Aside from occasional jumping between layers, the conductance is quite stable. The solvation forces are holding the tip a specific number of layers above the surface with an accuracy that far exceeds the capabilities of the AFM itself.

The stability of these "liquid" barriers may make them useful for tunneling spectroscopy measurements of a variety of surfaces or nanostructures. To this end, figure 5-10 depicts the response of the differential conductance of the tip-HOPG system as a function of tip-sample bias. The response is seen to be an approximately exponential function of bias. The loop on the right is due to hysteretic response of the tip-sample interface and is a commonly observed, yet not understood, feature of similar measurements. We have also observed that spectra taken in hexadecane became unstable when the sample potential rose above a volt.

Another important effect of the hysteresis seen in figure 5-8 comes when one tries to map the impedance of the HOPG surface in a hexadecane environment. One such map appears in figure 5-11b. The fast scan direction for this image is left to right. Here we see the conductance staying at a constant value while the tip is scanned along a single atomic plane (as is the case in the middle of the image). However, when the tip climbs a step edge, it slides lower into the hexadecane ordered film and the conductance rises to a higher value; only to go back down as the tip leaves the higher plateau. Since lower plateaus are found on the bottom right and top left of the image, the upper terrace (running from the bottom left to the top right of the image) becomes more conducting, when a step to these levels is present. Such results illustrate that solvation forces are important when performing

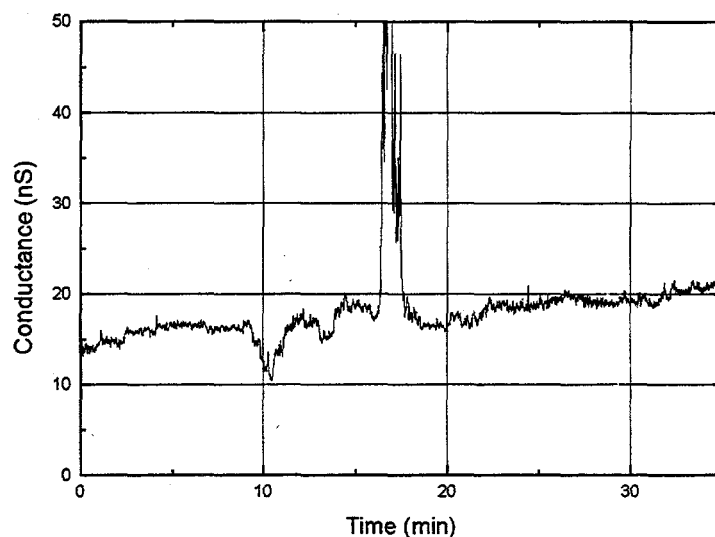


Figure 5-9: Time stability of the tip-sample interface for a Au coated Si_3N_4 tip pressing against HOPG in hexadecane with ~ 500 nN of force. The temporary rise in the conductance that occurs after fifteen minutes is likely a result of a sequence of changes in the number of layers beneath the tip.

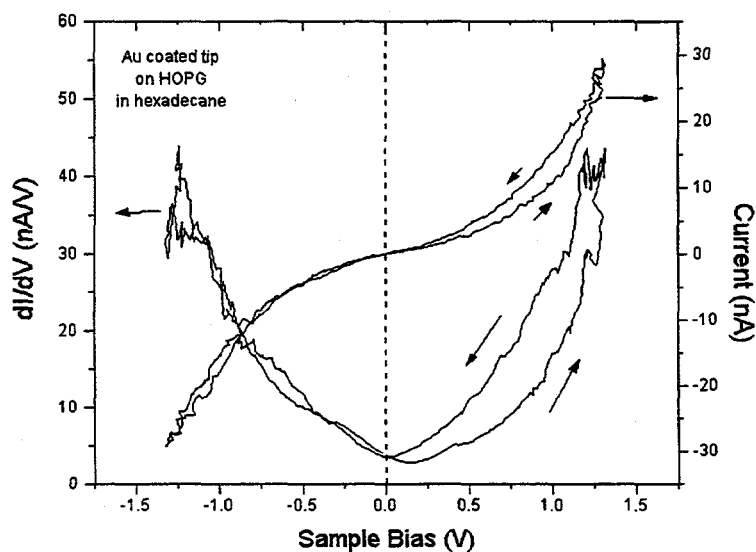
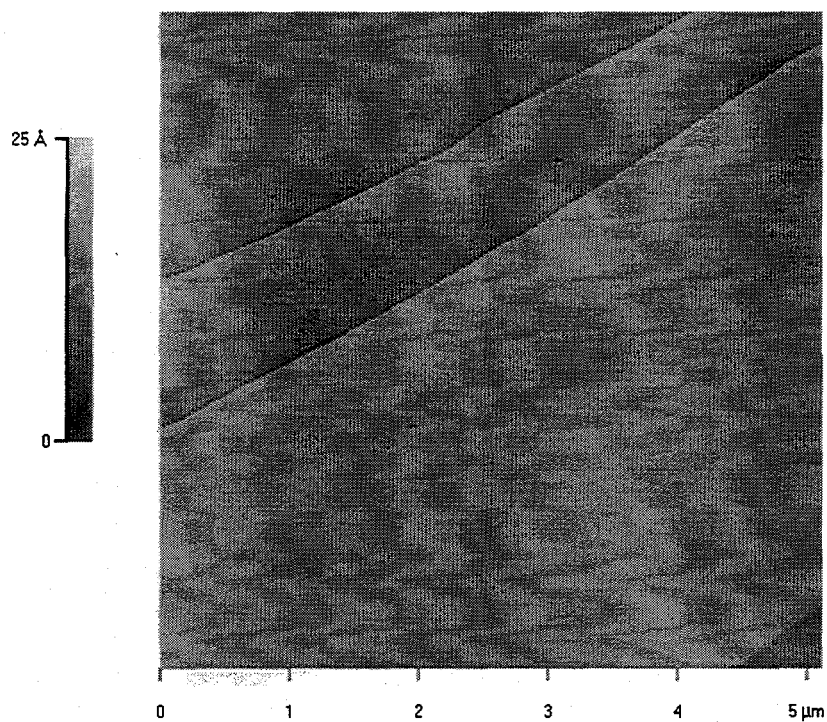


Figure 5-10: Current and differential conductivity measured as a function of bias for a Au coated Si tip placed on HOPG in hexadecane with ~ 100 nN of force.

a)



b)

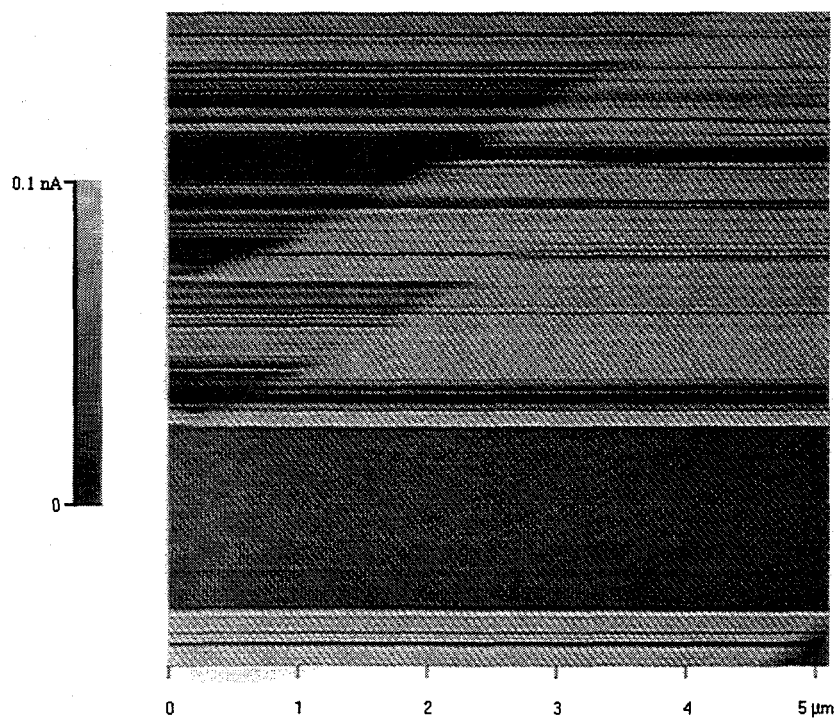


Figure 5-11: a) Topography of a region of HOPG measured in hexadecane with a Si stylus coated with Au. The normal force applied is approximately 40 nN. b) Simultaneously obtained tip-sample current map with a tip-sample bias of 6 mV.

electrical studies in liquid, complicating the use and interpretation of electrical measurements.

5.5 SUMMARY AND CONSEQUENCES

Now armed with a minimal understanding of what it means to bring an AFM tip onto a crystalline surface in a non-polar liquid, we can re-assess our desire to use such a probe in the investigation of nanocrystals. We have learned that we must consider the chemical nature of both the AFM's stylus and the nanocrystal's surface to minimize solvation forces. Further, we must take care in the methodology we choose to bring the tip towards the nanocrystal, else the hysteretic nature of solvation phenomena (figure 5-8) will present non-physical results (figure 5-11).

Being experimentalists, we tried to make the measurements none the less. In hexadecane and octane we tried to measure current through a surface covered with CdSe nanocrystals. No special care was taken to minimize solvation forces. Such a system could not be made to conduct with forces small enough to prevent damage to the surface. A solution might be found in taking care to create low energy surfaces which do not readily solvate molecules from the liquid environment. We choose not to take this path, based upon the complications found in the above set of experiments and instead shifted our efforts towards lithographic means to electrically isolate and study nanocrystals.

Chapter 6

Catalytic AFM

6.1 BACKGROUND

Given our disappointment at the prospects of easily using a SPM for electrical investigations of nanocrystals (chapter 5), we now focus on ways to incorporate molecules and nanocrystals into lithographically defined devices. As discussed in chapters 1 and 2, transport measurements of nanocrystals can reveal information on classical and quantum confinement effects, but to see these effects we must first learn how to place nanocrystals between leads. This chapter addresses this first step by exploring means to localize where nanocrystals deposit on a substrate.

There are several existing technologies for the patterning of features on a substrate, the most mature of which is resist-based lithography. This approach uses photons, electrons, or a SPM to selective remove regions of a resist layer that coats a substrate. Subsequent processing uses this patterned resist as a mask. The resolution and rate of the patterning for these techniques varies greatly. A benchmark can be taken as the fabrication-line optical lithography used in bulk processing of computer chips. The current generation of which has a resolution limit of ~ 350 nm and can pattern a 8" (12" in ~ 1998) wafer in ~ 1 min. For higher resolution we can move to X-ray, e-beam, or SPM [Dobisz and Marrian 1991, Majumdar *et al.* 1992, and Kim and Lieber 1992] patterning of resists. These approaches can push the resolution down to 10-20 nm. The price paid is in the processing rate. For a comparison of time scales we note that to expose 10% of a 8" wafer with 20 nm features takes ~ 1000 hrs using a e-beam* and ~ 200 hrs using a SPM†. While this is too slow (without parallel processing) for commercial processing, the rate is quite fast enough for basic research.

* Assuming a 1 nA beam used give a $100 \mu\text{C}/\text{cm}^2$ dosage

† Assuming a 1 MHz tip resonance (which gives a 20 mm/s write speed)

Our concern in this chapter is how we can localize nanocrystals or molecules with nanometer accuracy on a substrate. Optical lithography's resolution is not up to the task, but the higher resolution of e-beam or SPM lithography techniques does come close to meeting our needs. We must be careful, however, to make sure that the resist chemistry and nanocrystal/molecule chemistry is compatible. Further, this approach is not fully satisfying, for it does not exploit the inherent chemical selectivity available in nanocrystal and molecular systems.

To avoid lithography, several researchers have simply used a SPM to push molecules [Weisenhorn *et al.* 1990], nanocrystals [Junno *et al.* 1995], or atoms [Eigler and Schweizer 1990] into the complex patterns on a surface. Others have developed the means to use a SPM to create nanoparticles where they are wanted [Mamin *et al.* 1990 and McCord and Awschalom 1990 for example]. Such approaches are intriguing in that they allow us to position or create nanostructures in complex patterns on a surface. In practice however, it has proven difficult to construct working devices by these means. Pushing particles about on a surface with patterned leads or other features is difficult. Further, to be able to push particles around requires that they are lightly bound to the substrate and hence the resultant structures can be fleeting. Direct deposition of nanostructures allows the use of more complex geometries, but only allows the use of a limited number of materials.

Another recent patterning approach is to locally define the chemical nature of a substrate's surface. By patterning the chemistry of a surface, one can then localize the subsequent binding of molecules and nanocrystals. One example of this approach comes from Kumar and Whitesides [1993] who demonstrated the ability to "ink" an elastomeric stamp with alkanethiols, and thereby stamp a patterned self assembled monolayer (SAM) onto a substrate. Others [Kuramochi *et al.* 1994 and McIntyre *et al.* 1994] have used a STM tip to field emit atomic hydrogen, and thereby passivate high energy surfaces.

Along these lines, I will now discuss our efforts to use an AFM to selectively catalyze chemical reactions on a substrate. Such an approach allows us to perform *chemical lithography* and thus pattern where subsequent chemical bonding reactions will occur. This patterning should (but has not yet) provide a path for the introduction of complex patterns of nanocrystals into an electrical circuit. A further discussion of our efforts can be found in the previously published work of Müller *et al.* [1995].

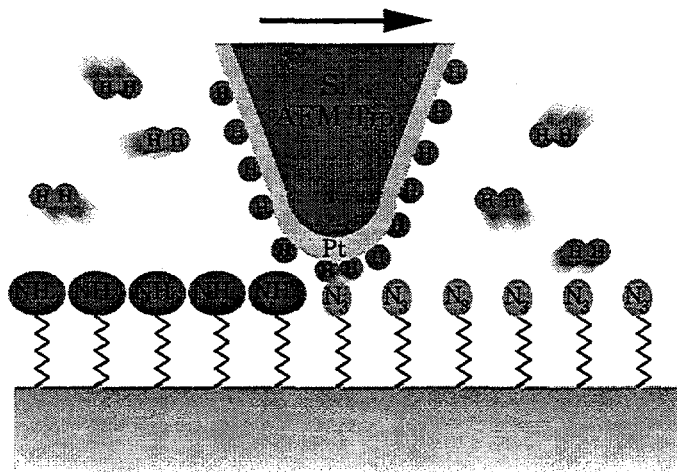
6.2 INTRODUCTION

In this chapter, we present work on using an AFM's tip as a catalyst to chemically modify functional end groups exposed on the surface of a self assembled monolayer (SAM). By scanning a Pt coated AFM stylus in a hydrogen rich environment over a surface of a SAM which has terminal azide [$-N_3$] groups, we catalytically convert the azide groups to amino [$-NH_2$] groups (figure 6-1a). The amino groups formed by this process can then be selectively modified with a variety of reagents in a second step to generate more complex structures (figure 6-1b). Covalent bonding between the derivatization groups* and the SAM and between the SAM and the substrate results in the long term stability of any formed structures. By using a catalyst rather than an electrochemical or field emission process we eliminate the need to apply a potential between the tip and the surface and significantly expand the range of surface transformations that can be explored [Rylander 1973].

The catalytic hydrogenation of azides was chosen for this study. Pt likely acts as a catalyst here because it readily disassociates H_2 molecules onto its surface to form a metal bound hydride. Unlike molecular hydrogen, this metal bound hydride can react with the azide functional groups to form amino groups [Horinti and Polanyi 1934]. Because the Pt catalyst is localized to the AFM tip, amino groups should only be formed at those sites where the metallic AFM tip contacts the surface. This reaction is known to have a very low activation energy and yields no by-products that could inactivate the catalytic tip [Wienhaus

*i.e. Aldehyde-modified latex beads or ATTO-TAG (see section 6.4).

a)



b)

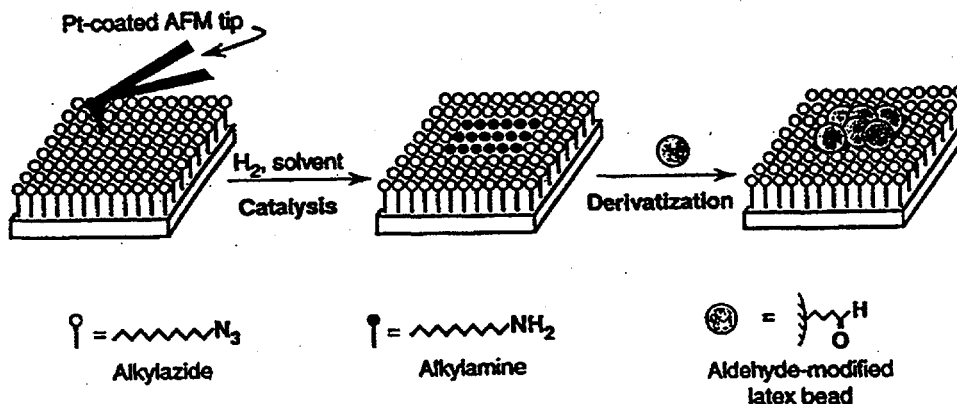


Figure 6-1: a) Schematic of the use of a Pt coated AFM stylus operating in a hydrogen environment for the reduction of azide end groups to primary amino groups. Here, the molecular hydrogen is unable to drive the hydrogenolysis reaction, but the metal-bound hydride groups on the Pt tip can. b) Overview of the catalysis and derivatization process employed. First we scan over the SAM with a Pt coated AFM tip in a hydrogen environment. This locally reduces surface azide groups to primary amino groups. Derivatization of the resulting amine surface with aldehyde-modified latex beads or ATTO-TAG results in specific labeling of the reduced areas.

and Ziehl 1932, Levene and Kuna 1936, Levene and Kuna 1937]. The free amino groups generated in the catalytic reaction can be derivatized in high yield by a variety of molecules including acids, aldehydes, and metal complexes [see, for example March 1985]. Both the catalytic step and subsequent chemical modification steps were carried out in solution to ensure compatibility with the largest number of systems.

6.3 FORMATION AND CATALYSIS OF THE SAM.

The SAM used is formed by the self-assembly of 11-bromoundecyltrichlorosilane $[\text{Br}(\text{CH}_2)_{11}\text{SiCl}_3]$ on glass slides or Si wafers. The Br end groups are then displaced with azide groups to form an axylazide SAM (for preparation details, please see appendix D).

Our catalytic AFM stylus is made from a $0.8\text{ }\mu\text{m}$ thick Park Scientific Ultralever (see appendix B). Onto this stylus we use an e-beam evaporator to deposit a 3 nm thick Cr adhesion layer followed by a 7 nm thick Pt film. These metal coated styli are very similar to those used for our conducting AFM experiments (chapter 5). We used evaporation rather than RF sputtering for these tips in the belief that it forms a cleaner film. Although evaporation is directional and will therefore not deposit much metal on the sides of the high aspect ratio AFM tip, the film about the tip was found to be contiguous via tip-substrate conductance measurements of same type discussed in chapter 5.

To perform the catalysis we assemble a sealed liquid cell containing the SAM substrate beneath a Pt coated AFM tip and flush the cell with isopropanol that has been saturated with hydrogen. The hydrogen saturated isopropanol is formed by drawing a vacuum over the isopropanol, thereby driving out dissolved gasses, and then back filling the vessel with hydrogen gas. This process was repeated several times and the resultant hydrogen saturated isopropanol is stable in a sealed container for several days or longer.

Catalysis is performed by scanning the AFM's tip at a speed of $1\text{ }\mu\text{m/s}$ and a force of $\sim 400\text{ nN}$ in hydrogen saturated isopropanol over our axylazide SAM. Each region was scanned 3 times to maximize the reaction yield. The use of a faster scanning speed or a

reduced tip pressure on the substrate during catalysis led to a decrease in the number of reduced azide groups as measured by a weaker fluorescence signal after derivatization (see below). After scanning, the sample was removed from the liquid cell, rinsed with ethanol and water, and then covalently derivatized with a label to identify the hydrogenated regions.

6.4 DERIVATIZATION OF THE SAM

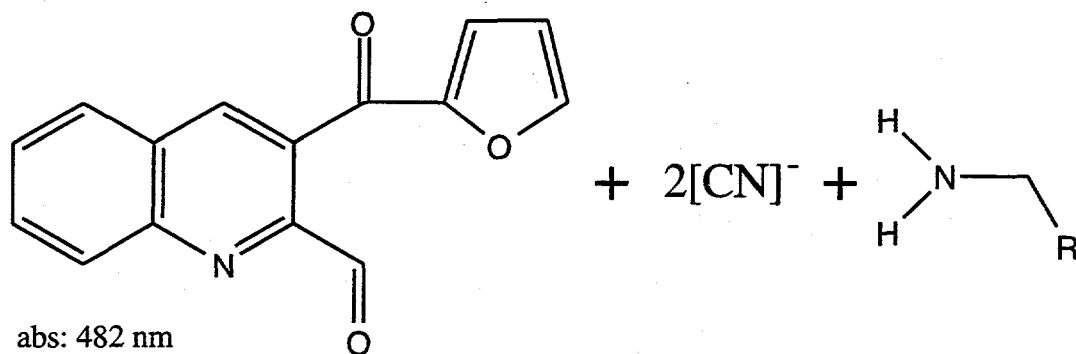
To visualize the amino groups, we covalently modify the surface with either fluorescein-labeled, aldehyde-modified, 290 Å latex beads [Molecular Probes, Eugene, Oregon] or 3-(2-furoyl)quinoline-2-carboxaldehyde (ATTO-TAG) [Molecular Probes] [Beale *et al.* 1990]. For an outline of these processes, please see appendix D. The aldehyde groups on the latex beads bind to the substrate's amino end groups, but not to its azide groups. This means that by using fluorescence to map where the fluorescein* labeled beads bind, we learn where the amino groups lie. ATTO-TAG (depicted in figure 6-2a) is a more powerful label for it is not fluorescent, but reacts with primary amines in the presence of cyanide ions to form a fluorescent† isoindole derivative (figure 6-2b). Consequently, detection of a fluorescence signal demonstrates unequivocally the conversion of the surface azide groups to primary amino groups.

Optimization of the conditions for derivatizing of the amine surfaces with the fluorescent latex beads or the fluorogenic reagent (ATTO-TAG) was done with SAMs formed from aminopropyltriethoxysilane [Haller 1978]. Control experiments with azide surfaces showed very little nonspecific binding of the beads and no detectable nonspecific labeling with ATTO-TAG. When pure amine control surfaces were derivatized with the beads or ATTO-TAG reagent, the signal strength was more than 10 times that of the azide control surfaces.

*Fluorescein has an excitation maximum at 494 nm and emission maximum at 520 nm.

†This species has a excitation maximum at 486 nm and a fluorescence maximum at 591 nm.

a)



b)

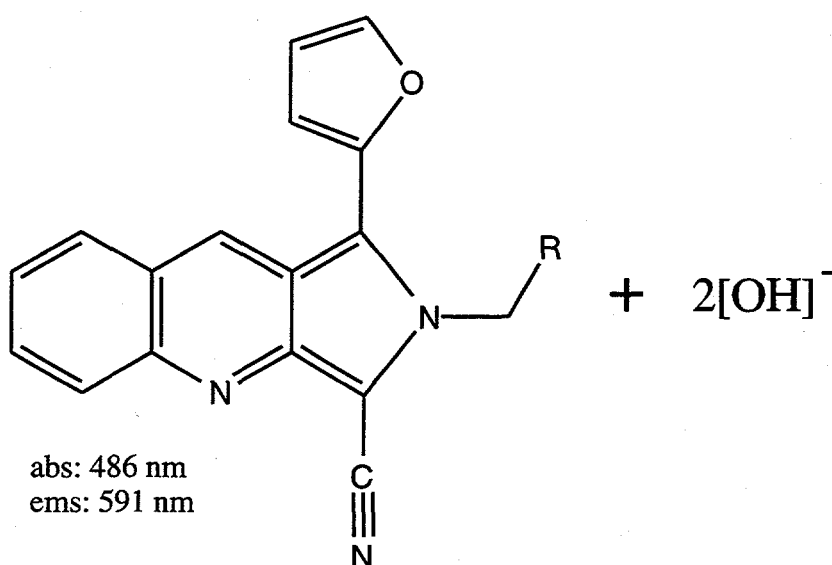


Figure 6-2: a) Starting materials for labeling amino groups with the ATTO-TAG reagent. The unmodified ATTO-TAG absorbs at 482 nm, and does not fluoresce. When exposed to a primary amino group (attach to our SAM) in a phosphate buffer which contains an excess of cyanide ions, the ATTO-TAG reacts to form the species depicted in (b). This new species, bound to our alkane SAM via the primary amino group fluoresces at 591 nm, and has an absorption maximum at 486 nm.

6.5 IMAGING AND RESULTS

Fluorescence imaging of the catalyzed regions was performed with a confocal scanning laser microscope (CLSM) [Molecular Dynamics]. Here, an excitation laser is focused onto a sample and the same lens is used for fluorescence detection. A dichroic mirror is used to isolate the fluorescence signal which is then measured by a photo multiplier tube (PMT) as the laser is rastered over the substrate. Figure 6-3a shows the CLSM fluorescence image of region in which a 10 μm square was catalyzed and then derivatized with fluorescent latex beads. Figure 6-3b is a CLSM fluorescence image of a different region, in which a 10 μm square was catalyzed and then derivatized with ATTO-TAG. Bright 10 μm fluorescent squares are visible in both regions, indicating successful catalysis. Scanning over the azide-terminated surface with an untreated, fresh Si tip, or a tip coated with gold (a catalytically inactive metal) in hydrogen-saturated isopropanol did not result in any detectable structures after derivatization with either fluorescent latex beads or ATTO-TAG reagent (figure 6-3c).

The same tip used for the catalysis can be used with lower force to image the catalyzed region and look for changes in surface morphology. No measurable ($>2 \text{ \AA}$) differences were observed between the scanned and unscanned areas; this finding indicates that the tip did not significantly perturb the SAM. This is consistent with previous results on similar covalently linked SAMs [Tsukruk *et al.* 1994].

These results indicate that during scanning with the Pt tip, the surface azide groups of the SAM are catalytically reduced to amino groups. These groups can then be covalently labeled with either fluorescent latex beads or ATTO-TAG reagent in a spatially defined fashion. To estimate the degree of hydrogenolysis of the surface azide groups in the scanned areas, we derivatized the amine and azide control surfaces as well as the catalytically reduced surfaces with ATTO-TAG reagent and quantified the fluorescence intensities. These measurements indicate that $\sim 10\%$ of the total surface azide groups are

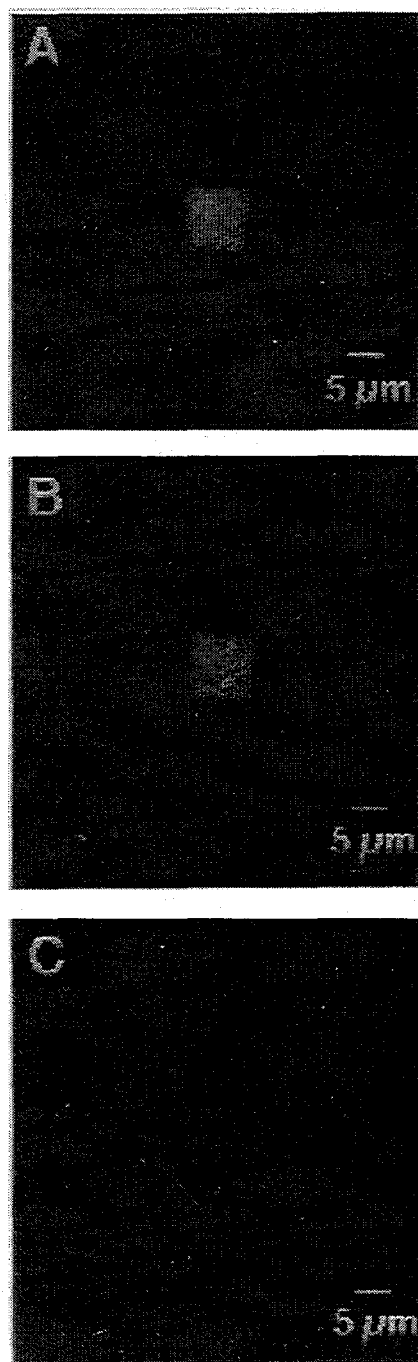


Figure 6-3: Fluorescence micrographs of surface azide groups derivatized after scanning under different conditions with an AFM. a) A 10 μm square area scanned with a Pt coated AFM tip in hydrogen saturated isopropanol and derivatized with fluorescent aldehyde-modified latex beads. b) A 10 μm square area scanned as in (a), but now derivatized with ATTO-TAG reagent. c) A 10 μm square area scanned with a uncoated Si tip under the same conditions as (a) and derivatized with ATTO-TAG reagent (the same picture was obtained when the surface was derivatized with aldehyde-modified latex beads).

converted to amino groups by the scanning catalyst tip. Improvements in yield may result from changes in tip morphology, reaction conditions, or the nature of the surface.

We can also use an AFM to image surfaces which are derivatized with latex beads (figure 6-4). Here we find that the edge of the derivatized region is defined with ~40 nm resolution. This observation indicates that resolution is thus far limited only by the size of the derivatization agent used (here 29 nm spheres which are bloated to ~40 nm by the AFM's tip geometry). Hence the edge definition of the catalyzed region, and the ultimate resolution of this technique is yet to be determined.

6.6 CONCLUSIONS

We have learned how to catalyze the hydrogenolysis of surface azide groups to form surface amino groups. The ultimate resolution of our technique is yet to be determined, but is better than 40 nm. Given the large number of heterogeneous catalytic reactions involving transition metal catalysts, the approach described above may provide a general strategy for performing chemistry on the nanometer scale.

This ability to locally define the chemical reactivity of a surface, should provide an excellent technique for the creation of complex patterns of molecules and nanocrystals for electrical investigations. We have yet to realize this potential however. The primary reason is that while this fabrication technique does work, it does *not* work reliably. This is likely because we rely upon a bare Pt tip to catalyze chemical reactions; we must insure that the tip remains clean during scanning. Any amount of dirt that adheres to the end of the tip will inactivate it. Further, silanated molecules can easily polymerize and form globules of organic material on the surface of our substrate. These particles effectively create a dirty substrate which can easily deactivate the catalytic potential of our tip.

Before this technique can be used to fabricate electrical devices, we must learn how to make it more reliable. This primarily involves finding a way to clean the tip *in situ*. One possible way that this can be done is to apply a voltage spike to the tip, thereby field

emitting a bit of the tip's apex, and creating a clean Pt surface. This approach has yet to be explored.

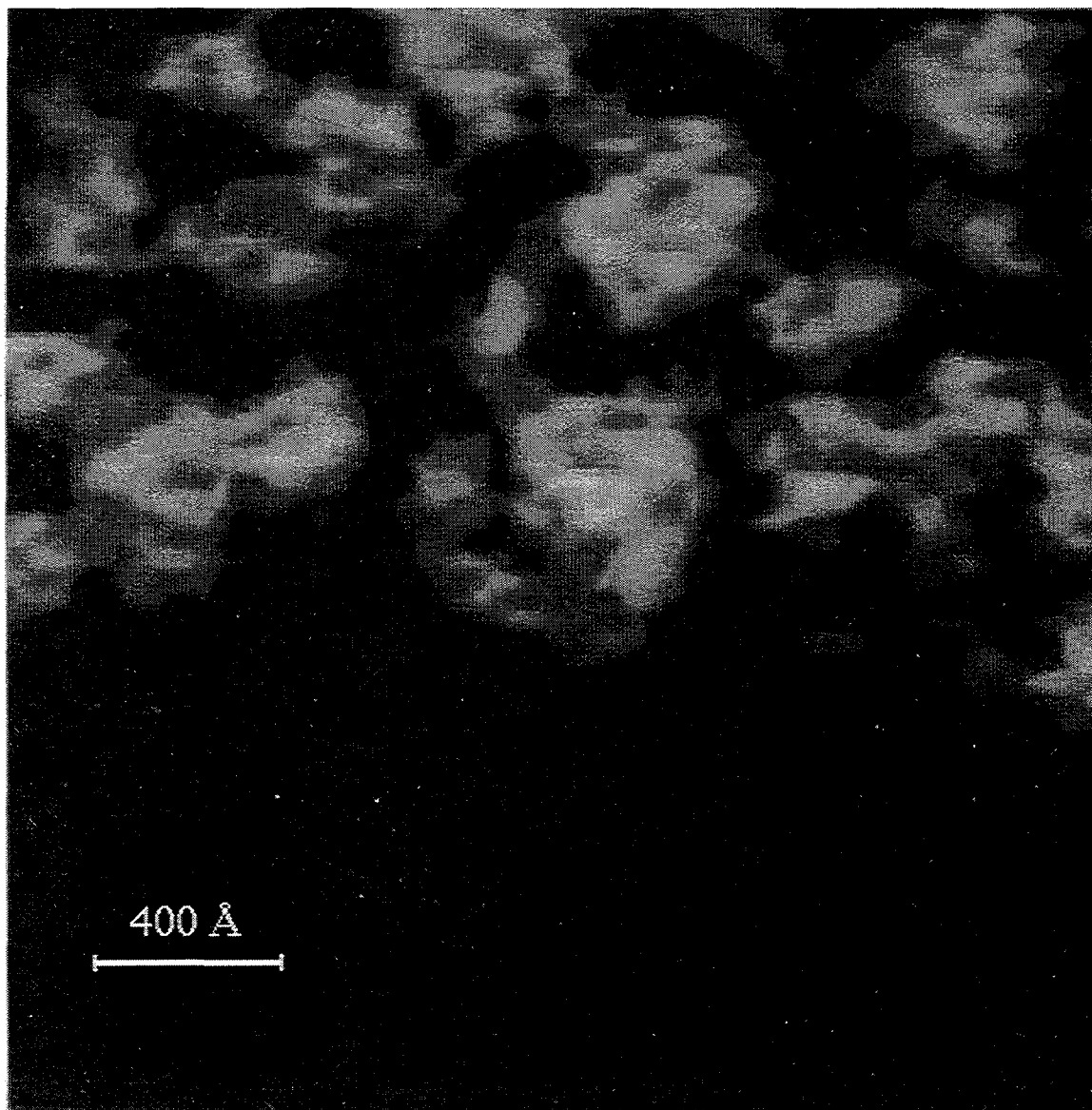


Figure 6-4: Contact AFM image of the bottom edge of a region that had first been catalytically modified with a Pt coated AFM tip, then labeled with 290 Å latex beads. The roughly spherical latex beads are bloated by the AFM's Si stylus and so appear as ~400 Å mounds. The edge of the labeled region is seen to be defined with a roughness comparable to that of the latex balls' size, ~400 Å.

Chapter 7

Fabrication of a Nanocrystal Based Single Electron Transistor

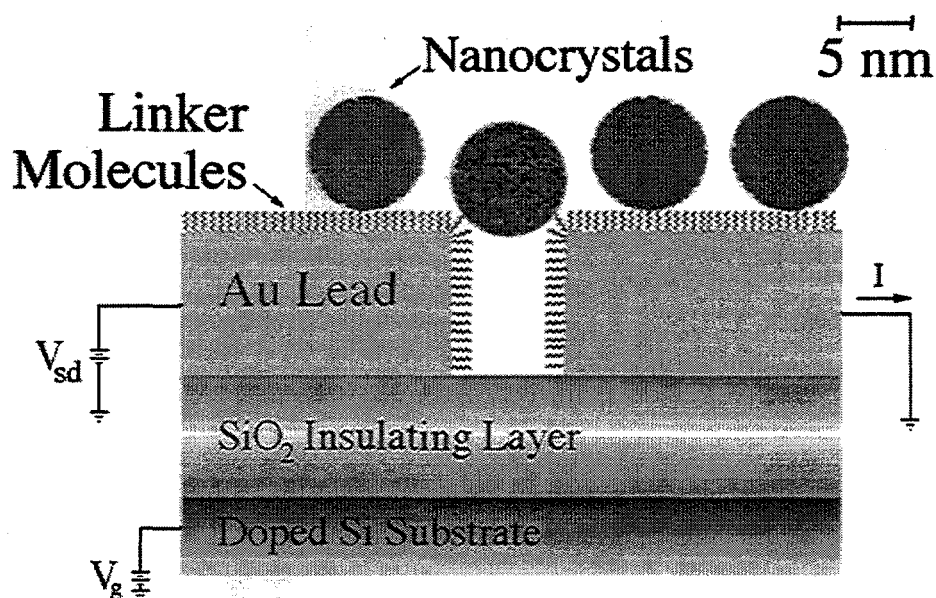
7.1 INTRODUCTION

In this chapter, we present a hybrid assembly scheme for the fabrication of a nanocrystal based single electron transistor (SET). In this device, a nanocrystal is placed in tunneling contact between source and drain leads and electrostatically coupled to a gate. As discussed in chapter 2, single electron effects in the nanocrystal will lead to transport phenomena such as Coulomb blockade and Coulomb oscillations in these devices. In nanocrystals, the energy scale for these effects ranges from tens to hundreds of meV (chapter 1). As a result, a nanocrystal based SET can show single electron effects at room temperature. Our efforts (chapter 8), however, will tend to focus on lower temperatures. Here, quantitative studies on the nature of the electronic states in a nanocrystal can be performed.

Figure 7-1 shows idealized schematics of the devices that we fabricate. Here nanocrystals coat two closely spaced Au leads. The nanocrystals are bound to the leads with an insulating monolayer of bifunctional linker molecules. By measuring the source-drain conductance, we probe only the nanocrystal that best bridges the gap between the leads. The leads are fabricated on a degenerately doped silicon wafer which can be used as a back-gate to shift the electrochemical potential of the nanocrystal under study.

In appendix E a step-by-step recipe for the fabrication of the devices can be found and in appendix F is a list all of the devices that have been fabricated. Further discussions of the work described here can be found in Klein *et al.* [1996a, 1997].

a)



b)

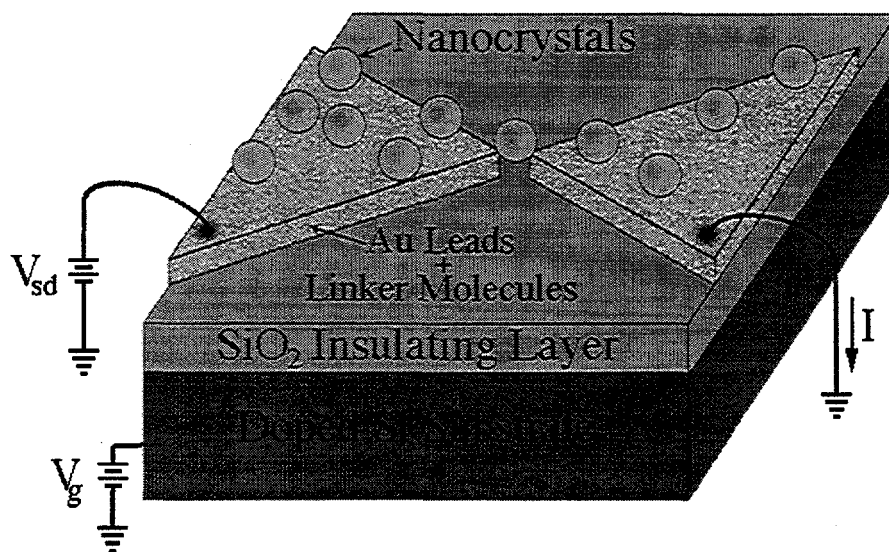


Figure 7-1: (a) 2d and (b) 3d schematic profiles of the device. Nanocrystals are bound to source and drain leads with a monolayer of bifunctional linker molecules. Transport measurements probe the nanocrystal that bridges the gap between the leads. The electrochemical potential of this nanocrystal can be tuned by applying a gate voltage to the substrate.

7.2 OPTICAL LITHOGRAPHY

7.2.1 Overview

The current device fabrication uses four optical lithography steps followed by one electron beam (e-beam) lithography step. The optical lithography is done on a 4" wafer and yields 80 chips. Each chip has 43 leads and can be used to fabricate 42 single electron transistors*.

Figure 7-2 shows an optical micrograph of the chips that we fabricate. 42 Au *source*-leads can be seen running horizontally in this figure, while a single Au *drain* lead runs vertically along the length of the chip. The majority of the wafer is coated with a ~900 nm thick layer of silicon dioxide. In the central region (dark gray) of the chip, the oxide is thinned to ~55 nm thick. On the four corners of the chip lie Al gate contacts that penetrate the surface oxide and provide electrical access to the substrate.

7.2.2 Step 1 - Oxide Growth and Patterning

The wafer that we use is a 4", n-type, degenerately doped Si wafer [from PCA corporation]. The room temperature resistivity of this wafer is less than $0.008 \Omega\text{-cm}$ and it is metallic in nature[†]. Over the majority of this wafer, a thick silicon dioxide barrier layer is grown. This protects against the accidental shorting of leads to the wafer during wire bonding. Furthermore, a thick oxide layer minimizes leakage current and maximizes the breakdown voltage of our gate. To grow the layer, we first use HF to strip any pre-existing silicon dioxide from the wafer and then grow a ~900 nm thick *wet oxide*. This oxide grows in 2.5 hours at 1050 °C under a flowing mixture of N₂, O₂, and H₂O[‡]. We have found that with an oxide of this thickness, one can wire-bond to surface features with minimal danger of penetration to the underlying substrate.

*Although we have never successfully made more than four devices on a chip.

[†]In other words, this wafer's carriers do not freeze out and it remains conductive at low temperatures.

[‡]The H₂O is introduced by bubbling the N₂ gas through water.

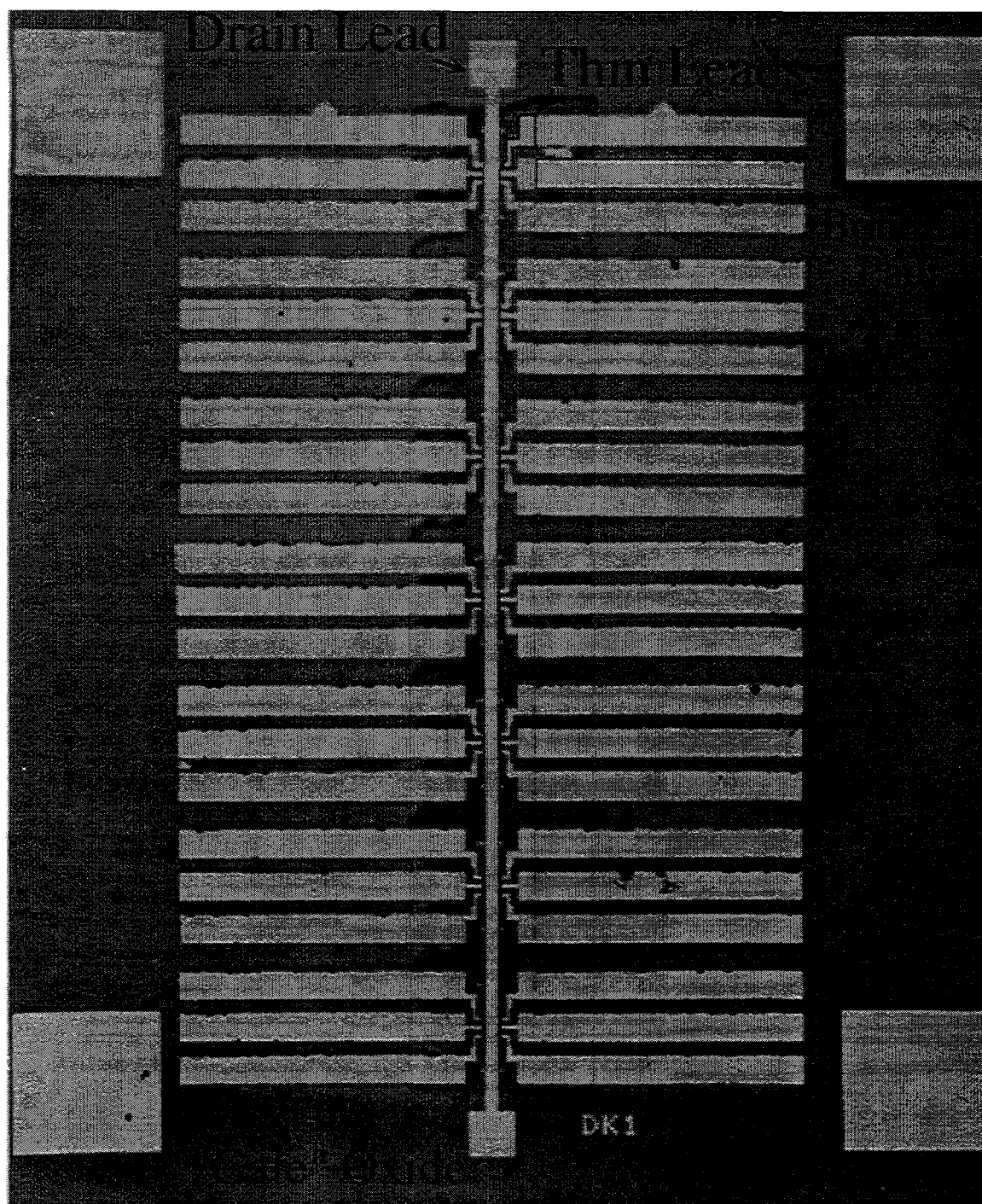


Figure 7-2: Optical micrograph of a fabricated chip. The Au drain lead can be seen running vertically and 42 Au source leads can be seen running horizontally in this figure. The substrate is a degenerately doped Si wafer on which a thick (900 nm) oxide has been grown. In the central (dark) rectangle, the oxide has been thinned to 55 nm. 4 Al gate contacts appear on the corners of this image.

In the active region of our devices, we would like to maximize the capacitive coupling between the substrate (which is used as a gate) and surface features (figure 7-1). This means that we would like to minimize the thickness of the silicon dioxide layer in this region. This is done by first applying a layer of photoresist to the substrate. Optical lithography is then used to pattern holes into this film. Subsequent immersion in HF will etch the exposed regions of SiO_2 , while the areas protected by the photoresist will remain unchanged. The photoresist is then removed, the wafer is cleaned, and 55 nm thick *dry oxide* is grown (seen as a dark gray rectangle in the center of figure 7-2). This oxide (grown in 2 hours in a dry N_2/O_2 , 950 °C environment) grows more slowly than does a wet oxide, but has a higher impedance and dielectric strength.

7.2.3 Step 2 - Definition of Gate Bonding Pads

Next, we provide electrical access to the substrate. This is done by first using optical lithography to pattern a photoresist layer and then using HF to etch holes into the surface oxide. Immediately after etching these holes, 350 nm of Al is evaporated onto the wafer. The wafer is then placed into an acetone bath to dissolve the photoresist and *lift-off* the Al film from the bulk of the wafer. Al will be left in the areas in which holes have been patterned into the photoresist (and subsequently into the SiO_2). These Al pads can be seen in the four coners of figure 7-2. To ensure ohmic contact between the Al and the Si substrate, the wafer is then annealed for 30 min. at 350 °C. During this time, the Al and Si react to form a low impedance silicide.

7.2.4 Step 3 - Definition of Source and Drain Leads

We now pattern all but the finest features of our source and drain leads*. This is done using two lift-off procedures. First, we use optical lithography to pattern the entire lead structure (seen in figure 7-2) into photoresist. We next evaporate 10 nm of Cr

* The fine features will be drawn by electron beam lithography (section 7.3).

followed by 30 nm of Au and then dissolve the photoresist in acetone (thereby lifting off the bulk of the Cr/Au film). Left behind is a Cr/Au film patterned to the form of the leads seen in figure 7-2.

We deposit a film which is only 40 nm thick to ensure reliable contact to the 100 nm thick electron beam defined features that we will draw later (section 7.3). It has been found that if we try to evaporate a thin metal film atop a thicker film, the thin film will occasionally be discontinuous near the edges of the underlying thicker film. By making the above described features thinner than 100 nm, we allow the to-be-deposited leads (section 7.3) to envelop these features and provide reliable electrical contact.

A problem with thin leads, however, is that they cannot be easily wire-bonded (section 7.4); a bond can only be reliably made to a Au film that is greater than 200 nm thick. We thus do a second lift-off process to thicken all but the innermost regions of our leads. During this step, 15 nm of Cr and then 200 nm of Au are deposited. In figure 7-2, the transition between the thick and thin regions of the leads can be seen as faint lines at the innermost portion of the horizontal leads.

7.3 ELECTRON BEAM LITHOGRAPHY

The fine details of the leads are defined by electron beam lithography. Figure 7-3, shows a scanning electron micrograph of a set of leads that we have fashioned. Here we see six optically defined source leads which are separated from a central drain lead by 14 μm . Bridging the gap between these features are 6 finer leads that have been fashioned by electron beam lithography.

To make these diminutive leads, we first coat the entire wafer with 2 layers of e-beam resist. The bottom layer is a ~400 nm thick film of P(MMA-MAA) and the top is a ~100 nm thick film of PMMA. P(MMA-MAA) is much more sensitive to electrons than is PMMA. As a result, a drastic undercut of features will occur. This effect is depicted in figure 7-4 and will be exploited below.

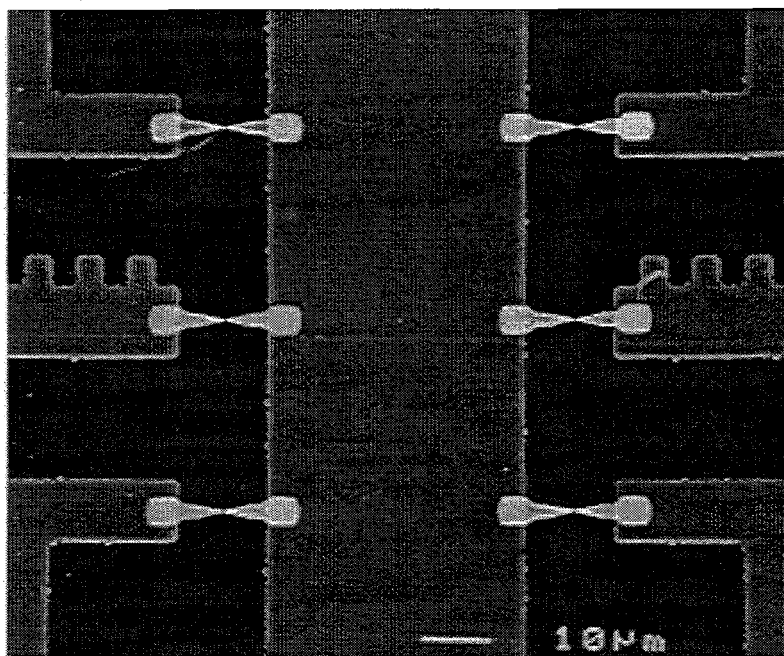


Figure 7-3: Overall view of a set of six electron beam leads (small bright features) sitting atop larger scale optical features.

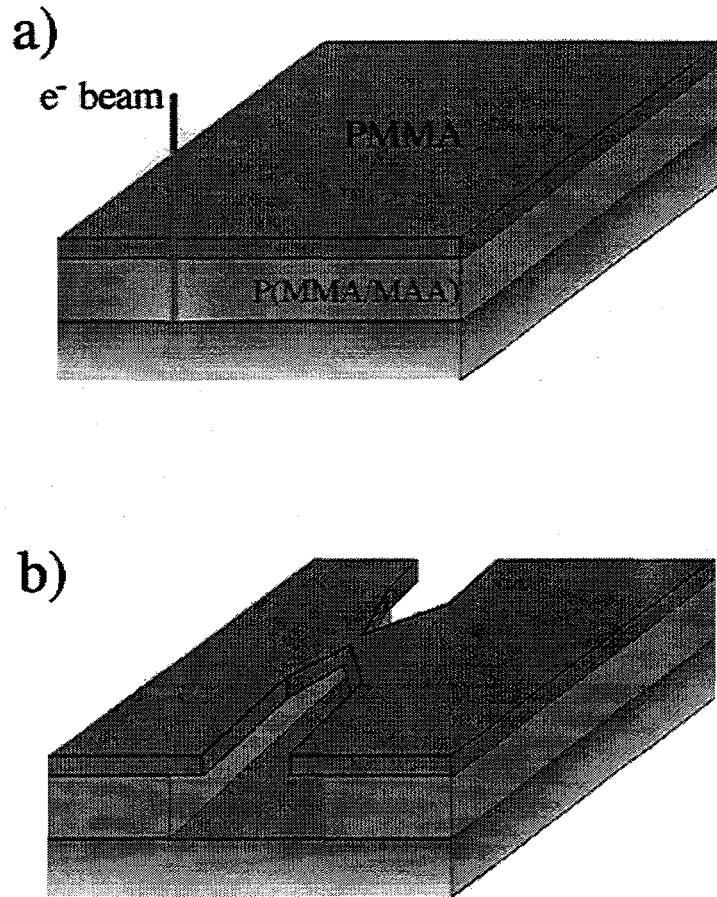


Figure 7-4: A sketch showing the use of electron beam lithography and two resist layers to form a suspended mask. a) An electron beam is used to draw two closely spaced features. Secondary electrons scattered from the substrate (shown here with a bright hemisphere) will expose the resist over a region larger than the primary electron beam. b) During development, the more sensitive, lower resist layer will then be over-developed, leaving us with an overhanging bridge formed by the upper resist layer.

After the resist has been deposited, the wafer is scribed into smaller chips (a single chip is shown in figure 7-2). Electron beam lithography is done on one chip at a time in a modified JEOL 6400 SEM. The lithography is performed with a beam current of 5 pA and an accelerating voltage of 20 kV. Typical exposure dosages are $900 \mu\text{C}/\text{cm}^2$ for fine features and $150 \mu\text{C}/\text{cm}^2$ for coarser ($> 500 \text{ nm}$) features. Development is done in 3:1 IPA:MIBK for 1 minute.

In figure 7-4 we sketch the patterned e-beam resist for a pair of leads. The typical patterning draws two leads which are separated by $\sim 200 \text{ nm}$. The dosage is chosen so that the top layer faithfully reproduces the pattern drawn with the electron beam. However, as the bottom resist layer is much more sensitive to the electron beam, it is drastically overexposed by secondary electrons (as seen in figure 7-4). As a result, the region in-between the source and drain lead is only covered by *abridge* of the upper resist layer.

We exploit this bridge to narrow the gap between our leads. This variation on the Dolan bridge technique [Dolan 1977, Dolan *et al.* 1981, Bishop *et al.* 1985, Fulton and Dolan 1987; see also section 3.3.2] is sketched in figure 7-5. Here three sequential evaporations are performed. First, 3.5 nm of Cr and 10 nm of Au is evaporated at $+15^\circ$ relative to normal. This is then repeated at -15° relative to normal. As evaporation is a highly directional process, each of these steps will create an image of the upper resist that has been shifted by $\sim 100 \text{ nm}$ on the underlying substrate and the final leads will be separated by only a few nanometers. To ensure a reliable bond to the optically defined features, 3.5 nm of Cr and 80 nm of Au is then evaporated straight down onto the sample. The sample is then placed into acetone and the e-beam resist (and overlying Cr/Au film) is removed.

Figure 7-6 shows the structure of the resultant leads (after the attachment of nanocrystals as described in section 7.4). Here we can see that we have successfully created two leads which are separated by less than 10 nm.

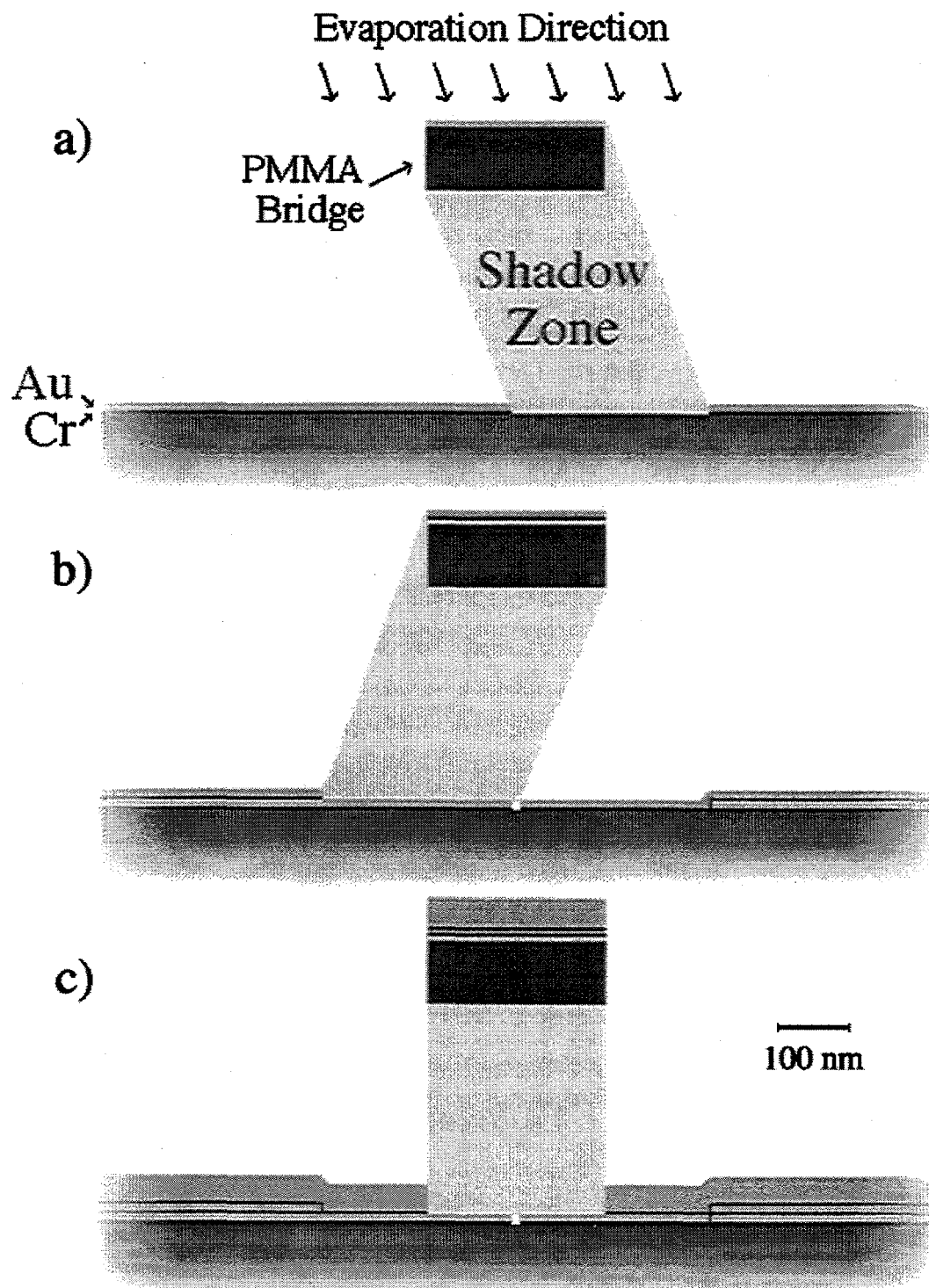


Figure 7-5: A sketch showing the use of angled evaporations to fabricate two closely spaced leads. a) Cr and Au are evaporated at an angle of 15° relative to normal. This will shift the position of features of a suspended mask by about 100 nm. b) A second evaporation at -15° yields features which are shifted by about -100 nm. This leaves us with two closely spaced leads. c) A final evaporation at normal incidence is used to thicken the body of these leads.

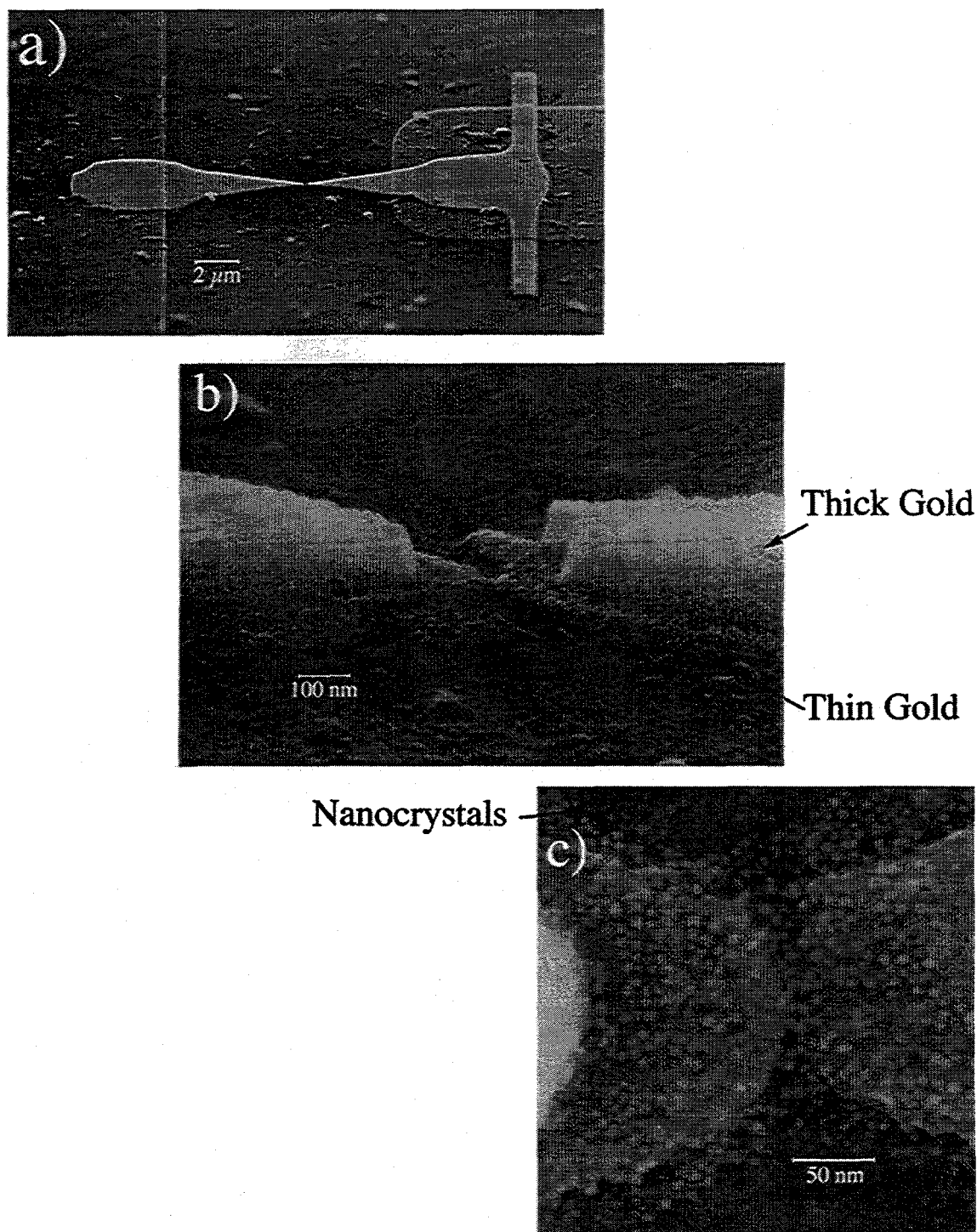


Figure 7-6: Field emission scanning electron micrographs of a pair of leads onto which 5.5 nm CdSe nanocrystals have been deposited. a) Low magnification image of the overall lead geometry (taken at a tilt of 60° from normal). b) Higher magnification image, showing the ends of the two leads. These leads are separated by a ~5 nm gap. About the gap, the leads are ~13 nm thick, while the main body of the leads is ~100 nm thick. The CdSe nanocrystals are not resolved at this magnification, and appear as a mottling of the surface. c) Higher magnification micrograph taken at the center of (b), now at normal incidence. Here we have a better view of the CdSe nanocrystals and the gap between the leads.

7.4 ATTACHMENT OF NANOCRYSTALS

At this point, the lithography is complete and nanocrystals are attached to the Au leads via a bifunctional linker molecule. For the work described in chapter 8, Au and CdSe nanocrystals were used. The colloidal Au particles were obtained from a commercial distributor [BBI International], had a coefficient of variation of 15%, and were dispersed in water. The CdSe nanocrystals were made by previously described methods [Murray *et al.* 1993, and Bowen-Katari *et al.* 1994; see appendix C for details], had a 5% coefficient of variation, were capped with tri-*n*-octylphosphine oxide (TOPO), and were dispersed in toluene.

The procedure for the attachment of these nanocrystals is the same for both Au and CdSe. Immediately prior to attachment of the linker molecules to the substrate, the sample is plasma cleaned for 1 min. in a N₂ plasma. Then the sample is placed in a solution of 5 mmol/L 1,6-hexanedithiol in electronic grade isopropanol. The linear dithiol molecules bind one of their thiol endgroups to the Au leads, thereby forming a 1.2 nm thick monolayer [Porter *et al.* 1987 and Bain *et al.* 1989]. After approximately 24 hours in this solution, the sample is transferred to a solution of nanocrystals and left for approximately 24 hours. During this step the nanocrystals bind to the exposed endgroups of the linker molecules which envelop the Au leads [Colvin *et al.* 1992].

XPS and RBS show about 30% coverage of CdSe nanocrystals when bound to a Au substrate in the above fashion. RBS measurements of Au nanocrystals bound to a Ag substrate show only 1% coverage. This low coverage of Au is likely due to problems in forming the thiol bond when the nanocrystals are suspended in water.

After the nanocrystals are attached, the chip is glued into a 16 pin dip package. An ultrasonic wedge bonder is then used to attach wires (typically 25 μ m in diameter) to the device for electrical studies.

7.5 THE COMPLETED DEVICE

Figure 7-6 shows several field emission scanning electron micrographs of a completed single electron transistor. This device (which aims to be a manifestation of the idealized system introduced in figure 7-1) consists of two leads that are separated by less than 10 nm and coated with nanocrystals. As current passes from the source (right side of figure 7-6) to the drain (left side of the figure), the transport behavior of the nanocrystal that best bridges the gap between the leads is probed. Ideally this would be an isolated nanocrystal, however in figure 7-6 several nanocrystals can be seen in the near the gap between the leads. This issue will be further addressed in chapter 8.

Having now described the fabrication of nanocrystal based single electron transistors, in chapter 8 we discuss their transport behavior.

Chapter 8

Nanocrystal Transport Experiments

8.1 OVERVIEW

In this chapter, I will present the electrical measurements that we have made on the nanocrystal devices whose fabrication was described in chapter 7. First, I will discuss the measurements that we have made on Au nanoparticles. The quantum levels in these metallic particles are very closely spaced* (see chapter 1) and so the observed transport behavior can be described by an orthodox Coulomb blockade model. I will then discuss our measurements of CdSe nanocrystals. The lower carrier density in these nanocrystals yields richer I - V_{sd} characteristics whose structure can be interpreted to learn about the nature of electronic states in CdSe nanocrystals.

8.2 AU NANOPARTICLES

8.2.1 Overview

We have deposited Au nanocrystals on 10 chips (see appendix F). Among various mistakes and failures†, studies on 3 working Au nanoparticle devices have resulted from these chips. All three devices were two terminal and did not have a gate. I will describe and discuss the measurements that were made on two of these devices below‡.

8.2.2 A 5.8 nm Au Nanoparticle Device

Figure 8-1a shows the measured current, I , as a function of the applied source-drain bias, V_{sd} , for a two terminal, 5.8 nm diameter Au nanoparticle system at 77 K. A Coulomb staircase is observed due to the incremental charging of the dot by single

*A 6 nm diameter Au particle has a quantum level spacing of ~ 0.7 meV. This is much smaller than the charging energy of these particles and comparable to kT at 4.2 K (the temperature of our measurements).

†Including a chip that disappeared into a fume hood and many blown leads.

‡The third device used aminothiophenol as a linker molecule. Most likely as a result of charging effects in this molecule, rather complex, hard to interpret I - V_{sd} were obtained.

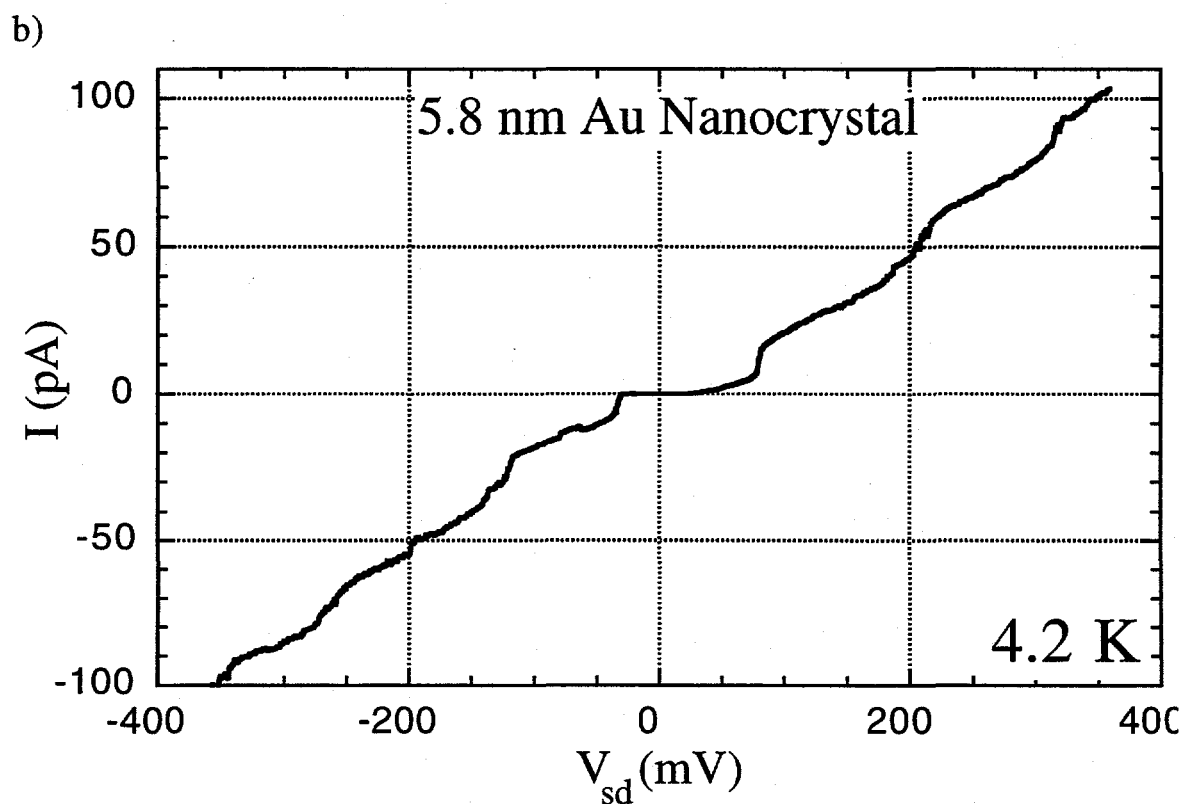
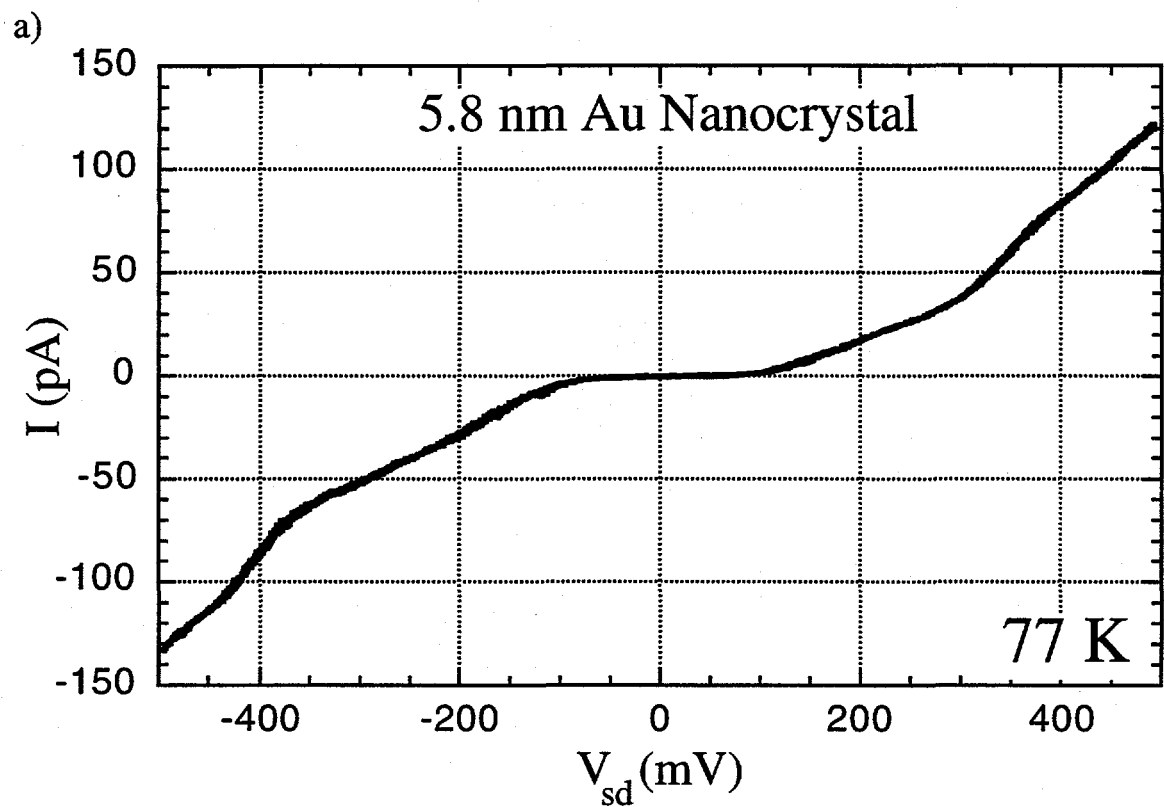


Figure 8-1: a) I - V_{sd} characteristic of a 5.8 nm diameter Au nanoparticle measured at 77 K. b) I - V_{sd} characteristic of the same nanoparticle at 4.2 K. In both cases a Coulomb staircase can be seen.

electrons with increasing V_{sd} . The period of the steps, ΔV_{sd} , is ~ 200 mV. Figure 8-1b depicts the I - V_{sd} characteristic of the same device, now cooled to 4.2 K. Here the Coulomb staircase is more pronounced as a result of decreased thermal broadening.

Figure 8-2 depicts the Coulomb gap of same the device at 4.2 K. Here, we show several measurements which were made over the course of a few days. Each curve is well modeled by the standard two junction Coulomb blockade model [Averin and Likharev, 1991]. Fitting the data with this model (with the program described in appendix A) yields the resistance and capacitance of the system's two tunnel junctions (see figure 2-1) as well as the offset potential of the unbiased nanocrystal. A fit with the parameters: $C_s = 2.1$ aF, $C_d = 1.5$ aF, $R_s = 32$ M Ω , $R_d = 2$ G Ω and differing offset potentials appears above each data trace. Here C_s and R_s are the capacitance and resistance of the source-dot tunnel junction, while C_d and R_d are for the dot-drain junction*. The overall charging energy of the dot, E_c , is $e^2/(C_s+C_d) = 44$ meV. The curves' differences arise as a result of occasional changes in the local charge environment about the nanocrystal. These changes cause abrupt shifts in the electrostatic offset potential of the dot and will be further discussed in section 8.3.4.

8.2.3 A 2 nm Au Nanoparticle Device

Figure 8-3 shows the I - V_{sd} characteristic of a 2 nm diameter Au nanoparticle device cooled to 4.2 K. A large Coulomb gap is seen and the onset of conductance is very noisy, especially at negative biases where at the device was observed to repeatedly switch between a high current and a low current state.

This figure represents the maximal V_{sd} range that we can explore without inducing lasting, electric-field-related, changes in the device's response characteristic. This range is not sufficient for the observation of a Coulomb staircase. Even the biases required

*Without a gate, we can not differentiate the source-dot junction from the dot-drain junction and so the source and drain assignment is arbitrary.

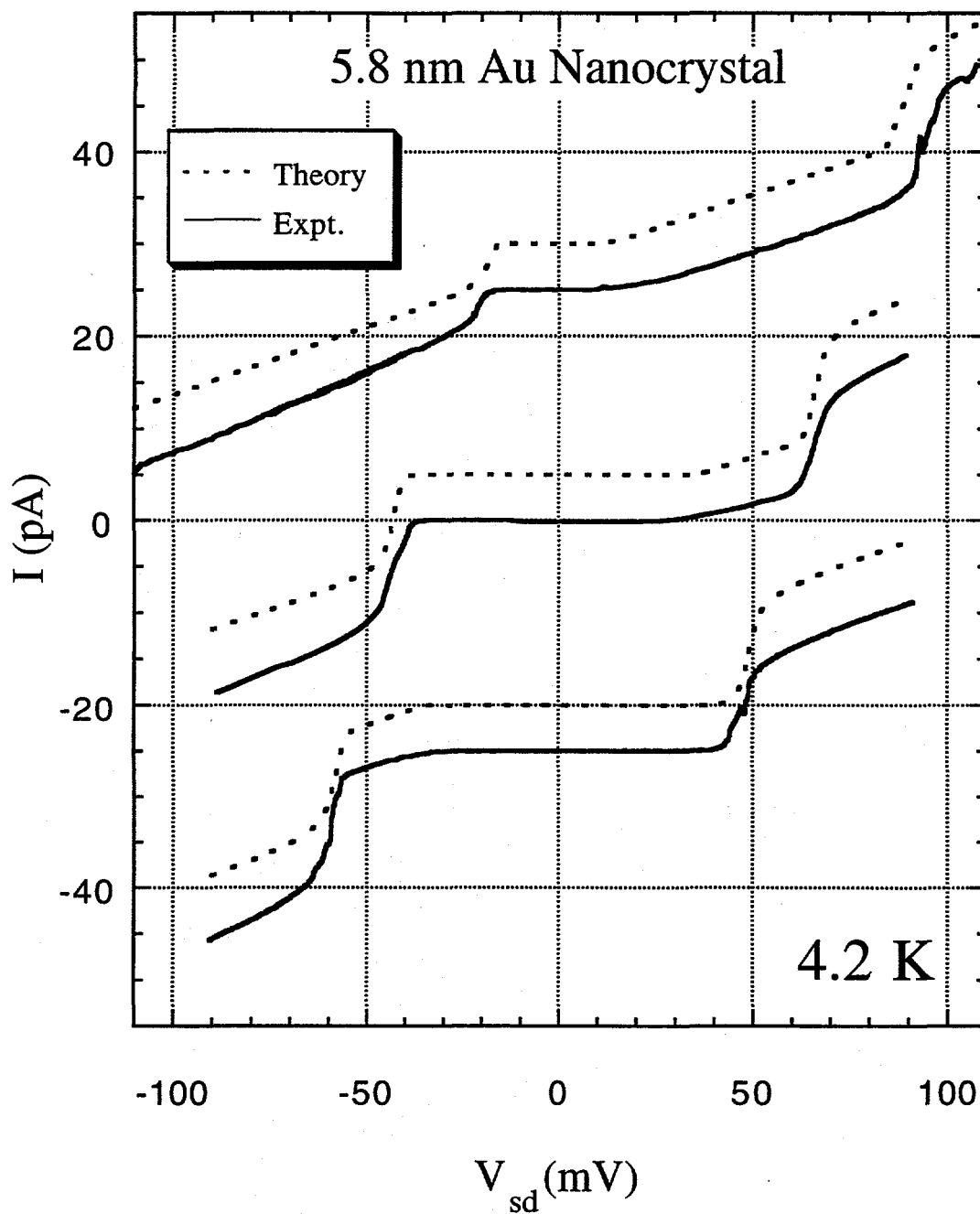


Figure 8-2: I - V_{sd} characteristic of a 5.8 nm diameter Au nanocrystal measured at 4.2 K. The solid lines show three I - V curves measured over the course of several days. Each is offset for clarity. These different curves result from changes in the local charge distribution about the dot. The dashed lines are fits to the data using the orthodox Coulomb blockade model as discussed in the text.

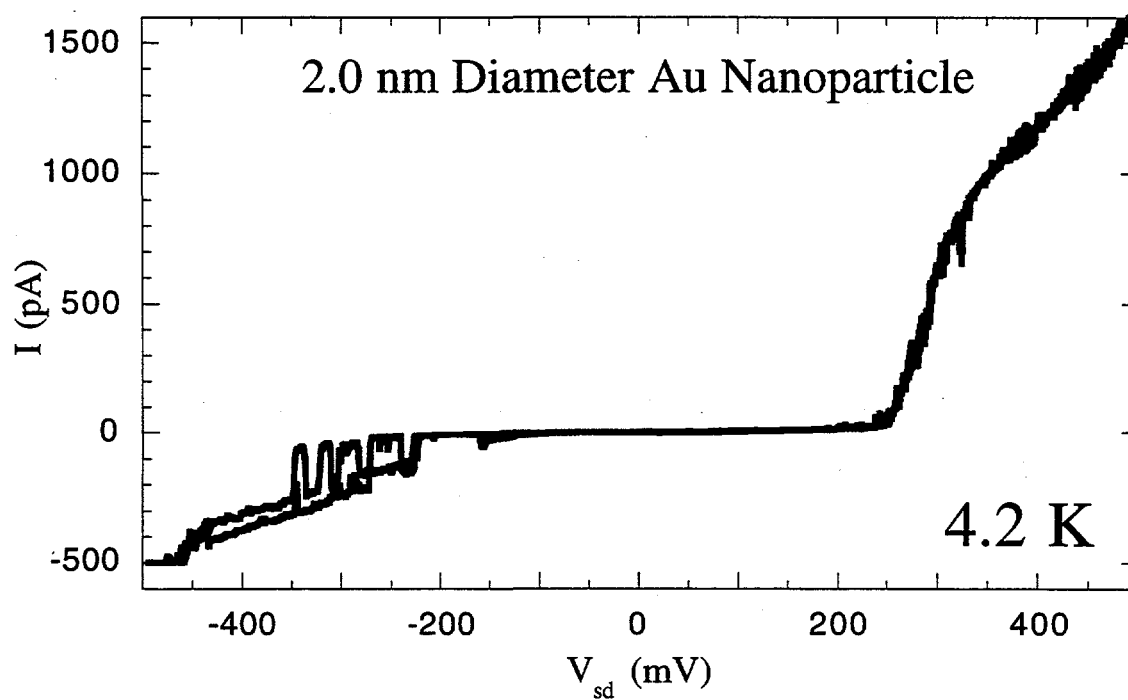


Figure 8-3: I - V_{sd} characteristic of a 2 nm diameter Au nanoparticle measured at 4.2 K. A large, ~200 mV Coulomb gap can be seen.

to study the Coulomb gap are observed to induce significant system noise, as seen in figure 8-3.

As a result, a detailed characterization (like that performed in section 8.2.2) of this device is not possible. We can say, however, that this 2 nm Au nanoparticle system has a charging energy of ~ 200 meV. This energy is estimated by noting the maximal Coulomb gap seen during the course of our measurements (section 2.3). More detailed studies of such a small nanocrystal have proven difficult as a result of the large voltages required. We could, but have yet to, improve the studies of such diminutive particles by using a gate to reduce the size of the Coulomb gap.

8.2.4 Discussion

As seen above, a Au nanoparticle can be incorporated between our leads to form a Coulomb blockade device. The transport behavior is well modeled as that of a classical dot.

The charging energy of a 5.8 nm diameter Au particle device was found to be 44 meV, while the charging energy of a 2.0 nm Au particle device was found to be ~ 200 meV. A simple estimation of the charging energy (equation 1-4) of a 5.8 nm diameter metallic sphere placed 1.2 nm away from two leads in a dielectric medium of $\epsilon = 2.6$ (appropriate for a 1,6 hexanedithiol linker molecule [Porter *et al.* 1987]) is 42 meV. A comparable estimation of the expected charging energy of a 2.0 nm Au particle is 190 meV. These values are in good agreement with the data.

In general, gold nanoparticle devices are observed to be relatively stable in ambient conditions for a few weeks. However, it was found that a large V_{sd} could change a device's properties. In particular, source-drain biases greater than ~ 0.2 V occasionally caused small changes in the offset potential of the nanocrystal (see, for example, the different measurements in figure 8-2). The application of $V_{sd} > 1$ V (which represents an electric field of $\sim 10^6$ V/cm) often drastically changed the resistances and capacitances of the system and occasionally destroyed the device. For example, between the measurement

of the 77 K characteristic of a Au nanoparticle (figure 8-1a) and the 4.2 K characteristic (figure 8-1b), room temperature measurements with a V_{sd} of up to 2 V were performed. These measurements led to rapid jumps in the impedance of the device, and, upon subsequent cooling, the period of the Coulomb staircase had significantly changed. These devices are thus relatively stable, but can be modified or destroyed by the application of a large source-drain bias.

8.3 CDSE NANOCRYSTALS - TWO TERMINAL MEASUREMENTS

8.3.1 Introduction

We have also made significant efforts in the study of CdSe nanocrystals. CdSe is a semiconductor and, as a result, CdSe nanocrystals have far fewer carriers than do metallic nanocrystals. As discussed in chapter 1, a lower carrier density means a larger spacing between quantum levels. By contrasting the results obtained on CdSe quantum dots to those obtained on Au classical dots, we can learn about the nature of these quantum levels.

We have deposited CdSe nanocrystals on over 40 chips (see appendix F). Among various mistakes and failures*, we have made and studied ~20 working CdSe nanocrystal devices of varying quality. I will describe and discuss the two terminal measurements that we have made on some of these devices below. Three terminal measurements will be discussed in section 8.4.

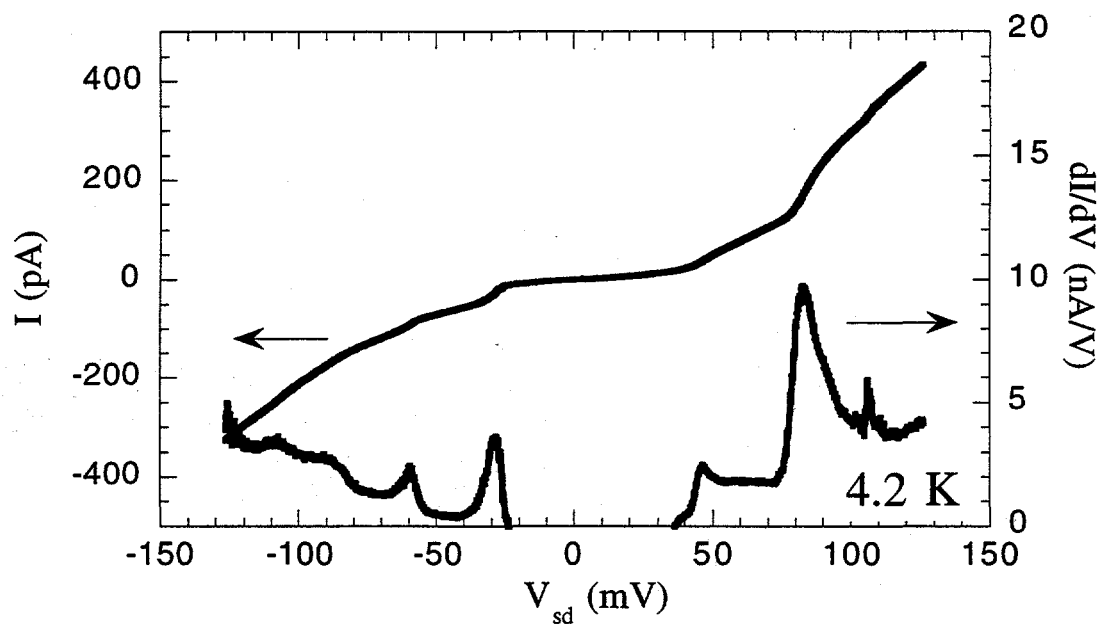
8.3.2 Overview

Figure 8-4 presents a smorgasbord of I - V_{sd} characteristics taken on 5.5 nm diameter CdSe nanocrystal devices. Each I - V_{sd} is from a different device. Coulomb blockade characteristics are seen in all of these I - V_{sd} 's. Unlike the Au measurements discussed above, these devices have additional structure superimposed upon their Coulomb staircase type response†. The observed device impedances tend to be on the order of

*This time including chemistry problems, lithography problems, and many, many blown leads.

†For example, at the onset of conductance in figure 8-4b several conductance peaks are seen.

a)



b)

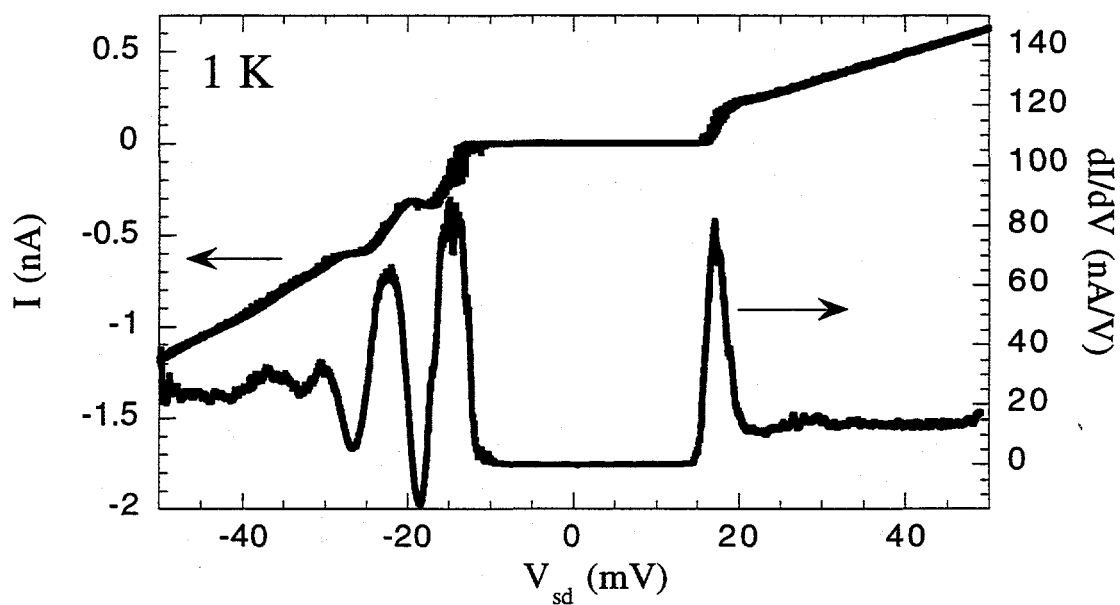
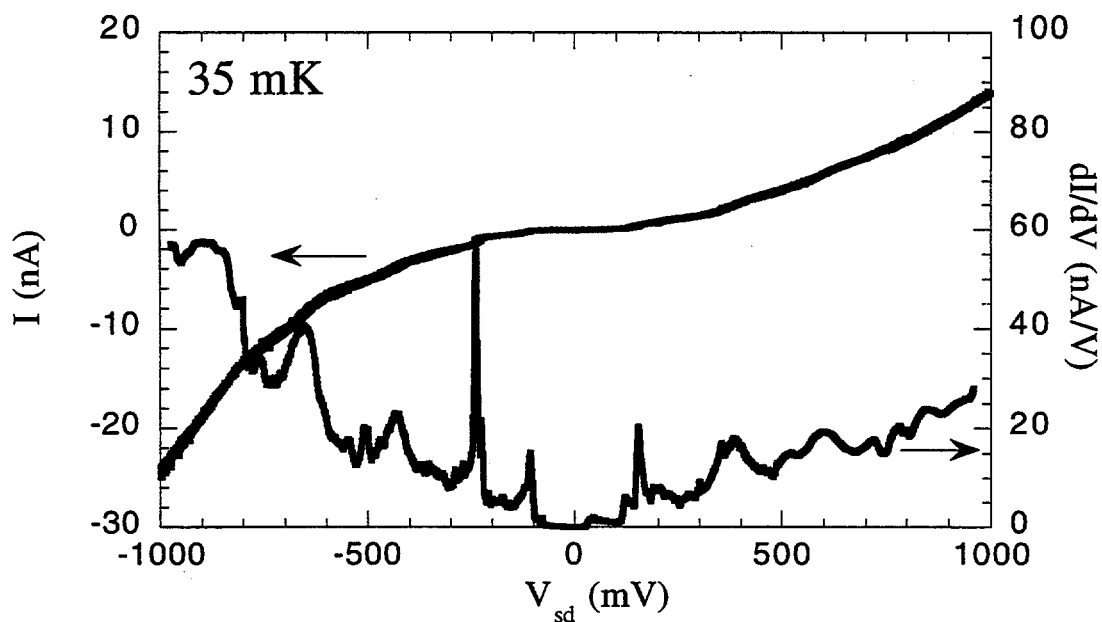


Figure 8-4: The current, I , and differential conductance, dI/dV_{sd} plotted as a function of the source-drain bias, V_{sd} , for various 5.5 nm diameter CdSe nanocrystal Coulomb blockade devices. a) The response of device B10-4b. b) The response of device B10-6c.

Figure 8-4 is continued on the next page.

c)



d)

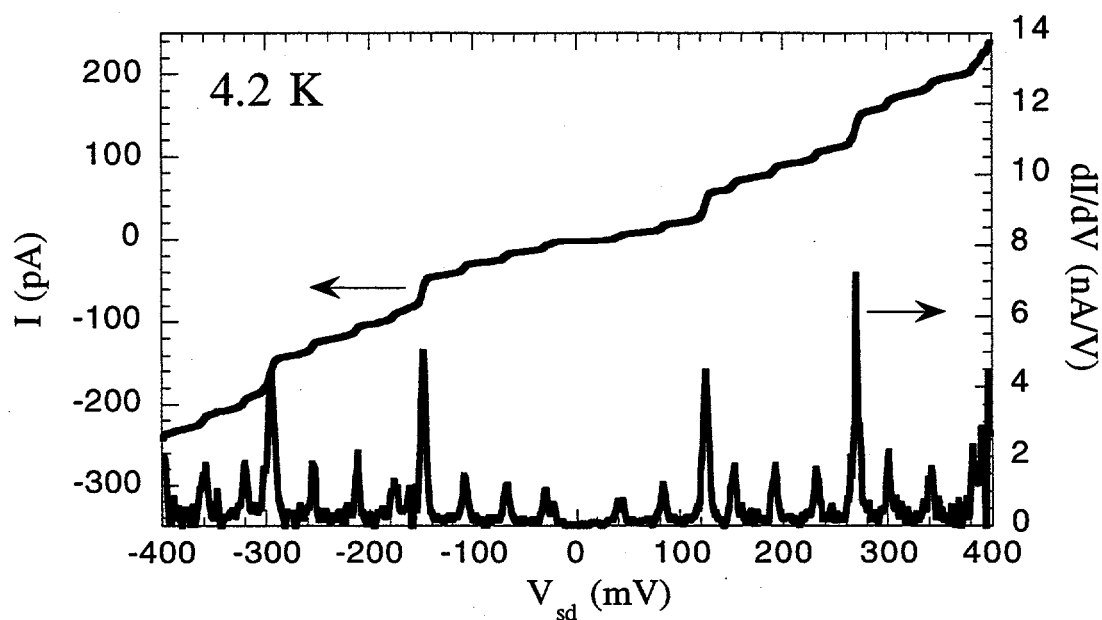
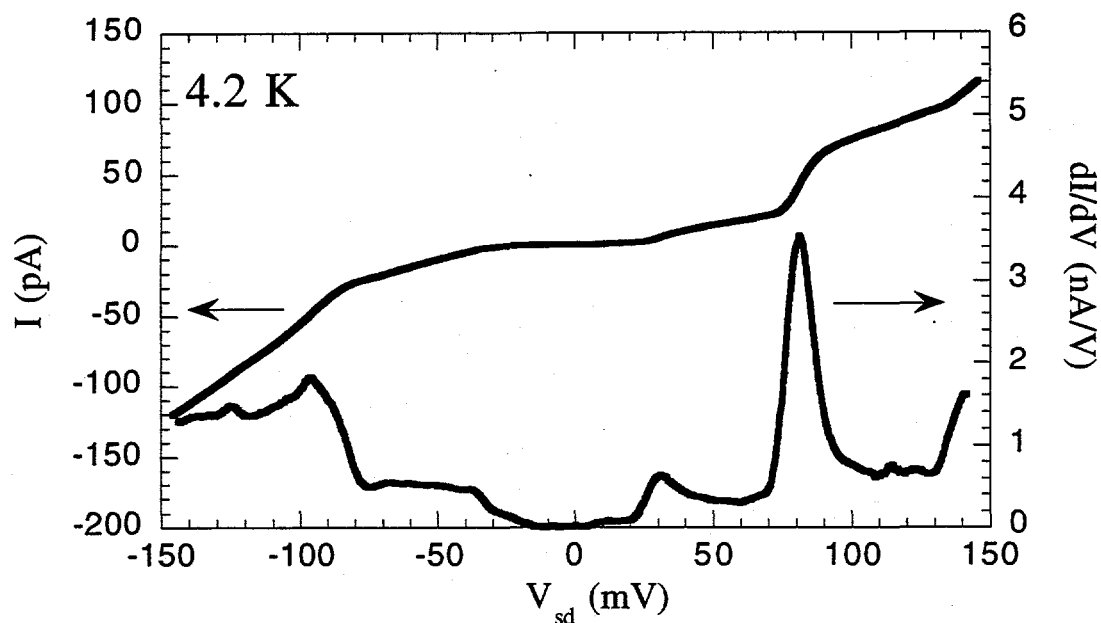


Figure 8-4 continued: The current, I , and differential conductance, dI/dV_{sd} plotted as a function of the source-drain bias, V_{sd} , for various 5.5 nm diameter CdSe nanocrystal Coulomb blockade devices. c) The response of device B10-5e. d) The response of device B16-1d.

Figure 8-4 is continued on the next page.

e)



f)

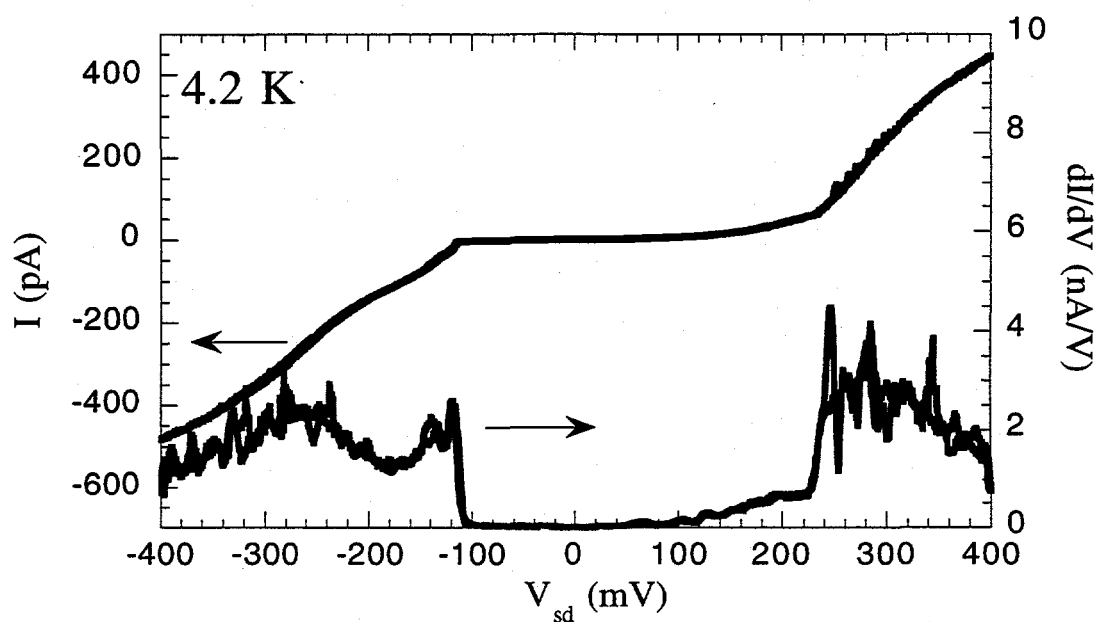


Figure 8-4 continued: The current, I , and differential conductance, dI/dV_{sd} plotted as a function of the source-drain bias, V_{sd} , for various 5.5 nm diameter CdSe nanocrystal Coulomb blockade devices. e) The response of device B24-3f. f) The response of device B24-6b.

Figure 8-4 is continued on the next page.

g)

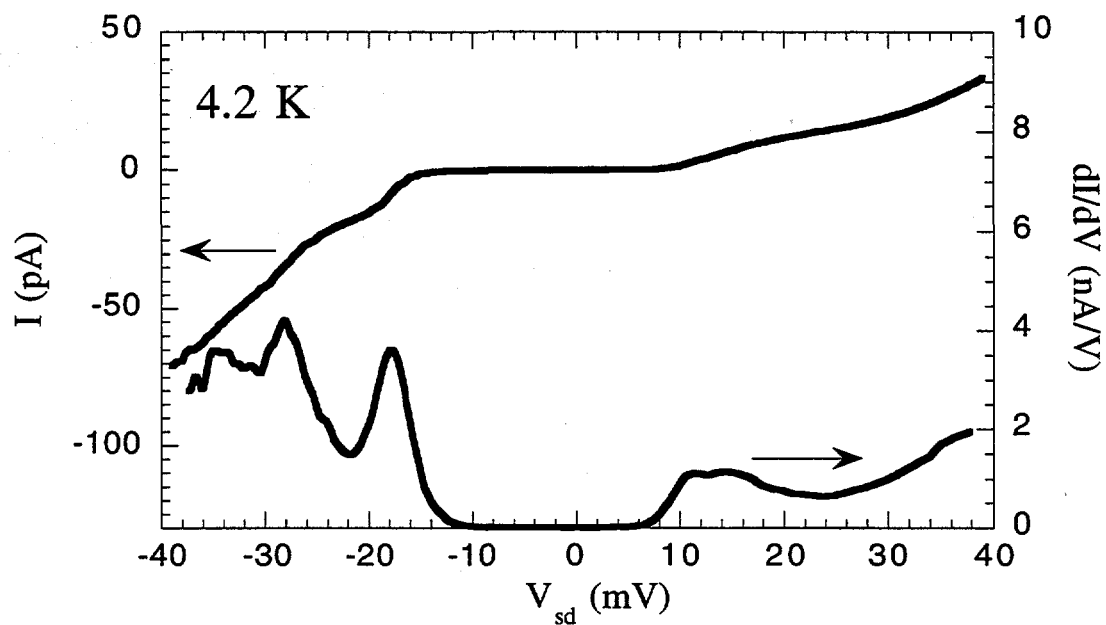


Figure 8-4 continued: The current, I , and differential conductance, dI/dV_{sd} plotted as a function of the source-drain bias, V_{sd} , for various 5.5 nm diameter CdSe nanocrystal Coulomb blockade devices. g) The response of device G3-5d.

100 M Ω - 10 G Ω with addition energies in the 35 meV regime* (appendix G). Below, we will discuss some of the particular traits of these devices and the measurements that we have made on them.

8.3.3 Temperature Dependence

Figure 8-5 shows the overall temperature dependence of the I - V_{sd} characteristic of the 5.5 nm diameter CdSe nanocrystal device introduced in figure 8-4a. We see that as the temperature is lowered from 300 K to 77 K, the conductance of the system drops and some features emerge in the I - V_{sd} characteristic. In the transition from 77 K to 4.2 K even more structure emerges and the conductance stays about the same (in fact it rises slightly).

The sharpening of features is a result of a decrease in the thermal broadening at low temperatures. A derivative of the 77 K I - V_{sd} of figure 8-5 reveals that features at this temperature have a breadth of ~ 60 mV, while the 4.2 K I - V_{sd} has features that are ~ 5 mV wide. The thermal energy, kT , at 77 K is 6.6 meV, while the thermal energy at 4.2 K is 0.36 meV. As discussed in chapter 2, the expected thermal broadening of Coulomb blockade type features is $\sim 4 kT$. In I - V_{sd} measurements, this must be multiplied by a factor of about two to account for dot-lead capacitive coupling. This then gives an expected broadening at 77 K of order 50 meV and an expected broadening at 4.2 K of order 3 meV, in good agreement with the data.

8.3.4 Random Telegraph Noise

In our measurements of nanocrystals, noise is a frequent problem. This noise is often manifested as a lateral shifting of the I - V_{sd} characteristics. An example of this noise at

*Typically the addition energies (defined as the sum of the charging and quantum energies) of these devices was estimated by noting the maximal the Coulomb gap seen during their measurement. Some devices proved stable enough that high bias I - V_{sd} 's could be taken. On these devices we estimated the addition energy as $\sim 1/2$ the Coulomb staircase period. For gated devices, we could explicitly measure the addition energy as discussed in section 8.4.

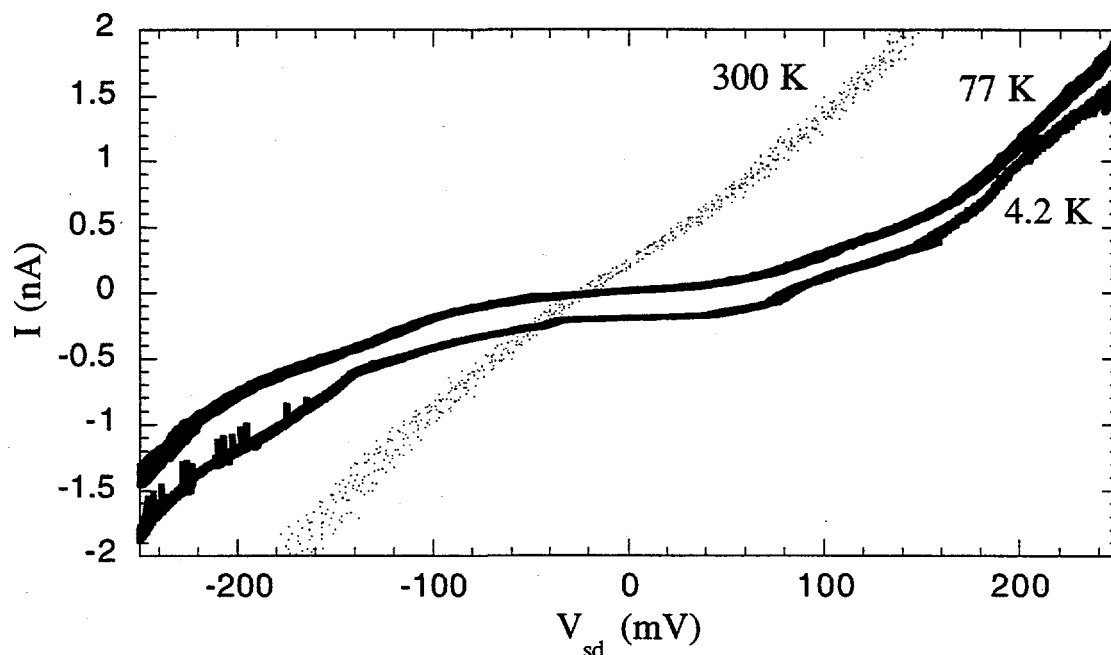


Figure 8-5: The dependence of the measured I - V_{sd} characteristic upon temperature for the 5.5 nm diameter CdSe nanocrystal device introduced in figure 7-4a. Each curve is offset for clarity. We see that the conductance drops by a factor of ~ 2 as we go from 300 K to 77 K and some structure emerges. The conductance remains about constant as we cool the sample to 4.2 K and further structure becomes visible.

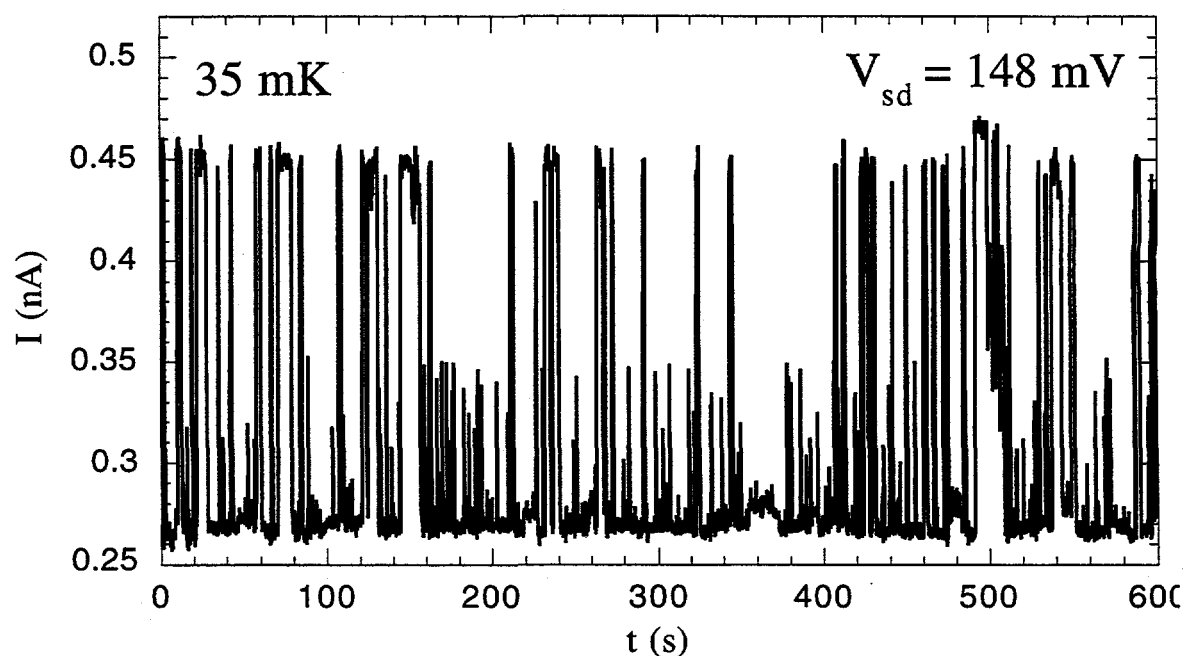


Figure 8-6: Time evolution of the current at a fixed source drain bias of 148 meV applied to the 5.5 nm diameter CdSe nanocrystal device introduced in figure 8-4c. A rapid switching (random telegraph noise) between a few current levels is seen.

a fixed V_{sd} is given in figure 8-6. This dataset was taken on the device originally shown in figure 8-4c, on the edge of a Coulomb step, at a fixed V_{sd} of +148 mV.

This switching is interpreted to be a result of jumps in the offset potential of the nanocrystal (chapter 2). Near the nanocrystal under study lies several other nanocrystals and assorted impurities. Electrons will occasionally jump into or out of metastable states in these energy wells. As they do so, they change the local charge environment about the nanocrystal and induce a shift in its offset potential. Sometimes the shift is persistent and causes a lasting change in the system's behavior (for example, see figure 8-2). More often, the shift will only be transient and results in noise. This noise, caused by repeated changes in the charge states of electron traps near a nanocrystal, is referred to as random telegraph noise* [Kirton and Uren, 1988]. Such noise is a common *feature* of mesoscopic systems and, as seen in figure 8-6, is also a common feature of our devices.

8.3.5 The Death of a Device

Typically the devices would die when a large V_{sd} was applied or when left exposed to ambient conditions for multiple weeks. However, a couple of devices went into a permanent non-conducting state spontaneously. Figure 8-7 shows *before* and *after* I - V_{sd} 's of a device (originally introduced in figure 8-4b) that spontaneously jumped into a non-conducting state. We see that after the device's "death" the conductance is much lower and no Coulomb blockade type structure is seen. The conductance level in this latter state is very comparable to that seen in the Coulomb gap of the earlier state. Upon warming the device to room temperature, its conduction remained very low†.

We interpret this change to be the result of the disappearance of the nanocrystal under study. In the alive state, a nanocrystal bridges the gap between the leads and, when the Coulomb gap is surpassed, dominates the current flow. For an unknown reason this

*Or random telegraph signal if it the feature under study.

†This rules out intradot effects such as the shifting of the electrochemical potential to within the bandgap of the nanocrystal (see section 8.4.2).

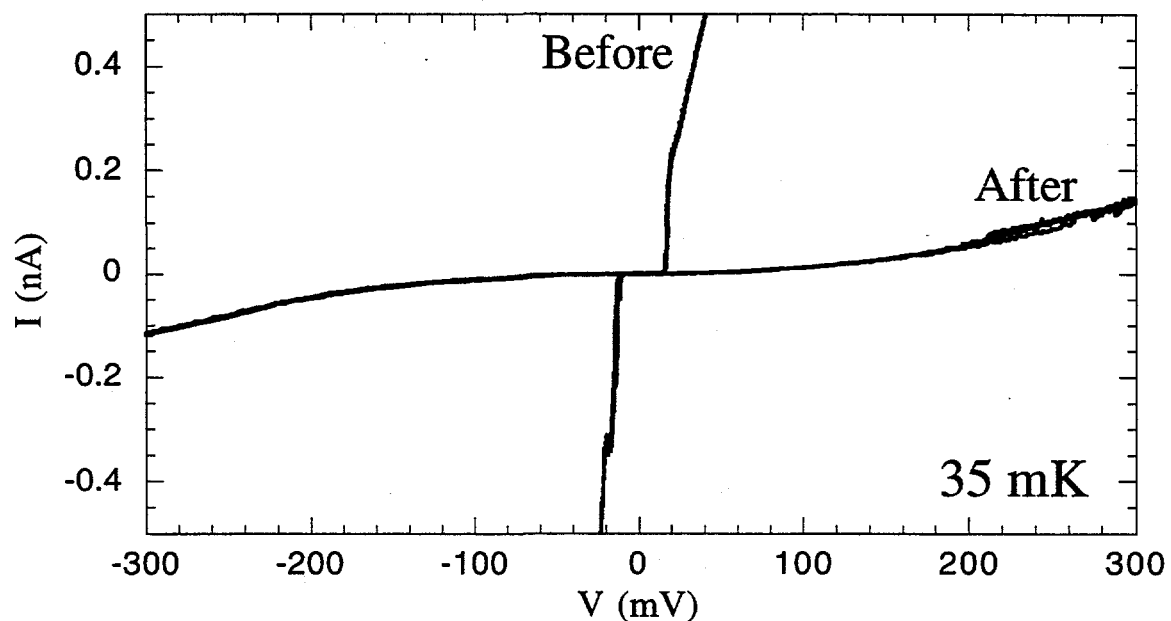


Figure 8-7: The death of the 5.5 nm diameter CdSe nanocrystal device originally introduced in figure 8-4b. In the original ("before") state, a Coulomb blockade like I - V_{sd} characteristic is seen. After the device spontaneously switched to a new, non-conducting ("after") state, the current level has dropped precipitously. The conductance of this new state is consistent with that seen in the Coulomb gap of the original state.

nanocrystal then moved out of position or was damaged. As a result the only conduction pathway is direct tunneling between the leads, a much higher impedance process.

8.3.6 Summary

In the above presentation, we have seen that CdSe nanocrystals can be deposited between two metallic leads for electrical study. Like Au nanoparticles, a Coulomb gap and staircase is seen in the I - V_{sd} characteristics of these devices. The addition energy of these particles is ~ 35 meV; comparable to similarly sized Au particles. However, for each charge state of the nanocrystal, additional peaks in dI/dV_{sd} are seen. Such substructure is a general feature of the measurements of CdSe nanocrystals and is not present in the measurements of Au particles. As CdSe has a lower electron density and a higher ionicity than Au, the substructure likely arises from quantum levels and/or LO-phonon interactions. To understand these peaks, we need another parameter to adjust; a gate*. By using a gate to tune the electrochemical potential of our nanocrystal, we can watch how the I - V_{sd} characteristic evolves and gain a quantitative understanding of the transport in our system.

8.4 CDSE NANOCRYSTALS - THREE TERMINAL MEASUREMENTS

8.4.1 Introduction

Figure 8-8a plots the 4.2 K linear response conductance of a 5.5 nm diameter CdSe nanocrystal transistor[†] as a function of the gate voltage, V_g , applied to the substrate. As the gate bias is raised, the conductance of the nanocrystal transistor, initially zero, grows to a peak and then declines back to zero. This conduction peak, or Coulomb oscillation, is a consequence of the finite energy required to add (or remove) an electron to (from) the

*One could also use a magnetic field. Such studies have been made on 2-terminal devices, yet occasional changes in the devices' offset potential have made the results difficult to interpret.

[†]Originally shown in figure 7-4g.

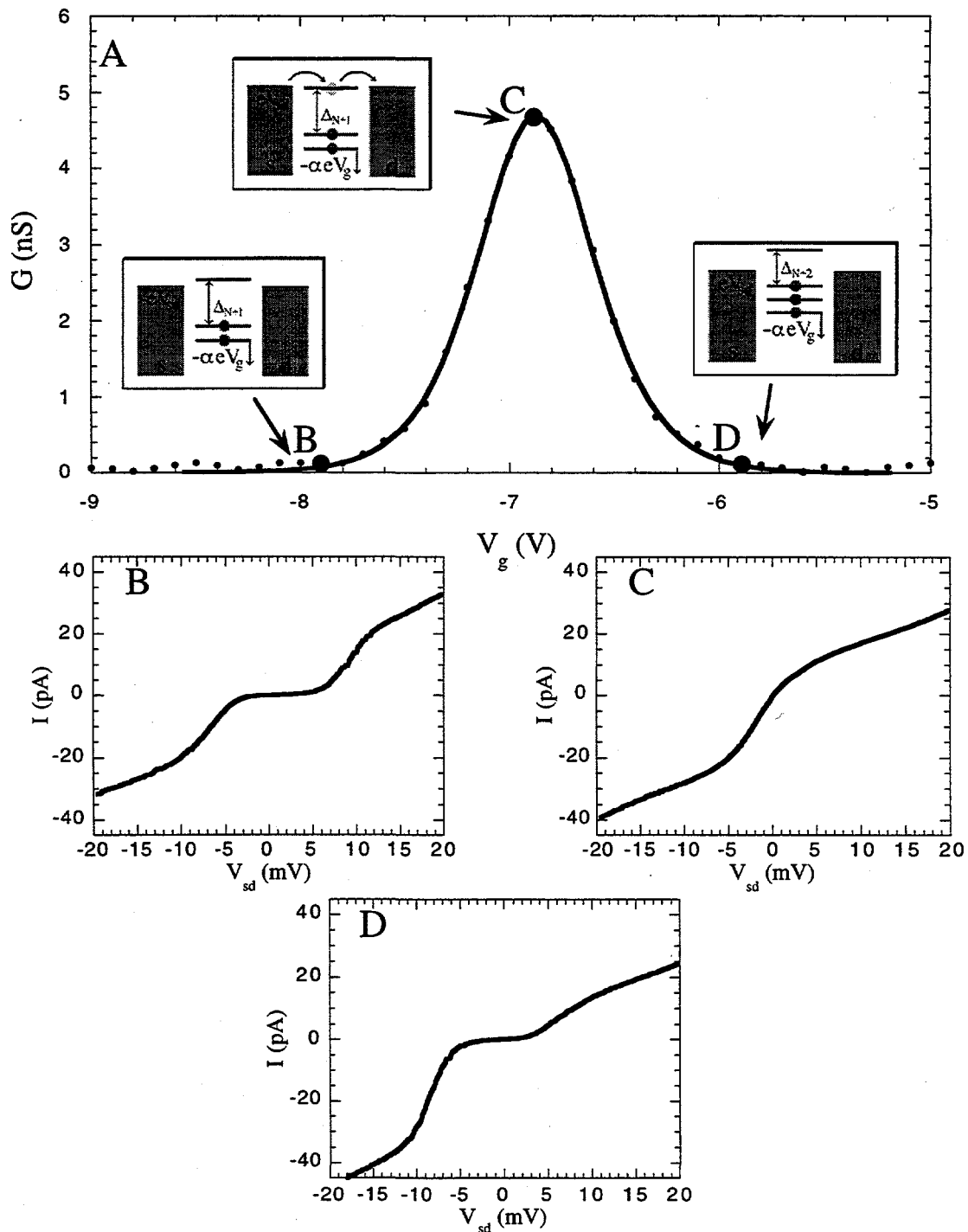


Figure 8-8: a) Conductance versus gate voltage for a 5.5 nm CdSe nanocrystal measured at 4.2 K. The solid curve is a fit to the data of form $[kT \cdot \cosh^2(\mu_N/2kT)]^{-1}$. This is the appropriate fit for Coulomb oscillations (see chapter 2) in a single electron transistor and gives $T = 5 \pm 1$ K. (b) I - V_{sd} characteristics measured at a fixed gate voltages of -7.9 V. (c), (d) the same with V_g equal to -6.9 and -5.9 V respectively.

nanocrystal and is analogous to the electron affinity (ionization energy) of a molecule. A further discussion of the physics of Coulomb oscillations can be found in chapter 2.

In figures 8-8b, c, and d; we plot the source-drain current, I , as a function of the source-drain bias, V_{sd} , at three fixed values of V_g about the Coulomb oscillation shown in figure 8-8a. The I - V_{sd} 's taken with a V_g that is 1 V off the linear response peak show a suppressed conductance at small V_{sd} , i.e. a Coulomb gap, while the I - V_{sd} characteristic taken at the linear response peak shows a finite conductance at zero bias.

In figure 8-9, we plot the differential conductance of the same CdSe nanocrystal transistor, now as a function of both V_g and V_{sd} . This is essentially a plot of how the I - V_{sd} characteristic of the dot evolves as a function of the applied gate voltage, V_g . A G - V_g plot like the one shown in figure 8-8a is a horizontal slice of this dataset taken at $V_{sd} = 0$. Vertical slices of this dataset gives dI/dV_{sd} as a function of V_{sd} , the derivative of plots similar to figures 8-4 and 8-8b, c, and d.

The analysis of this dataset proceeds in a manner similar to that presented for figure 8-8. As we apply sufficient V_{sd} (y axis of figure 8-9) to surmount the nanocrystal's Coulomb gap, there will be a sharp rise in the current, a peak in dI/dV_{sd} . Peaks in dI/dV_{sd} seen at higher V_{sd} can occur as a result of transport through excited states of the nanocrystal. An increased gate voltage (x-axis of figures 8-9) will lower the electrochemical potential of the nanocrystal and shift the position of these peaks. As a result, the edge of the Coulomb gap and features in the nanocrystal's level structure appear as lines in figure 8-9. Lines moving with positive slope* occur when a conductance feature of the nanocrystal is coincident with the source's Fermi level, while lines of negative slope occur when nanocrystal features match the Fermi level of the drain. At the charge degeneracy point of the nanocrystal, the lines corresponding to the onset of conduction in the nanocrystal (the edges of the Coulomb gap) cross and form an X-like pattern.

*With respect to a grayscale plot of V_{sd} versus V_g .

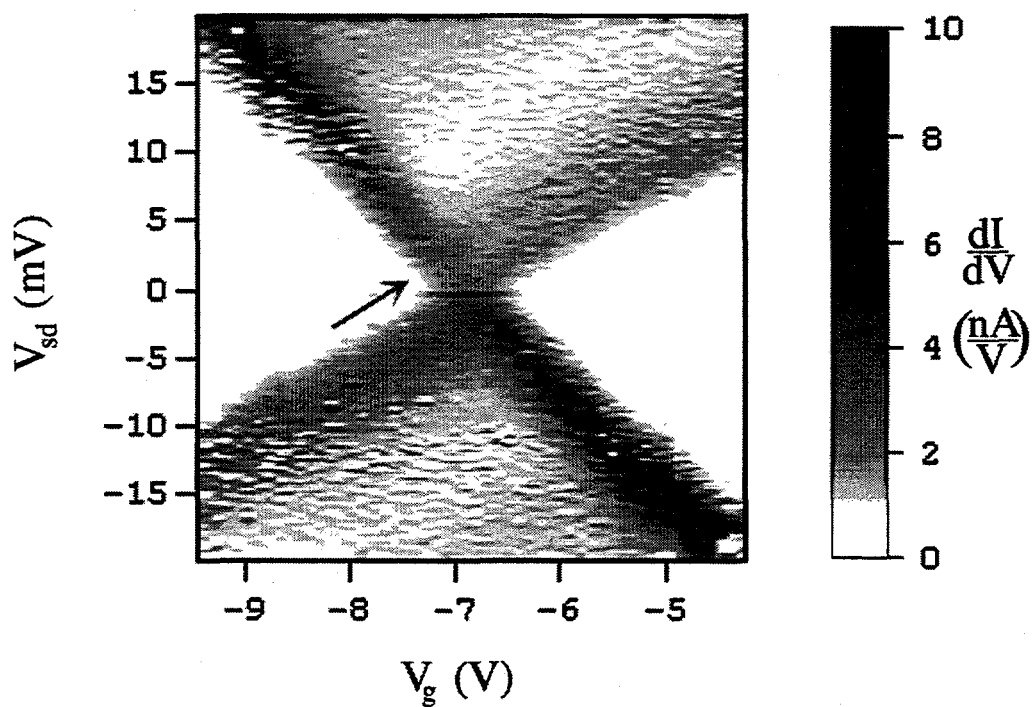


Figure 8-9: Differential conductance, dI/dV_{sd} of a CdSe nanocrystal plotted as a function of gate and source-drain bias. A barely resolved excited state is marked with an arrow, and further discussed in the text.

This then demonstrates the ability of a back gate to vary the electrochemical potential of our dot. As we will now discuss, the ability to tune the Coulomb gap and induce Coulomb oscillations greatly expands the range of transport phenomena that can be explored in our devices.

8.4.2 Depletion of a Nanocrystal

In figures 8-10a and 8-10b, we again plot the differential conductance, dI/dV_{sd} , as a function of both V_g and V_{sd} ; this time over a larger range*. These gray-scale plots are shown abreast of each other to reflect their relative positioning in the overall response characteristic of the transistor. In figures 8-10a and 8-10b, we see that the Coulomb gap evolves to form an aperiodic diamond-like pattern as we sweep V_g . Random telegraph noise (section 8.3.4) is seen for $V_{sd} > 20$ mV. A change in the offset potential occurred between the acquisition of figures 8-10a and 8-10b. During the acquisition of figure 8-10a, 2 smaller shifts in the offset potential occurred. To account for this, we shifted some parts of this dataset. A schematic of the evolution of the Coulomb gap seen in figures 8-10a and 8-10b is shown in figure 8-10c.

Each time the Coulomb gap is tuned to zero in figures 8-10a and 8-10b, we are changing the charge state of the nanocrystal. By comparing the difference in gate voltage required to effect this change to the maximal Coulomb gap observed between the two charge degeneracy points, we can determine the coupling of the gate to the nanocrystal. For this device, we find that one volt applied to V_g lowers the electrochemical potential of the nanocrystal by 2.7 meV.

On the right side of figure 8-10, we see that after a number of oscillations there exists a large barrier to electron addition. For a gate bias of up to 40 V (the largest that we can apply) no additional Coulomb oscillations are observed. Here, the Coulomb gap only

*Figure 8-9 was taken about the right-most charge degeneracy point of these figures.

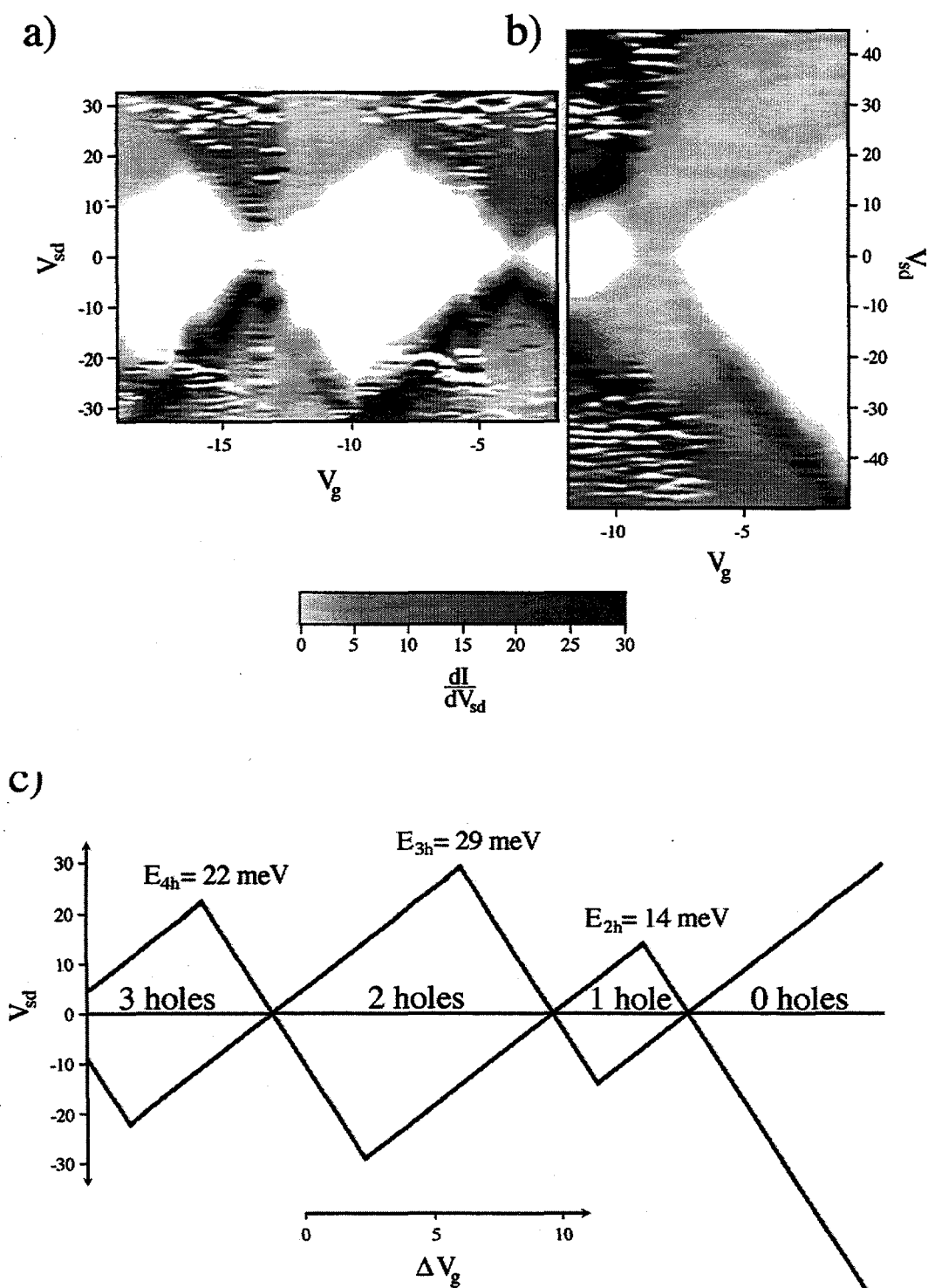


Figure 8-10: (a),(b) Gray scale plots of the differential conductance, dI/dV_{sd} of a CdSe nanocrystal plotted as a function of the applied gate and source-drain bias. (c) A sketch of the evolution of (a) and (b).

grows with V_g and eventually exceeds* 150 mV. This is in sharp contrast to negative gate voltages, for which the diamond-like pattern of figure 8-10 persists down to the largest negative gate voltage that we can apply (~ -40 V)

The large electron affinity seen at positive gate bias is interpreted to be the result of a filled nanocrystal valence band. With the gate, we have lowered the energy of the nanocrystal to the point at which the every state in the valence band has been filled with an electron. The next extended state of the nanocrystal lies in its conduction band, 2.0 eV higher in energy [Murray *et al.* 1993].

The rightmost Coulomb oscillation of figure 8-10b (and 8-10c) then represents the removal of the first electron from the valence band (alternately the addition of the first hole). A further decrease in V_g causes additional ionizations. We find that, for this nanocrystal, the ionization energy for the 2nd electron is 14 ± 2 meV and that it takes a further 29 ± 3 meV and 22 ± 2 meV to remove the 3rd and 4th electrons respectively. We discuss these values within the context of current models for the electronic structure of CdSe nanocrystals in section 8.5.

8.4.3 LO Phonon Emission

Once the nanocrystal is conducting, a further increase of V_{sd} will probe non-equilibrium modes of transport. Conductance features seen here correspond to resonant tunneling through excited states of the nanocrystal and to energy loss mechanisms such as LO-phonon emission. In figure 8-11, we enlarge the region about the rightmost Coulomb oscillation of figure 8-10, the zero to one hole transition. Here, a rather pronounced conductance feature (marked with an arrow) can be seen at negative V_{sd} . The source-drain bias at which this feature is coincident with the Coulomb gap tells us the energy difference between this state and the ground state of the nanocrystal. Such analysis reveals that this particular conduction channel lies 25 ± 2 meV above the valence band edge of the

*As we could not apply a greater V_g , we do not know how much larger the Coulomb gap becomes.

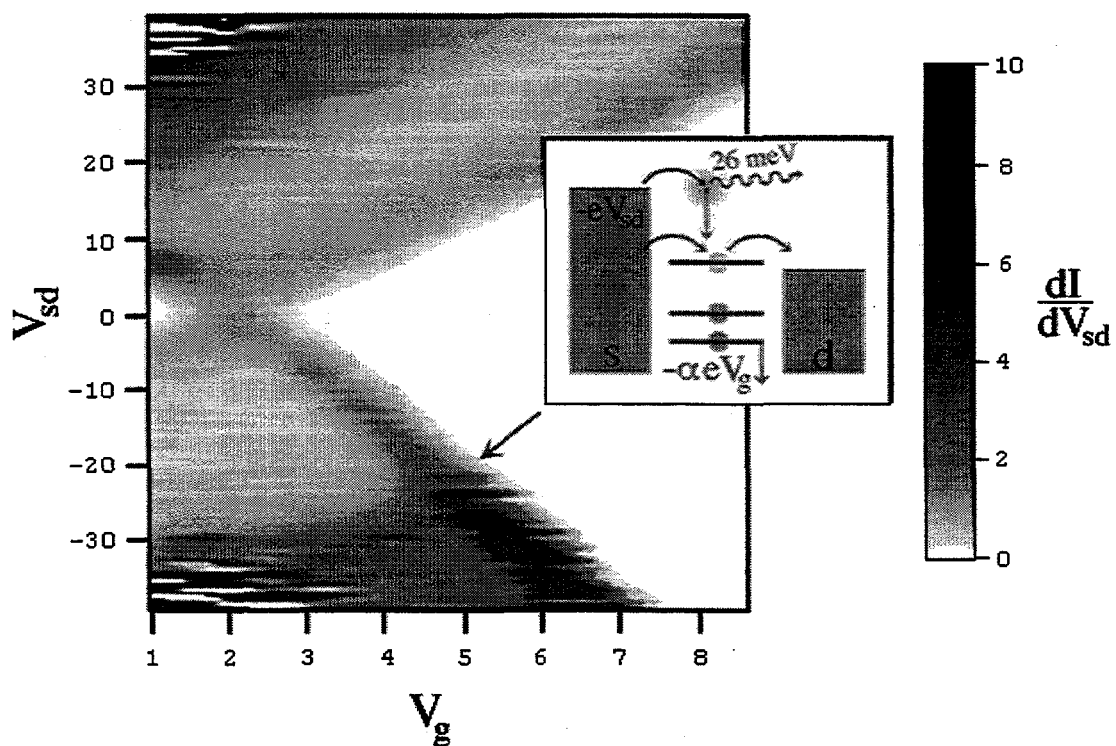


Figure 8-11: Grayscale plot of the differential conductance, dI/dV_{sd} of a CdSe nanocrystal plotted as a function of the applied gate and source-drain bias. This data was taken about the rightmost Coulomb oscillation of figure 8-9b. With an arrow (and an inset) we mark an conductance feature that heralds the emission of a phonons by tunneling electrons.

nanocrystal, an energy regime devoid of extended states. We thus interpret this feature to be the result of LO phonon emission. When eV_{sd} exceeds ϵ_{LO} (26 meV for CdSe), electrons tunneling from the source lead to the nanocrystal* can emit a phonon. This opens a new channel for conduction and results in a sharp rise in the current (a peak in dI/dV_{sd}).

8.4.4 Transport Via Excited States

In figure 8-10 and other datasets (such as figure 8-4), there exist additional broad peaks with spacings that range from the thermal resolution limit (<1 meV at 4.2 K) to ~ 15 meV. Many of these are likely the result of transport via excited states of the nanocrystal. Figure 8-9 shows the low bias response immediately about the rightmost Coulomb oscillation of Figure 8-10. Here, a barely resolved second peak is seen running parallel to the Coulomb gap in the top right quadrant of the figure (marked with an arrow). As discussed above, we can determine the position of this state relative to the ground state of the nanocrystal by noting the position at which the level intercepts the Coulomb gap. Such an analysis reveals that this feature lies 3 meV below the ground state of the 1 hole nanocrystal. We interpret this feature to be an excited state of the 1 hole nanocrystal†.

8.4.5 On the Number of Nanocrystals in Our Device

In general, in our devices, the transport appears to be dominated by single nanocrystals. For Au nanoparticles this statement is easily justified by the fact that the data can be best understood by using an orthodox single dot model. For CdSe nanocrystals, the transport behavior is more complex and determining the number of nanocrystals through which transport occurs is a bit more difficult. As an aid, we below discuss the expected nature of transport for multiple nanocrystal systems.

For two (or more) nanocrystals placed in parallel between two leads, the observed current flow is the sum of the current flow through each nanocrystal. As a result, we expect

*Alternately, holes transiting from the nanocrystal to the source.

†Recall that for holes (which have negative mass) an excited state lies *lower* in an energy diagram.

to see two superimposed staircases in the measured I - V_{sd} characteristic; one staircase for each nanocrystal. Typically, every nanocrystal will have a slightly different nature and position and so the period and offset potential of these staircases will differ. The observed Coulomb gap in this system is the lesser of the Coulomb gap of either nanocrystal.

For two dots placed in series, the behavior is more complex [Livermore *et al* 1996, Dixon *et al.* 1996, van der Vaart *et al.* 1995, Hofmann *et al.*,1995]. Now, the source-drain current is that which is able to pass through both nanocrystals and so is regulated by the less compliant of the two. As a result, the overall system's Coulomb gap is greater than that of the constituent nanocrystals. Furthermore, the linear response conductance of the system will only be finite when both nanocrystals are at a charge degeneracy point, a rare occurrence.

The best approach to determine the number of nanocrystals in our system is to use a gate. This allows us to watch the evolution of the Coulomb gap and staircase as we change the electrochemical potential of the nanocrystal. As any two nanocrystals will differ in their gate coupling (C_g/C_{tot}) and in the details of their nature, we can differentiate a single dot system from a multiple dot one by examining the transport through the dot as we vary V_g . In plots like those shown in figure 8-9, 10, and 11; multiple nanocrystals in parallel would produce multiple sets of overlapping diamonds. Nanocrystals in series would have suppressed transport at low V_{sd} and Coulomb oscillations would generally not be seen. Neither type of behavior properly describes the transport that we see in these figures. Rather, a single nanocrystal model best describes the observed transport behavior. This is also the case for the two other single electron transistors that we have studied.

The majority of our sample did not have an incorporated gate, however. For these devices, we must examine the system's response as the offset potential is shifted by changes in the local charge environment. This is essentially the same as a gate-type study, with the exception being that we have minimal control over the applied gate bias.

In all but one of the two terminal devices that we have measured, the response is best characterized as that of a single nanocrystal. The dot shown in figure 8-4d is an exception to this rule. Here, two staircases are clearly seen. The first has a period of 40 mV, while the second has a period of 146 mV. If these two dots were to conduct in parallel, the system's Coulomb gap would never grow larger than 40 mV. If the dots are in series, we would typically not observe low bias conduction and the Coulomb gap could grow as large as ~160 mV. We observe the latter case to be correct for this particular device. Because the steps of the 40 mV period staircase are perfectly periodic and equal in height, we believe that this staircase is not the result of a second CdSe particle, but is rather the result of a metallic grain. Likely this grain was formed by a small break in the tip of one of the leads.

At first blush, the notion that the transport is dominated by a single nanocrystal is in conflict with figure 7-6, in which several nanocrystals can be seen bridging the gap between the two leads. However, we must keep in mind that tunneling current decays exponentially with distance [Simmons 1963]. Our tunnel barrier (1,6 hexanedithiol) is over 1 eV high* [Porter *et al.* 1987, Bain *et al.* 1989, Chidsey 1992, and Boulas *et al.* 1996]. The tunneling current through such a barrier decays with a characteristic length of less than 1 Å. This means that only a well positioned nanocrystal can contribute to the observed transport. This need for a good deal of luck is the reason for the low rate of success in device fabrication†. The odds of two nanocrystals successfully bridging the gap in series or parallel is much lower and so transport of our devices will generally be dominated by a single nanocrystal.

*This can also be seen in the high voltage region of the $I-V_{sd}$ characteristics (see 7-4c for example). As the transport remains roughly linear for high voltages, we find that our barriers must be over 1 eV high.

†Of the 500-1000 tunneling junctions measured, only ~20 had measurable conduction.

8.5 DISCUSSION

We now integrate the above described results to paint a portrait of our current understanding of the transport through CdSe nanocrystals.

To start, we look at the results obtained on Au nanoparticles (figures 8-1, 8-2, and 8-3). We find that $I-V_{sd}$'s of these system are well described by an orthodox Coulomb blockade model and that the transport is dominated by a single dot whose charging energy ranges from 44 meV (for a 6 nm diameter particle) to ~200 meV (for a 2 nm diameter particle). These values compare well to simple estimates of the expected charging energies (section 1.3). The tunneling impedances range from tens of $M\Omega$ to a few $G\Omega$ in these devices. This is consistent with tunneling through an order eV high barrier whose width is approximately 1 nm.

We can then use these well-understood results as a basis for the interpretation of the transport phenomena observed in CdSe nanocrystals (figures 8-4 through 8-11). We start by noting that the transport again appears to be the result of tunneling through a single nanocrystal (with the exception of 8-4d). Like Au, the tunnel barriers for CdSe appear to be greater than 1 eV high and the device impedances range from 10 $M\Omega$ to 10 $G\Omega$.

Let us now address the nature of the addition energy in CdSe nanocrystals. Typically, the addition energy for 5.5 nm diameter CdSe nanocrystals falls in the range of 30 to 80 meV; comparable to the values seen in Au particles. In section 8.4.2 (and associated figure 8-10), we are able to observe the addition of the first through fourth holes to the valence band of CdSe (alternately, the ionization of the first through fourth electrons). Here, we find that the addition energies for the 2nd, 3rd, and 4th holes are 14 ± 2 meV, 29 ± 3 meV, and 22 ± 2 meV respectively*. These values are a fair bit smaller than the typical addition energies seen in other, comparable CdSe nanocrystal systems.

*The ionization energy of the first electron is essential equal to the band gap (2.0 eV), an energy scale not accessible in these measurements.

The simplest model for understand these energies (introduced in section 2.4) is to say that the energy required to add the N^{th} hole to a $N-1$ hole nanocrystal is given as:

$$E_c + \Delta E_N. \quad (8-1)$$

Here, E_c is the charging energy of the nanocrystal and ΔE_N is the energetic difference between the N^{th} and the $(N-1)^{\text{th}}$ single particle hole state. When we are adding a hole to a partially filled degenerate quantum level, ΔE_N is zero and the addition energy is equal to the charging energy. When we are adding a hole to a *filled shell* nanocrystal*, the addition energy is ΔE_N greater than the charging energy of the particle. This model has been used with success in semiconductor heterostructures [Tarucha *et al.* 1996]. A complete theory of the single particle states of the valence band of CdSe has yet to be fully developed (section 4.3.2). In general, it is believed that the first two holes lie in a doubly degenerate quantum level†. The next hole level is 10-20 meV higher in energy and is at least doubly degenerate. We would thus expect the addition energy for the second and fourth holes to be equal, while the addition energy for the third hole should be 10-20 meV larger. Our data does follow a small-large-small trend for the 2nd through 4th addition energies. However, such a model can not be complete, for the addition energy for the 4th hole is 60% larger than that of the 2nd.

Thus a simple model which combines a capacitive charging energy with single particle quantum levels is not adequate to fully understand the addition energies. This is because, for nanocrystal with only a few carriers, correlation energies and variations in the system's effective capacitance are quite important [Tarucha *et al.* 1996 and Iafrante *et al.* 1995]. A yet to be performed, self-consistent calculation of the energy required to place the first few valence band holes onto a CdSe nanocrystal from a weakly coupled Au reservoir would offer valuable insights to these measurements.

*i.e. a nanocrystal whose uppermost quantum level is filled. This would be analogous to adding a electron to Ne. As Ne has a filled $2p^6$ shell, a rather substantial (0.3 eV [CRC, 73rd ed. 1992]) is required to add another electron (to the $3s^0$ shell).

†Assuming spin degeneracy.

Excited state spectroscopy should allow us to observe the higher lying quantum levels in our system. In figure 8-9, the first observed excited state occurs 3 meV above the ground state. This is a fair bit lower than the expected position of the first excited state of a 1 hole, 5.5 nm diameter CdSe nanocrystal (10-20 meV). In general, however, detailed studies of the excited states of a nanocrystal have been difficult and we have typically not been able to satisfactorily resolve and study these levels. This is because the levels appear to be quite broad* compared to their spacing. This is likely the result of fast decay rates in these nanocrystals. Mittleman *et al.* [1994] have found that the intraband decay rates in CdSe nanocrystals are on the order of a few ps. This corresponds to a few meV lifetime broadening of nanocrystal's excited states†. This is comparable to the energy level spacing in our nanocrystal. As a result, excited state spectroscopy is difficult in this system. It has been shown that capping CdSe nanocrystals with an higher bandgap material, like CdS [Peng *et al.* 1997] or ZnS [Hines and Guyot-Sionnest 1996], greatly increases the lifetime of its carriers. Future work on such sample may enable higher resolution excited state spectroscopy.

*Broader than expected for thermal broadening alone.

†A 1 ps lifetime state will have a natural linewidth of 4 meV.

Chapter 9

Summary and Future Directions

9.1 SUMMARY

In this thesis we have presented our efforts towards the electrical characterization of nanocrystals. We have found that both electrostatic and quantum mechanical confinement is important in the electronic transport through nanocrystals and leads to phenomena such as Coulomb blockade.

The largest barrier to these measurements has been in finding ways to attach leads to nanocrystals. The first approach that we discussed used a scanning probe microscope to image and then make electrical contact to nanocrystals which are bound to a substrate. Here, it was found that very low forces (< 25 nN) and a liquid environment are required to avoid dislodging nanocrystals. It was also found that electrical measurements in a liquid environment can be complicated by the solvation of molecules about the surface under study.

We next discussed a method to pattern the functionality of a surface and localize where nanocrystals will subsequently bind. It was found that such an approach can be used to create complex arrangements of molecules or nanocrystals on surfaces. However, changes must be made to improve the reliability of the technique before it can be used to fabricate working devices.

Finally we discussed the fabrication and measurement of a nanocrystal based single electron transistor. Here, we peppered a surface with Au and CdSe nanocrystals and then measured those nanocrystals that bridged a gap between closely spaced leads. It was found that the transport behavior of Au nanoparticles is well described by the standard Coulomb blockade model, while the transport behavior of CdSe nanocrystals is more complex. Low source-drain bias, Coulomb oscillation type studies on CdSe nanocrystals reveal irregularly spaced peaks. The analysis of these peaks has yielded information about the energies

needed to add or remove electrons to/from the nanocrystal. Larger source-drain bias studies have probed non-equilibrium transport in CdSe. Here, transport via excited states and by LO phonon emission has been observed. Further work will be needed to fully understand the nature of the addition energies and excited states of this system.

9.2 FUTURE DIRECTIONS

The technique which currently offers the best promise for future electrical studies of nanocrystals is a combination of electron beam lithography and luck to form a single electron transistor (chapters 7 and 8). This fabrication technique is readily suited to a host of chemically derived structures and its open planar geometry allows for optical studies and the inclusion of more complicated, multiple-nanocrystal systems.

Several improvements should be made to this system, however. First and foremost, the current fabrication yield is quite variable. At some times, one of five devices will show Coulomb blockade; while at other times the yield can fall to less than one in a hundred. This indicates that we do not have a full understanding of the important parameters to device fabrication and a systematic study of each constituent process is in order. Also a problem is the substantial random telegraph noise seen in our system. This noise is most likely a result of electrons jumping into either trap states in the underlying SiO₂ or nearby nanocrystals. The SiO₂ traps can be minimized by including a H₂ passivation step to the fabrication process, while the removal of nearby nanocrystals is a more difficult task. One approach is to use a catalytic atomic force microscope (chapter 6) or resist-based lithography to allow only one or two nanocrystals to bind between the leads. Another is to use *in-situ* monitoring as the nanocrystals deposit. By then terminating the deposition of nanocrystals as soon as one is observed to bridge the leads, the number of nanocrystals in the system can be minimized.

With these improvements to the fabrication, the nanocrystal based single electron transistor described in this thesis can and will be used to study a wide variety of systems such as core-shell nanocrystals [Hines and Guyot-Sionnest 1996], dimers [Alivisatos *et al.* 1996], and conducting molecules [Schumm *et al.* 1996]].

Appendix A

Coulomb Blockade Modeling

A.1 INTRODUCTION

Below, is a description of the Coulomb blockade modeling program that we use to simulate the response of single, classical dots of the type sketched in figure 2-1 and discussed in sections 2.2 and 2.3. This model is based upon the work of Averin and Likharev [1991] and Amman *et al.* [1991].

A.2 THE MODEL

We consider the device depicted in figure 2-1. The probability that this dot has n electrons is given as ρ_n . The tunneling rate from the source to an n electron dot is given as $\bar{\Gamma}_n^s$, while the tunneling rate from an n dot to the source is given as $\bar{\Gamma}_n^s$. Likewise, the tunneling rate from an n electron dot to the drain is given as $\bar{\Gamma}_n^d$, while the tunneling rate from the drain to an n electron dot is given as $\bar{\Gamma}_n^d$. We then define the rate at which an n electron nanocrystal gains (Γ_n^+) and sheds (Γ_n^-) electrons as

$$\begin{aligned}\Gamma_n^+ &= \bar{\Gamma}_n^s + \bar{\Gamma}_n^d \\ \Gamma_n^- &= \bar{\Gamma}_n^s + \bar{\Gamma}_n^d\end{aligned}\tag{A-1}$$

We can then describe the evolution of an n electron dot as:

$$\frac{\partial \rho_n}{\partial t} = \Gamma_{n-1}^+ \rho_{n-1} + \Gamma_{n+1}^- \rho_{n+1} - (\Gamma_n^+ + \Gamma_n^-) \rho_n.\tag{A-2}$$

For steady state transport, we require that $\frac{\partial \rho_n}{\partial t} = 0$. This condition can be met via detailed balance:

$$\Gamma_n^- \rho_n = \Gamma_{n-1}^+ \rho_{n-1}.\tag{A-3}$$

We consider the $-N$ to N electron states of a dot and assume the probability of the dot having a charge state outside of this range is zero. Using A-3 we can express the probability of the electron having n electrons as:

$$\rho_n = \left(\prod_{i=-N}^{n-1} \frac{\Gamma_i^+}{\Gamma_i^-} \right) \rho_{-N}. \quad (\text{A-4})$$

Multiplying A-4 by one, we obtain

$$\begin{aligned} \rho_n &= \left(\frac{\prod_{i=-N}^{n-1} \Gamma_i^+}{\prod_{i=-N+1}^n \Gamma_i^-} \right) \left[\frac{\prod_{i=-N+1}^N \Gamma_i^-}{\prod_{i=-N+1}^N \Gamma_i^-} \right] \rho_{-N} \\ &= \left(\frac{\prod_{i=-N}^{n-1} \Gamma_i^+ \prod_{i=-n+1}^N \Gamma_i^-}{\prod_{i=-N+1}^N \Gamma_i^-} \right) \rho_{-N} \end{aligned} \quad (\text{A-5})$$

Normalization by

$$\sum_{j=-N}^N \rho_j = 1 = \left(\sum_{j=-N}^N \prod_{i=-N}^{j-1} \Gamma_i^+ \prod_{i=-j+1}^N \Gamma_i^- \right) \frac{\rho_{-N}}{\prod_{i=-N+1}^N \Gamma_i^-}, \quad (\text{A-6})$$

then gives

$$\rho_n = \frac{\prod_{i=-N}^{n-1} \Gamma_i^+ \prod_{i=-n+1}^N \Gamma_i^-}{\sum_{j=-N}^N \prod_{i=-N}^{j-1} \Gamma_i^+ \prod_{i=-j+1}^N \Gamma_i^-}. \quad (\text{A-7})$$

Using A-7 we can then calculate the total current flow from the source to the dot, I_s , and from the dot to the drain, I_d , as:

$$\begin{aligned} I_s &= -e \sum_{n=-N}^N (\bar{\Gamma}_n^s - \bar{\Gamma}_n^s) \rho_n \\ I_d &= -e \sum_{n=-N}^N (\bar{\Gamma}_n^d - \bar{\Gamma}_n^d) \rho_n \end{aligned} \quad (\text{A-8})$$

I_s should equal I_d , so long as the calculation is properly performed.

So far, we have said nothing about the nature of the tunneling rates, and our conversation is equally valid for both quantum and classical dots. We now focus upon a classical dot and assume that the dot and leads can be modeled with featureless Fermi seas. From Simmons [1963] and Beenakker [1991], we find that the tunneling rates from a Fermi sea to one whose electrochemical potential is $\Delta\mu$, lower is given as:

$$\Gamma(\Delta\mu) = \left(\frac{\Delta\mu}{e^2 R} \right) \frac{1}{1 - e^{\beta\Delta\mu}}. \quad (\text{A-9})$$

Using equation 2-13 to express the electrochemical potential of the dot, we find that the electrochemical difference between the source and an n electron dot, $\Delta\mu_n^s$, and the electrochemical difference between an n electron dot and the drain, $\Delta\mu_n^d$, are given as:

$$\begin{aligned} \Delta\mu_n^s &= -eV_{sd} - \mu_n^{dot} = \mu_o - \frac{C_d}{C_{tot}} eV_{sd} + \frac{C_g}{C_{tot}} eV_g - \frac{ne^2}{C_{tot}} \\ \Delta\mu_n^d &= \mu_n^{dot} = -\mu_o - \frac{C_s}{C_{tot}} eV_{sd} - \frac{C_g}{C_{tot}} eV_g + \frac{ne^2}{C_{tot}} \end{aligned} \quad (\text{A-10})$$

We can combine (A-9) and (A-10) to find the tunneling rates into and out of each charge state of the nanocrystal;

$$\begin{aligned} \bar{\Gamma}_n^s &= \Gamma(\Delta\mu_n^s); \quad \bar{\Gamma}_n^s = \Gamma(-\Delta\mu_n^s) \\ \bar{\Gamma}_n^d &= \Gamma(\Delta\mu_n^d); \quad \bar{\Gamma}_n^d = \Gamma(-\Delta\mu_n^d) \end{aligned} \quad (\text{A-11})$$

It is then with a combination of (A-7), (A-8), (A-9), and (A-11) that we calculate the current through a nanocrystal.

A.3 THE PROGRAM

I have written a series of routines within LabView to implement the above model. They exist within a library named *blockade.llb*, the latest version of which is in the labview/klein subdirectory of **Lemming**. The routine *Calc E.vi* calculates equation A-10, *Calc I.vi* calculates A-9, and *n level* calculates A-7. These three routines can then be used to calculate the total current in a single dot system. The program *grapher.vi* will do this simulation and then display and (if desired) save the results. The program *compare* will load in a data set for comparison to the simulation. The dataset to be loaded should be two columns of data; voltage (in V) on the left and current (in I) on the right.

Appendix B

Scanning Probe Microscopy

B.1 INTRODUCTION

Modern scanning probe microscopy (SPM) is generally traced to the scanning tunneling microscopy (STM) work of Binnig, Rohrer, and co-workers at IBM Zürich in the early eighties [Binnig *et al.* 1982a, Binnig *et al.* 1982b]. For their efforts, Binnig and Rohrer received the Nobel prize in physics in 1986. Another general class of SPM discussed in this thesis is the atomic force microscope (AFM) (a. k. a. surface force microscope (SFM)) and is also credited to Binnig and co-workers [1986]. These two general classes of SPM have spawned a plethora of novel SPM techniques. While new offspring are constantly arriving, a good review of the situation in 1994 can be found in Wiesendanger [1994].

B.2 SCANNING TUNNELING MICROSCOPY

The STM is nothing more than the end of a wire (the STM's tip) rastered in three dimensions above a substrate while the wire-substrate impedance is monitored. While its use is limited to conducting, clean surfaces, it can readily generate sub-atomic resolution images and local electronic spectra. The abilities and complexities of such a system are vast, and have been well discussed in several books and review articles [see, for example van de Leemput and van Kempen 1992, Wiesendanger 1994]. Below I will briefly sketch out some of the aspects of the STM as they pertain to the work presented in this thesis, but refer the reader to these review articles for an in depth treatment.

The STM obtains atomic resolution by exploiting the exponential dependence of the tunneling current on distance. For a square barrier between metals with a small differential bias [Simmons 1963], the tunneling current can be approximated as:

$$I \propto e^{-\sqrt{\Phi} \cdot z}, \quad (\text{B-1})$$

where Φ is the barrier height (essentially the mean work function of the two metals) in eV, and z is the barrier thickness in Å. Because the work function is typically on the order of several eV in metals, the characteristic decay length of the tunneling current is sub-Angstrom. This implies that a relatively blunt STM tip can provide sub-Angstrom resolution. Ideal tips are hard, oxide and contaminant free, and sharp (to allow faithful imaging of high aspect ratio features). Often tips are made from W which is cut and then electrochemically sharpened in a KOH or NaOH solution. These tips remain oxide free for part of a day. An alternate tip is made from Pt alloyed with Ir or Rh (for hardening the Pt). These tips remain oxide free, but sharpening is more difficult [Musselman and Russel 1990] and rarely done.

Typically one rasters a sample underneath the STM's tip using a piezoelectric tube. A piezoelectric material [Buchanan 1986, Moulson and Herbert 1990] is one which generates an electric field with the application of stress, and conversely will strain when a field is applied. To make a scanner, one takes a polycrystalline piezoelectric tube (typically PZT (Lead-Zinc-Titanate) doped with Nb or La), and plates quadrant electrodes onto the outside and a single reference electrode on the inside. By then applying a high radial field (1-4 V/ μm) at elevated temperatures ($\sim 100^\circ\text{C}$) one can pole all the crystal dipoles in a radial direction. Subsequent application of smaller differential biases to the quadrant electrodes will bend the tube as desired. The motion is slight (deflections of $\sim\mu\text{m}$ for $\sim\text{cm}$ length tubes). For a practical system, one is limited to X-Y motions of less than a few hundred μm and Z motion of less than a few μm . As a result a mechanical coarse approach is used to bring the sample into close proximity with the tip.

One generally uses an STM to generate a constant current image. To do so, one rasters the sample in the X-Y plane and adjusts the Z axis as needed to maintain a constant current. The resultant map, Z verses X-Y, is the constant current STM image of the surface. It is a convolution of the morphology and density of states over the sample's

surface. Numerous alternate imaging techniques also exist, but were not used in this thesis [for a review, please see Wiesendanger 1994].

All of our STM measurements were performed on a Park Scientific Autoprobe CP system operating on an air table in ambient conditions. All imaging was done with 20 mil Pt 13% Rh wire which was freshly cut with a wire cutter immediately prior to imaging. Either a 10 μm or a 100 μm travel piezo tube was used to raster the sample.

B.3 ATOMIC FORCE MICROSCOPY

The AFM scans a cantilever with a sharp tip at its end over a surface and watches how it deflects. Because force, rather than tunneling current, is used for probing the sample, non-conducting samples can be imaged. For this capability, we pay a price in resolution. This is because most forces felt by the AFM display a power law dependence upon distance, rather than the exponential dependence of the tunneling current by the STM.

The most common AFM imaging methodology is basically the same as that of the STM. Using a piezoelectric tube, a sample is laterally rastered underneath the AFM's stylus. A constant force image (rather than constant current) is taken by adjusting the sample's height, Z , as needed to maintain a constant tip-sample force. A plot of the applied Z against the X - Y position is the constant height image.

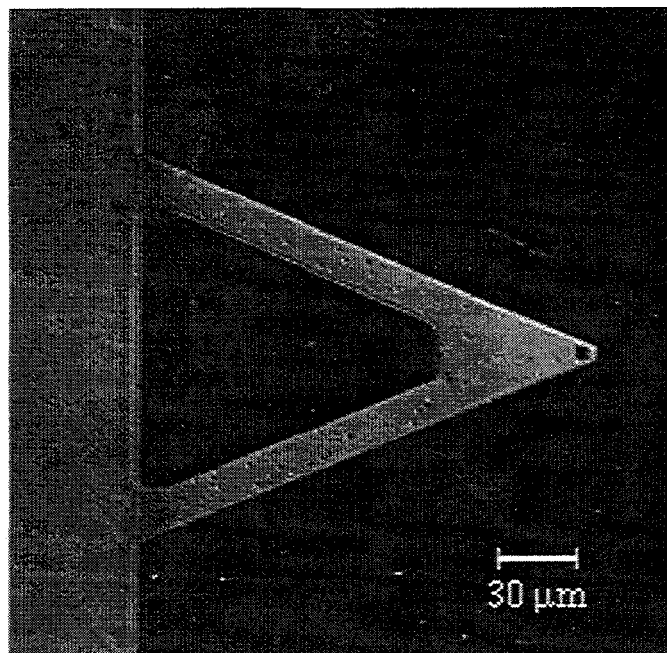
One can obtain such an image with the AFM's stylus in either attractive or repulsive interaction with the sample. The most common repulsive force imaging mode is contact AFM. Here one takes a weak cantilever (spring constant of 0.01 - 1 N/m) and lets it snap into contact with the sample. The tip-sample force is taken as the cantilever's static deflection from its neutral position. This deflection was first measured with a STM style tunneling tip positioned just above the cantilever [Binnig *et al.* 1986], but today is typically measured by optical deflection, optical interference, or piezo-resistive cantilevers [Tortonese *et al.* 1992]. Such detection techniques can also be used to measure the torsion

of the cantilever, thereby measuring lateral forces between the tip and sample [Meyer and Amer 1990].

To measure attractive forces, one typically brings a stiff cantilever (1-100 N/m) just over (<100 nm) a substrate. Instead of simply measuring the cantilever deflection, the weak tip-sample attractive forces are measured by oscillating the cantilever at a set frequency just off of its resonant frequency (10 kHz - 1 MHz). As the stylus feels an attractive pull from the sample, its resonant frequency will shift to lower frequencies. This shift will cause the oscillation amplitude and phase at the drive frequency to shift. This measured shift in the response of the cantilever gives us the tip-sample force with a sensitivity down to less than a fN [see for e.g. Rugar *et al* 1994]. This technique is generally referred to as non-contact AFM (NC-AFM). A variation on NC-AFM is to lower the oscillating cantilever towards the sample until a prompt upward shift in the resonant frequency occurs. This implies a repulsive tip-sample interaction and hence the technique is called tapping, or intermediate contact AFM.

Because most force laws are only power law in nature, special care must be taken to make a sharp AFM tip for imaging; we can't simply cut a wire and rely upon the exponential nature of tunneling current as we do in STM. Furthermore, as we want to oscillate this cantilever over a surface or let it lightly make contact, we must ensure that the tip is affixed to a well defined cantilever with a known spring constant. Luckily, these tip-cantilever systems are made commercially and a wide variety can be bought for tens of dollars. The older style AFM styli (which are still the most common type used) are made by depositing a patterned Si_3N_4 film over pyramidal etch pits made in a (100) Si substrate. The patterned Si_3N_4 film is then lifted off and affixed to a support. Figure B-1 shows a Park Scientific Si_3N_4 cantilever-tip assembly. A newer type of AFM stylus is made of single crystal Si [Wolter *et al.* 1991]. By patterning and then etching a Si wafer, free standing Si cantilevers can be made. To integrate a tip, a small etch-mask is applied where the tip is desired on the cantilever. An isotropic etch will then undercut this mask and generate a very

a)



b)

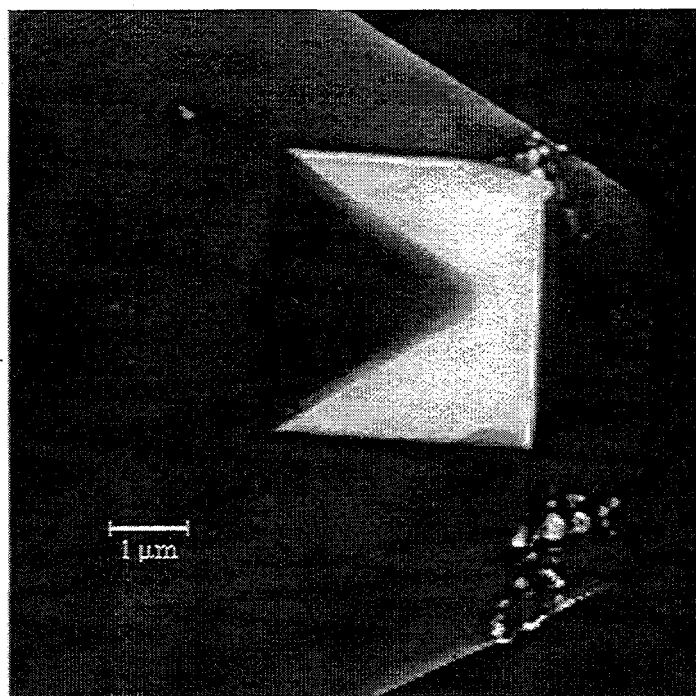
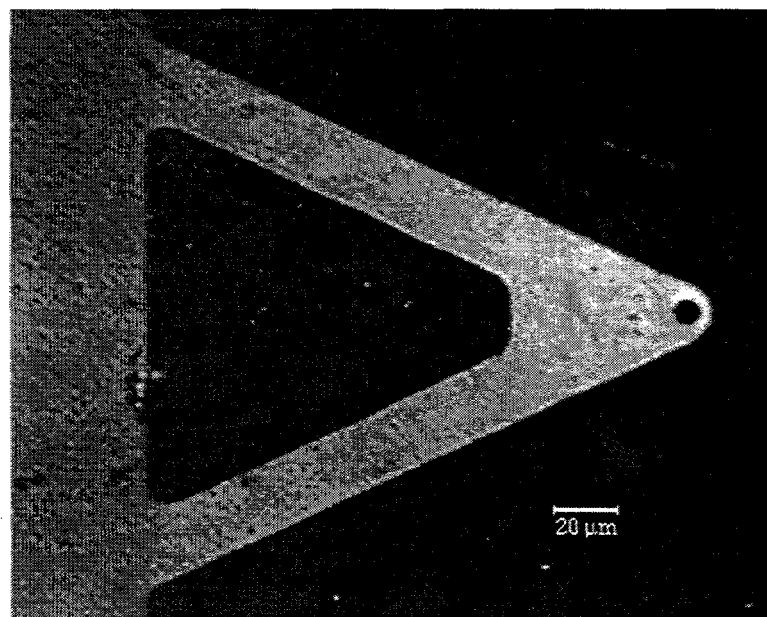


Figure B-1: a) Optical image of a Park Scientific Si_3N_4 *Microlever*. The pyramidal tip used for imaging is located on the end of the cantilever. The nominal spring constant of this cantilever is 0.05 N/m. b) SEM micrograph of the tip of a *Microlever* of the type shown in (a). This image with taken with a few tens of degrees tilt.

a)



b)

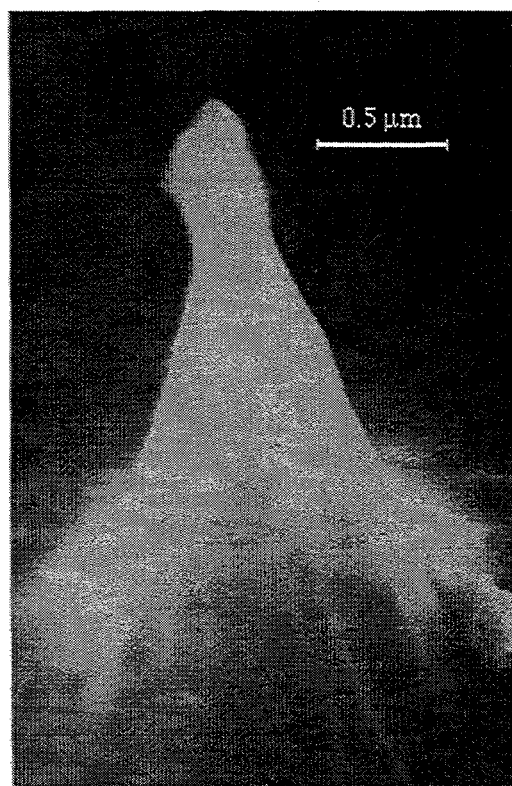


Figure B-2: a) Optical image of a Park Scientific Si *Ultralever*. The conical tip used for imaging is located on the end of the cantilever. The nominal spring constant of this cantilever is 0.03 N/m. b) SEM image of the tip of a *Ultralever* of the type shown in (a).

sharp tip as seen in figure B-2. There are many ways to improve the aspect ratio and sharpness of either type of tip. One approach is to extend the tip with features made of carbon nanotubes [Dai *et al.* 1996] or soot deposited under an electron beam [Keller and Chih-Chung 1992]. Such one-of-a-kind tips have been successfully used with greater resolution than commercial tips.

Generally, the AFM feels the sample via the van der Waals force. Such a force law felt between the AFM tip and a substrate dictates a weak dipole attraction ($\sim r^{-6}$) followed by a hard shell repulsion ($\sim 1/r^{12}$) as the tip makes "contact" with the surface. One can augment this force law to see other phenomena. By using a conducting tip with an applied bias, one can map potential distributions [Martin *et al.* 1988]. Likewise, a magnetic tip can be used to image magnetic features [Martin and Wickramasinghe 1987]. One can also use an AFM as a micro-positioner to place a secondary probe near the substrate. Such a system can measure optical properties (near-field scanning optical microscopy (NSOM)) [Betzig *et al.* 1992], tunneling current [Hosaka *et al.* 1992, Klein and McEuen 1995], temperature [Luo *et al.* 1996], magnetic fields [Chang *et al.* 1992], and so on. A good review of several of these hybrid techniques appears in Wiesendanger [1994].

For this thesis, all data was taken with a Park Autoprobe CP system operating in ambient conditions. If not otherwise stated, data was taken with a 0.6 μm thick Si cantilever [Park Scientific's *Ultralever* (figure B-2)] with a spring constant of ~ 0.06 N/m. Occasionally in Section 3, we chose to use stiffer Si cantilevers with a spring constant of ~ 14 N/m. The Si cantilevers have integrated $\sim 3:1$ aspect ratio conical Si tips with tip radii of ~ 10 nm. Some data was taken with aspect ratio $\sim 1:1$, pyramidal Si_3N_4 tips [Park Scientific *Microlevers* (figure B-1)] (tip radius: ~ 50 nm) integrated on a Si_3N_4 cantilevers with a ~ 0.5 N/m spring constant.

B.4 TIP CONVOLUTION EFFECTS IN AFM

B.4.1 A Model

When interpreting AFM and STM images, we must be mindful of the finite size of the probe's tip. As we discussed above, the best commercial Si AFM styli are 3:1 aspect ratio cones and end in a 10 nm radius of curvature point. This is relatively blunt in comparison to objects such as a 5 nm diameter spherical nanocrystals. Often these tips are even more blunt as a result of damage or material which has stuck on the apex. STM and AFM tips made from other materials tend to be more blunt. As a result of this, when we look at nanocrystals adhered to a substrate, we must be mindful of tip effects. Below we will discuss these effects in relation to the imaging of nanocrystals.

Consider a AFM stylus imaging a nanocrystal sitting on a flat substrate. We sketch this in figure B-3. Here we assume that the tip is hemispherical, with radius of curvature R ; that the nanocrystal is spherical, with radius r ; and that $R > r$. Simple geometry allows us to write the vertical displacement of the tip, Δz , as a function of its lateral displacement from the center of the nanocrystal, ρ (see figure B-3). When the tip is in contact with the nanocrystal, we write

$$\Delta z = r - R + \sqrt{(r + R)^2 - \rho^2}. \quad (\text{B-2})$$

When the tip is directly above the nanocrystal, we have an accurate measure of the nanocrystal's diameter. As we displace the tip, the height slowly falls until it touches the substrate ($\Delta z = 0$). We solve for the value of ρ for which $\Delta z = 0$, and find

$$\rho_o = 2\sqrt{rR}. \quad (\text{B-3})$$

Thus, even for a tip of the same radius of curvature as a nanocrystal ($\sim 2\text{-}3$ nm), we find that the apparent radius of the nanocrystal seen by an AFM will be $2r$.

Let us now consider the implications. In figure B-4a we plot the apparent morphology seen by an AFM of varying tip size scanning over two nanocrystals which are separated by 4 radii. Figure B-4b varies the nanocrystal separation for a fixed tip radius of

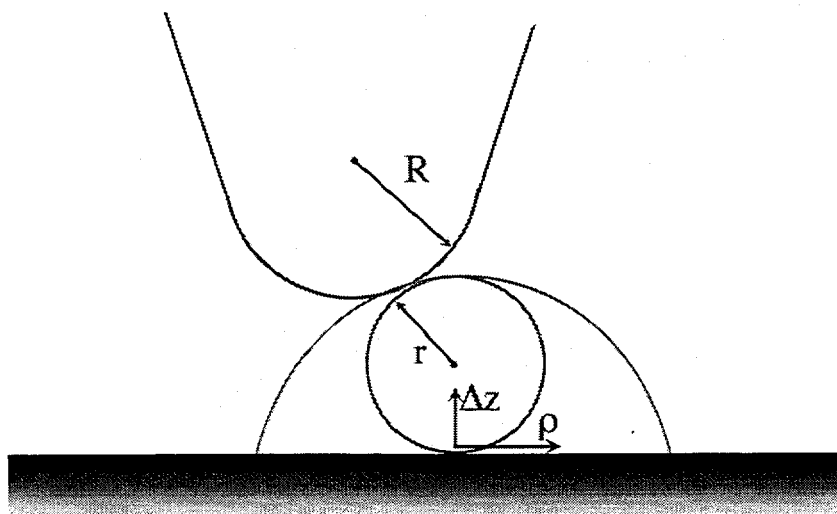


Figure B-3: Sketch of the tip convolution effect. When a AFM stylus with a hemispherical tip of radius R scans over a spherical nanocrystal of radius r , the measured width becomes bloated (gray line).

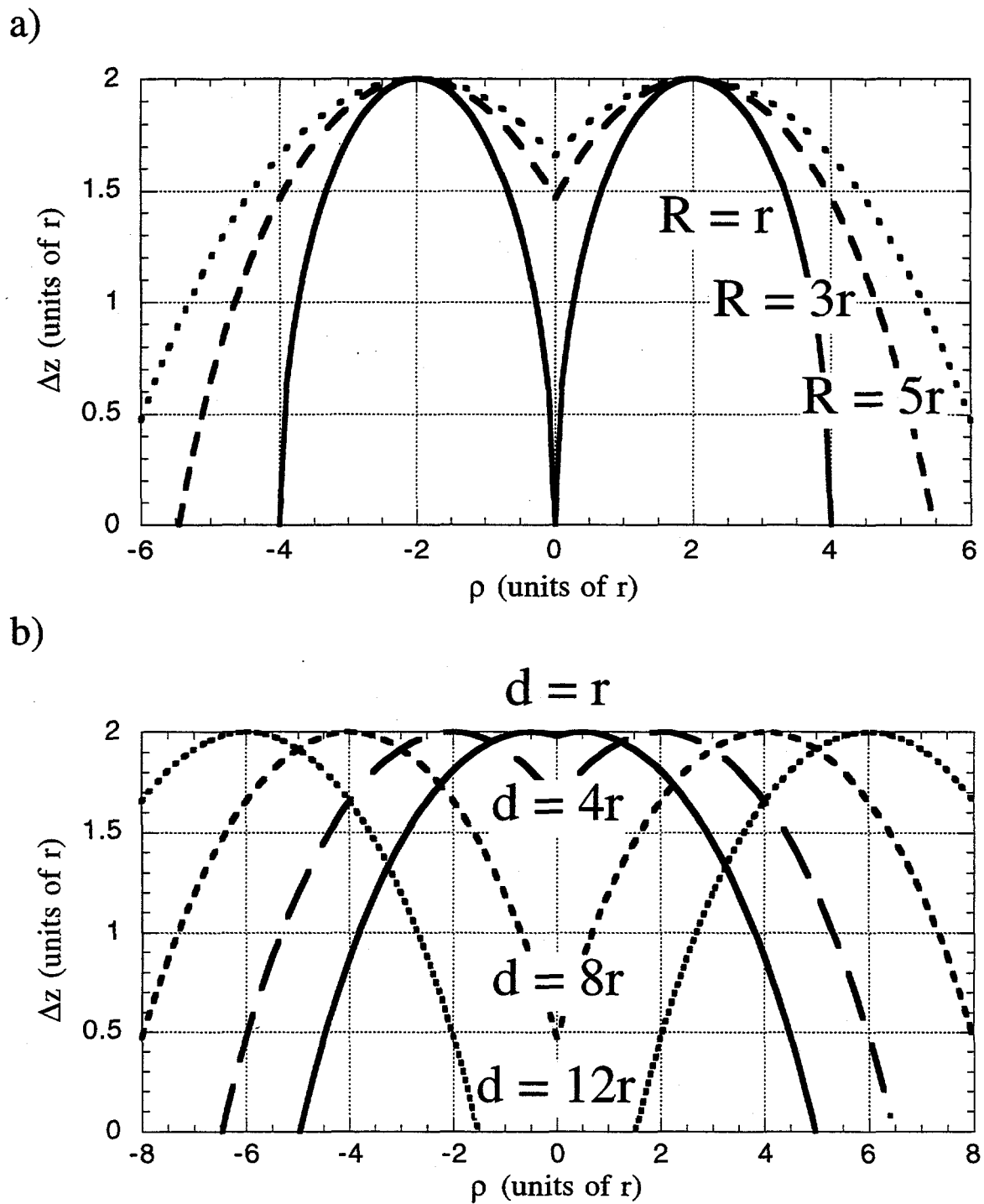


Figure B-4: Calculation of the tip convolution effect on AFM imaging of nanocrystals. Plots are in units of r , the radius of the nanocrystals. (a) The effect of the radius of the AFM tip, R , in the imaging two nanocrystals whose centers are separated by $4r$. (b) the effect of nanocrystal spacing when imaging with a tip of radius of curvature $5r$.

5r*. We note that in both cases even a relatively low density[†] of nanocrystals would appear to be a continuous film to the AFM.

B.4.2 Experiments

In figure 5-5a we saw an AFM micrograph of $r = 1.4$ nm CdSe nanocrystals imaged with a $R \sim 10$ nm AFM tip. This appears to be a continuous film of touching CdSe nanocrystals. However the apparent widths of the nanocrystals is much larger than expected, and much larger than the apparent heights. This is a result of the above described tip convolution effect.

For somewhat isolated nanocrystals in micrographs like figure 5-5a, we can measure both the apparent height and width of the nanocrystal. A histogram of our measurements on $r = 1.4$ nm CdSe nanocrystals appears in figure B-5. In figure B-5a, we plot a histogram of the apparent heights, and in figure B-5b we plot a histogram of the measured FWHM of the nanocrystals. The mean height is 38 ± 15 Å and the mean FWHM is 219 ± 73 Å. By equation B-3 we can thus estimate the tip radius to be 100 ± 50 Å, in good agreement with the nominal value.

*For a Park Scientific, Si tip ($R = 10$ nm) this would be a 2 nm radius nanocrystal. This is a typical size of the nanocrystals that we imaged.

[†]In these plots, the linear coverage of nanocrystals is 1/3. The 2d coverage would be less than 1/9.

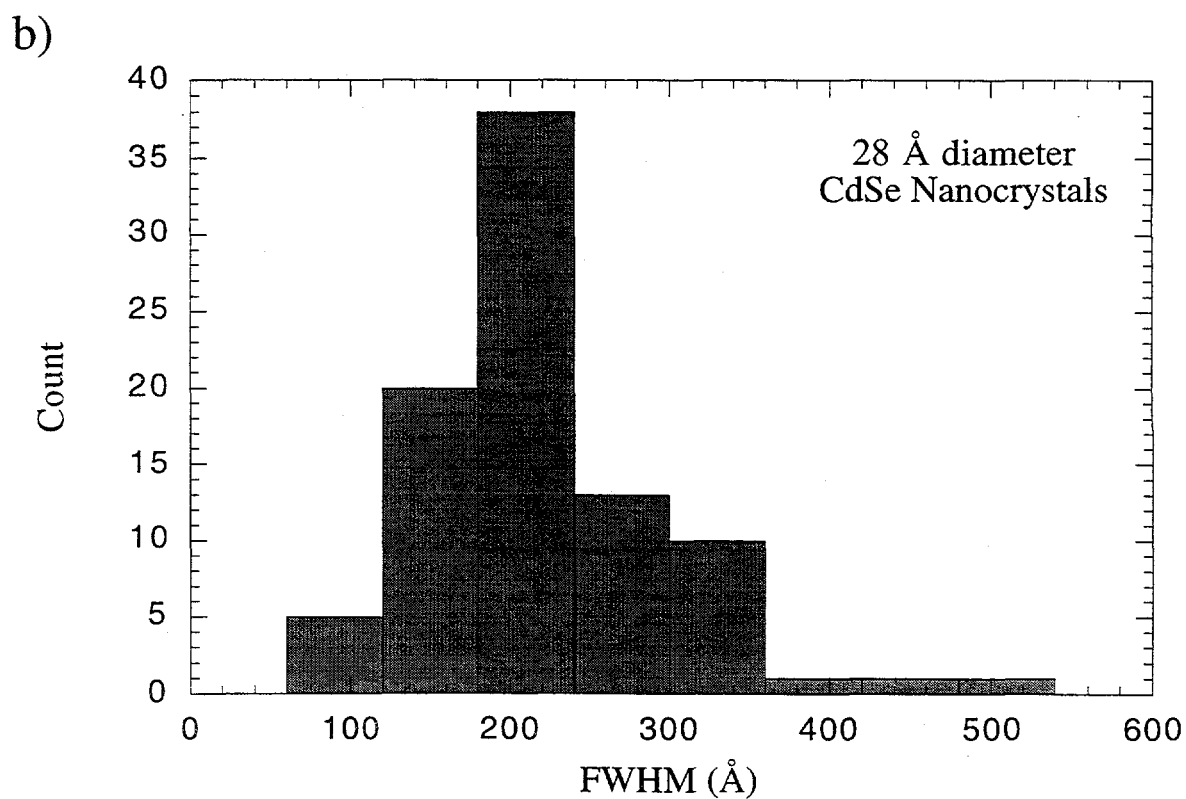
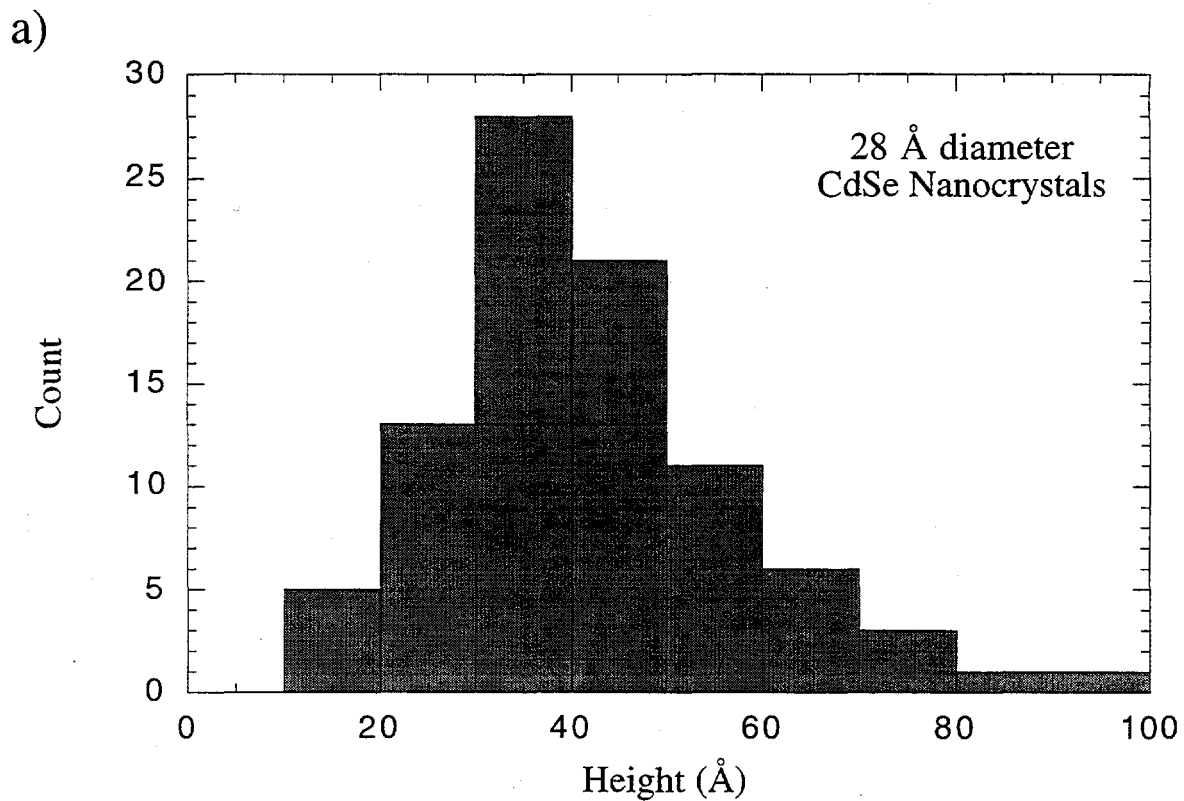


Figure B-5: AFM measurements of the size of a variety of 28 Å diameter CdSe nanocrystals using a tip with a 100 Å nominal radius of curvature. a) Measured heights of a variety of nanocrystals. b) The measured FWHM of the widths of the same nanocrystals.

Appendix C

Chemistry Related to Nanocrystals

•This was largely done in the Alivisatos lab by Janet Bowen Katari, Richard Roth, and Xiaogang Peng.

C.1 NANOCRYSTAL SYNTHESIS

*The below description of the procedure used to make our CdSe nanocrystals is based upon the thesis of Janet Bowen Katari [1995]. Murray *et al.* [1993] and Bowen Katari *et al.* [1994] further describe this procedure.

•Chemicals used:

Se (60 mesh) powder (Aldrich)

Dimethyl cadmium (Strem Scientific, filtered before use)

99% tri-n-octyl phosphine oxide (a.k.a. TOPO) (Aldrich)

Tri-butyl phosphine (TBP) (Aldrich)

Anhydrous methanol (Aldrich)

Toluene (Aldrich, distilled over sodium metal)

Anhydrous pyridine (Burdick and Jackson)

•Typical preparation:

- 1) In drybox, dissolve 0.8 g Se in 8.0 g TBP.
- 2) Add 2.0 g dimethyl cadmium.
- 3) Dilute 4:1 with TBP.
- 4) Septa cap and remove from drybox.
- 5) Heat 12 g of TOPO to 350° C. (careful, this is above TOPO's flash point!)
- 6) Let temp. stabilize to within 1° C of the desired temperature.

- 7) Add 0.4 mL of the Cd/Se solution to the TOPO; there should be prompt nucleation and a resulting color change.
- 8) Cool under Ar atmosphere
- 9) Transfer solution to dry box.
- 10) Add methanol to dissolve the TOPO and precipitate the nanocrystals.
- 11) Harvest the nanocrystals by filtering through a 0.1 μm filter and store under N_2 .

- These nanocrystals can be redispersed in a variety of solvents. Typically toluene or pyridine are used.
- Size is typically determined via optical spectroscopy.

C.2 ATTACHMENT OF NANOCRYSTALS TO AU

- 1) Fill petri dish with isopropanol.
- 2) Introduce 0.38 mL 1,6 hexanedithiol. This will make a ~5 mmol solution.
- 3) Plasma clean Au surface under N_2 for 1 minute
 - 3a) Clean plasma cleaner with isopropanol. Close and pump (mechanical pump with a LN_2 cold trap) and flush (with N_2) 3 times. Turn on plasma for 1 minute.
 - 3b) Place Au sample in the plasma cleaner. Pump and flush 3 times. Clean on *high* setting for 1 minute.
- 4) Place sample in a petri dish insert stirrer and cover.
- 5) Leave stirring in this solution for ~24 h.
- 6) Rinse sample with isopropanol and blow dry.
- 7) Place sample into a petri dish which contains ~100-200 mg of nanocrystals in toluene.
- 8) Leave stirring for ~24 h.
- 9) Rinse sample with toluene and blow dry.

Appendix D

Chemistry Related to Catalysis Experiments

*These procedures were developed and performed by Wolfgang Müller.

D.1 FORMATION OF AN ALKYBROMIDE SAM

- 1) Dissolve X mol. (*where X is about the desired amount of product*) 11-bromo-undec-1-ene $\text{CH}_2\text{CH}(\text{CH}_2)_9\text{Br}$ in $10 X$ mol. of trichlorosilane $[\text{SiCl}_3\text{H}]$. Mix and place in a sealed vessel.
- 2) Dissolve $\sim X/100$ mol of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ into isopropanol to form a 4 wt% solution. *This is a hydrosilation catalyst, as the Pt will act as an electron acceptor from the double bond of the $\text{CH}_2=\text{CH}-$ group and the Si-H bond of silane, thereby driving the silanation of the alkene group. The catalyst will not dissolve in trichlorosilane, hence the need to put it in isopropanol.*
- 3) Mix these two solutions, seal vessel, and place in a 60°C bath overnight.
- 4) Transfer to a pear flask, and evaporate excess trichlorosilane.
- 5) To separate out the 11-bromoundecyltrichlorosilane, form a 2 stage Kugelrohr vacuum still, heat the end to $140\text{--}150^\circ\text{C}$, and take the distillate from the 2nd stage. *A Kugelrohr still is a vacuum still with a series of bulbs (in this case 3). The still is placed horizontally and rotated while differential heat is applied (the starting bulb is the hottest).*

- 6) Into a set of individual sealed vials, dissolve 35 μL of the 11-bromoundecyltrichlorosilane distillate in 3.5 mL of bicyclohexane (or hexadecane).
- 6) (*Skip if using Si wafers*) Degrease glass cover slides by rinsing with acetone, then water, then acetone, then ethanol, then chloroform, then ethanol, then blow dry. Follow this with a soak in RGB soap at 50-60 °C for 2-3 min., a water rinse, a ethanol rinse, and blowing dry.
- 7) Clean degreased slides or fresh Si wafers by placing in a 90 °C piranha (hydrogen peroxide in concentrated sulfuric acid) solution for 30 min. Then rinse with water, ethanol, chloroform, and ethanol. Then blow dry.
- 8) Immediately place each substrate into its own vial of dissolved 11-bromoundecyltrichlorosilane. Let sit in solution for 4 minutes (*more can result in secondary layer formation*). Rinse with chloroform, ethanol, water, ethanol, then blow dry.
- 9) Immediately clean with chloroform in a Soxhlet extractor for 30 min.. *This gets rid of traces of bicyclohexane which may incorporate into the SAM. A Soxhlet extractor works by distilling the solvent into the vessel which has the object to be cleaned. An upside down U-shaped tube attached to the bottom of the cleaning vessel causes a siphon to form and drain the solvent out every time it reaches a set height.*

D.2 DISPLACEMENT OF BROMIDE WITH AN AZIDE

- 1) Place each substrate in its own vial which contains 30 mg of sodium azide [NaN_3] dissolved in 3.5 mL of dimethyl formaldehyde (DMF). *Sodium Azide is toxic, skin*

permeable, and a mutogen!. Let sit overnight, then rinse with water, ethanol, chloroform, and ethanol. Blow dry.

2) Clean with chloroform in a Soxhlet extractor for 30 min.

3) Store in a sealed, nitrogen filled amber glass vial until ready for use.

D.3 DERIVATIZATION OF AMINO GROUPS WITH ALDEHYDE-MODIFIED BEADS

1) Dissolve 30 μ l of an aqueous solution of fluorescein-labeled, aldehyde modified latex beads (2% solids in H₂O, mean diameter 290 Å) [Molecular Probes] into 3 mL of morpholinoethane sulfonic acid buffer (MES; 50 mM, pH 6.5).

2) Remove sample from the AFM liquid cell, and immediately immerse into this solution.

3) Let sit for 3 hours in the dark, remove, and blow dry.

D.4 DERIVATIZATION OF AMINO GROUPS WITH ATTO-TAG

1) To 1 mL of a 50 mM phosphate buffer (pH 8.2), add 50 μ l of a solution of 20 mM ATTO-TAG [Molecular Probes] in methanol and 25 μ l of an aqueous solution of 300 mM KCN.

2) Remove sample from the AFM liquid cell, and immediately immerse into this solution.

3) Let sit for 1 hour in the dark, remove, and blow dry.

Appendix E

Details of Device Fabrication

E.1 INTRODUCTION

Below I describe the current state of the procedure followed for forming devices on a degenerately doped Si wafer. Most processes are done in the EE microlab in Cory hall at U.C. Berkeley. The described technique tells how we did things for the last wafer, wafer G, and is by no means perfect. Figure 7-2 shows an optical micrograph of a completed chip.

E.2 FABRICATION OVERVIEW

- 1) Form 9000 Å of wet oxide.
- 2) Etch away gate regions, and grow a ~500 Å dry oxide.
- 3) Etch holes for bonding pads. Deposit Al gate bonding pads.
- 4) Deposit 300 Å Au leads.
- 5) Thicken bonding pads with 2500 Å more Au.
- 6) Spin on e-beam resist.
- 7) Expose chips as needed.

E.3 THE WAFER

We start with a 4" degenerately doped Si wafer. In particular they come from PCA, are n type, have 1 polished side and $\rho < 0.008 \Omega\text{-cm}$. They may have a grown oxide of some form.

E.4 FORMATION OF A THICK WET OXIDE

- 1) In *sink* 8, the wafer is placed into the 5:1 HF for 1.5 min. or until non-wetting to remove any starting oxide.

- 2) Standard cleaning (piranha-HF-H₂O) in *sink* 8 followed by *sink* 6.
- 3) In *tylan* 2 perform a 2.5 hour wet oxidation at 1050 °C using "swetoxb" program.
 - This should give ~9,000 Å of SiO₂.
- 4) Measure thickness on the *Nanospec*.

E.5 DEFINITION OF GATE REGIONS

- 1) Preclean *Tylan* 5 the night before using "STCA5-6" program. It takes ~8 hr. and should be done at night. Thus the following should be done in the morning.
- 2) Apply photoresist
 - i) Put in *HMDS bubbler* for 5 minutes.
 - ii) Spin Shipley S1818 5.5 krpm 30s on *spinner1*.
 - iii) Soft bake 5 min. at 90 °C.
- 3) Expose in *Quintel* for 8 s.
- 4) Develop in Shipley concentrated developer mixed 1:1 with water for 1 minute. Rinse with water and blow dry.
- 5) Hard bake at 120 °C for 30 minutes.
- 6) In *Old Lab Sink*, place in buffered HF 5:1 etch for 12 min.. Rinse w/ water; blow dry.
 - This should etch holes in the oxide at a rate of about 1,000 Å/min.
- 7) Place in acetone (to remove resist) for 2 min., wash w/ acetone then MeOH; blow dry.
- 8) Clean in *sink* 8 and 6 basically as normal, BUT skip the HF dip that follows the piranha clean in *sink* 8. When you get to the same point in *sink* 6, do a 30 s etch in the 10:1 VLSI HF. This should remove ~120 Å of SiO₂. This re-bares the gates.
- 9) In precleaned *Tylan* 5, grow a dry oxide at 950 °C for 2 hr., followed by a 30 min. anneal. This is done with "sgateox"
 - This should give ~550-600 Å of gate oxide and leave the thick regions unchanged.
- 10) One might do a H₂ passivation at this point; I currently don't.

E.6 MAKE GATE CONTACTS

- 1-5) Follow steps E.5-2, 3, 4, 5, and 6 using gate contact mask aligned as appropriate.
- 6) Hurry up hill and get the chip into the e-beam evaporator with the Al target.
- 7) Evaporate 3500 Å Al.
- 8) Do liftoff in acetone. This usually requires a few hours + ultra-sonication.
- 9) Rinse with acetone then methanol then blow dry.
- 10) Anneal and form silicide by placing in 350 °C furnace under flowing N₂ for 20 min.

•I usually use the annealing tube furnace in bldg. 2, room 216 (see Chris Olsen).

Due to overshoot issues, this is done with a program of 10 min. at 320 °C followed by 20 min. at 350 °C. Note that to fit into this furnace, a 4" wafer must be trimmed to a width of <2.5" or so at this point.

E.7 FORM SOURCE AND DRAIN LEADS

- 1) Apply Photoresist (note different procedure)
 - i) Put in *HMDS bubbler* for 5 minutes.
 - ii) Spin Shipley S1818, 5.5 krpm, 30s on *spinner1*.
 - iii) Soft bake for 5 min. at 90 °C.
 - iv) Cool, then place in chlorobenzine for 5 min. (this hardens the surface).
 - v) Bake 2 min. at 90 °C
- 2) Expose in *Quintel* for 8 s (using full lead pattern).
- 3) Develop in Shipley concentrated developer mixed 1:1 with water for 1 minute. Rinse with water and blow dry.
- 4) Place in 120 °C for 1 min. to remove any remaining water.
- 5) Descum in a 50 W O₂ plasma for 1 min. in *Technics-c*.
- 6) In e-beam evaporator, deposit 100 Å Cr then 300 Å Au.
- 7) Perform liftoff in acetone, this should take less than 1 hr.
- 8) To remove overhanging gold, place in acetone in ultra-sonic bath for 5 min.

9) Rinse w/ acetone, then methanol, then blow dry.

E.8 FORM SOURCE AND DRAIN BONDING PADS

Follow E.7:1-9 to put down a second layer of Au to thicken the bonding pads. In step 2, use the bonding pad mask (basically the lead mask without the innermost features). In step 6, evaporate 150 Å Cr and 2000 Å Au.

E.9 APPLY e-BEAM RESIST

1) Spin on 9% by wt. P(MMA(8.5)MAA)-E-9 in 2-ethoxyethanol (cellosolve)

Use 3 krpm, 30s; this gives a ~400 nm resist layer.

•This is M350009 from MCC.

2) Bake 150 °C for 1 hr.

3) Spin on 2% by wt. 950k PMMA-c-2 2% in chlorobenzene.

Use 3 krpm, 30s; this gives a ~100 nm resist layer.

•This is M240002 from MCC.

4) Bake 150 °C for 1 hr.

5) Use color to determine region which has a uniform resist coating. Use this region only.

6) Store in dissector, and cut off pieces as needed.

•The resist may leave a residue which results in poor electronic contact after ~6 mo.

E.10 e-BEAM LITHOGRAPHY AND EVAPORATION

1) Expose pattern in *Jeol107* at 1 kx, 5 pA beam current. One typically needs 150 $\mu\text{C}/\text{cm}^2$ for large features and up to 900 $\mu\text{C}/\text{cm}^2$ for the smallest features.

2) Develop in IPA/MIBK (methyl isobutyl ketone) 3:1 at 21°C for 1 min.

3) Dunk in IPA at 21°C for 30 s then blow dry.

4) Place on teeter-totter in e-beam evaporator.

5) At 15° tilt, evaporate 35 Å Cr then 100 Å Au.

- 6) At -15° tilt, evaporate 35 Å Cr then 100 Å Au.
- 7) at 0° tilt, evaporate 35 Å Cr then 800 Å Au.
- 8) Do liftoff in acetone. This should take 1 hr, and no ultra-sonication.
- 9) Rinse w/ acetone then methanol, then blow dry.

E.11 POSSIBLE IMPROVEMENTS

- 1) Do a H_2 passivation step after forming the dry oxide. This should reduce leakage current and maybe improve on device noise.
- 2) Better alignment marks in masks.
- 3) For Au lead deposition; do an etch, not a liftoff.

Appendix F

Summary of All Devices

Basic processing is described in appendix E. Further information is in appendix G

Wafer A: 2/8/95 (piece of Si wafer with 100 nm oxide. 1 layer; 100 Å Cr, 850 Å Au)

A1: *Normal 2 lead pattern and processing. 2 evaps: each were 30 Å Cr then 80 Å Au.*

No nanoxtals; Various shorts and opens.

A2: *Same processing as above.*

Some shorts and opens. Some problems contacting to optical pads

A3: *Now do 3 evaps, 30 Å Cr and 80 Å Au at $\pm 15^\circ$. Then 50 Å Cr and 500 Å Au at 0° .*

Janet deposited ~2.6 nm CdSe.

Probe stationed after making junctions: Combo of shorts and opens. Plasma cleaned by Janet. Same shorts and opens. SEMed then Janet put on nanoxtals. Did lots of measurements, in the end it turns out that we were bonding through the SiO₂.

A4: *Same processing as above.*

Used in an attempt to make a PPV LED.; no luck

A5: *Same processing as above. BUT I wirebonded before plasma-cleaning and cluster deposition.*

Initial junctions looked good. BUT after plasma cleaning and nanocrystal deposition, all bonded junctions were blown up.

Open: 10, Short: 2, tunneling: 2

A6: *Same processing as above. 5.8 nm Au.*

1 CB device, very well measured and discussed in the APL

Open: 9, Short: 4, Blockade: 1, Tunneling: 1

Wafer B: 6/8/95 (4" Si wafer w/ 100 nm oxide. 1 layer. 200 Å Cr, 3500 Å Au)

B1: *Normal 2 lead pattern, 30 Å Cr and 80 Å Au at $\pm 15^\circ$. Then 50 Å Cr and 500 Å Au at 0° . 10 nm Au.*

Blew entire first set of bonded leads, never knew why. No trouble, but no devices after that.

B2: *Same processing as above., no sure what nanocrystals were deposited.*

Open: 9, Short: 5.

B3: *Same processing as above. 2 nm Au nanocrystals*

1 CB device, Very large E_c .

Open: 9, Blockade: 1

B4: *Same processing as above. 5.6 nm Au*

lost by Janet

B5-7: *Same processing as above. not sure what was deposited*

Measured by Paul, nada.

B8: *Same processing as above. 5.8 nm Au nanocrystals now deposited by Richard.*

BUT SAM was aminothiophenol.

1 CB device, acted strange, likely aminothiophenol was "2nd dot"

Open: 11, Short: 2, Blockade: 1

B9: *Back to normal processing. 5.6 nm Au. *NEW DITHIOLS OPENED**

Open: 14

B10: *Same processing as above, 5.8 nm CdSe*

3 CB devices, very well measured; in APL.

Open: 9, Short: 2, Blockade: 3.

B11: *Same processing as above, 3.6 nm CdSe*

Open: 10, Short: 3, Tunneling: 1

B12-14 *Same processing as above, Overexposed*

B15: *Same processing as above, 5.8 nm CdSe*

Maybe 2 CB device, somehow blew up sample.

Open: 11, Blockade?: 2

B16: *Same processing as above, 5.8 nm CdSe*

1 CB device Probably 2 dots in series, *very stable*

Open: 9, Blockade: 1, tunneling: 1

B17: *Same processing as above, Apparently never used.*

B18: *Side gated device, same evaporation as above., 5.8 nm CdSe deposited*

Everything was open, even things that should have been shorts

B19: *New design, side gated device, same evap. as above. All gaps were too big.*

B20-23: *Same processing as above, smaller gaps though. 5.8 nm CdSe deposited*

Everything open, even things that should be shorts

B24: *Same processing as above (gated device) 5.8 nm CdSe deposited*

6 poor CB like devices. lots of gate-lead tunneling. Seems to be unclear as to what's tunneling via what lead.

Open: 11, Short: 6, Blockade: 5

B25: *Same processing as above (gated device) 5.8 nm CdSe nanoxxtals.*

All open

B26: *Made at same time in same way as B25 ONLY SAM, no nanoxxtal.*

All open

B27: *Go back to normal lead, but use small gaps, so all overlapping. No nanoxxtals*

All but 1 open even though they all should have been "shorts"

Wafer C: 4/14/96 (deg. Si. 970 Å of SiO₂, 3020 Å Al pads. 1 layer leads: 100 Å Cr, 2480 Å Au). Note Au did not stick well, and was a pain to bond to.

C1: *Normal 2 lead pattern, now 35 Å Cr and 100 Å Au at ± 15°. Then 35 Å Cr and 800 Å Au at 0°. no nanoxxtals*

Learned to bond, ended up commonly bonding *through* the gate oxide.

- C2: *All overexposed*
- C3: *All underexposed*
- C4: *Process as above (C1). 5.8 nm CdSe nanoxtals*
 Had trouble bonding. **Maybe 1 CB device, but I killed it.**
- C5: *Process as above (C1). 5.8 nm CdSe nanoxtals. Wirebonding done using I amp.*
 Did lots of weird stuff to this device. No CB measured probably.
- C6: *Same as above, 5.8 nm CdSe. Used I amp to monitor bonding again (rest of C too)*
1 CB device. lots of hassle making this chip work.
- C7: *Same as above, 5.8 nm CdSe.*
 Open: 13, Short: 2
- C8: *Same as above, 5.8 nm CdSe.*
 Open: 4, Short: 8
- C9: *Same as above, 5.8 nm CdSe.*
 Had trouble with bonding.
- C10: *Same as above, 5.8 nm CdSe.*
 Open: 12, Short: 3
- C11: *Same as above, 5.8 nm CdSe., Probably never measured*
- C12: *Same as above, 5.8 nm CdSe.*
 Open: 16, Short: 10

Wafer D: 8/23/96 Shattered during processing

Wafer E: 9/24/96 (deg. Si. 2 layer oxide: 9040 Å and 590 Å, 3500 Å Al pads. 1 layer leads: 200 Å Cr, 2500 Å Au). Note I made E1, then stripped PMMA US'ed and then made the rest.

E1: *Normal 2 lead pattern, now 35 Å Cr and 100 Å Au at $\pm 15^\circ$. Then 35 Å Cr and 800 Å Au at 0° . no nanoxtals. Leads look like shit. Damaged by PL edges*

- E2: *Processed as above. 5.8 nm CdSe*
All open
- E3: *Processed as above. 5.8 nm CdSe*
All but 1 open
- E4: *Processed as above. Except do de-scum after e-beam. All leads overlap*
All but 3 open.
- E5: *Processed as above. Do 2nd PL step on top of e-beam. Depo 5.8 nm CdSe*
All open.

Wafer F: *finished 10/28/96 (Same as wafer E.)*

- F1: *Normal 2 lead pattern, now 35 Å Cr and 100 Å Au at $\pm 15^\circ$. Then 35 Å Cr and 800 Å Au at 0° . 5.8 nm CdSe*
All open.
- F2: *Processed as above. Except do de-scum after e-beam. All leads overlap*
- F3: *Processed as in F1. 5.8 nm CdSe*
All open.

Wafer G: *11/19/97 (deg. Si. 2 layer oxide: 8930 Å and 530 Å, 3050 Å Al pads. 2 layer leads: 1st: 100 Å Cr, 300 Å Au, 2nd 150 Å Cr, 2000 Å Au (shorter mask)). Processing is described in Appendix F.*

- G1: *Normal 2 lead pattern, now 35 Å Cr and 100 Å Au at $\pm 15^\circ$. Then 35 Å Cr and 800 Å Au at 0° . 5.8 nm CdSe*
1 CB, but got blown up rather quickly, when trying to isolate the gate.
Open: 12, Short: 8, blockade: 1
- G2: *Process as above, 5.8 nm CdSe*
Open: 16, Short: 10. Note many shorts got blown during handling
- G3: *Process as above, 5.8 nm CdSe*

2 CB. 1 blown during cool down. lots of data on the second.

Open: 9, Short: 14, blockade: 2

G4: *Process as above, 5.8 nm CdSe*

Open: 13, Short: 11

G5: *Process as above, 5.8 nm CdSe*

Open: 11, Short: 20, Tunneling: 3

G6: *Process as above, 5.8 nm CdSe*

Open: 20, Short: 16 Tunneling: 3

G7: *Process as above, 5.8 nm CdSe*

Open: 4, Short: 8

G8: *Process as above, 5.8 nm CdSe*

Open: 13, Short: 13, Tunneling: 3

G9: *Process as above, 5.8 nm CdSe*

Open: 19, Short: 4

G10: *Process as above, 5.8 nm CdSe*

Short: 8, Open: 24, Tunneling: 1

G11: *Same as above, BUT now no SEM inspect. 5.8 nm CdSe, Richard had problems.*

2 CB device, but both died, 1 was killed in dipstick, 1 was killed by VTI.

Open: 18, Short: 20, Blockade: 2, Tunneling: 2

G12: *Process as above, 5.8 nm CdSe (again, no SEM)*

1 CB device?, but killed going into IHe.

Open: 26, Short: 14, Blockade: 1

G13: *Process as above, 5.8 nm CdSe (again, no SEM)*

Open: 6, Short: 28

G14: *Process as above, 5.8 nm CdSe (again, no SEM)*

Open: 13, Short: 25, tunneling: 3

G15: *Process as above, 5.8 nm CdSe (again, no SEM)*

More shorts and opens,

G16: *Process as above, 5.8 nm CdSe (again, no SEM)*

More shorts and opens

G17: *Process as above, 5.8 nm CdSe (again, no SEM)*

1 CB device? Blown up while going to 4 K. also more shorts and opens.

G18: *Process as above, 5.8 nm CdSe (again, no SEM)*

More shorts and opens

Appendix G

Working Device Factoids

Below are some factoids about the devices that data was taken upon. Some possible Coulomb blockade devices are **not** mentioned here, for they were not well enough measured for facts to come to light. Please see appendix F for a full device overview. I mention when the devices were made and where in my labbooks the data can be found. I also note which pins were of interest, tell what device that corresponds to, and the measured gap size (see chapter 7 for device fabrication details).

A3 - The Si device

Device A3 was made on March 7, 1995. 2.6 nm diameter CdSe nanocrystals were attached by Janet. SEM micrographs of several of the leads appear in my 2nd lab book, pages 87-90. IHe data was taken from March 17 (page 93 of 2nd lab book) to March 30. Note that it probably warmed up a bit on the night of March 29, no IHe was left when we pulled. 300 K measurements were made on April 3-4. 77 K measurements were made April 27 - 30. On September 12-13 we went back to this device (p85, 3rd lab book) and looked at 77 K transport as a function of the power applied to a nearby red LED. On Sept. 13 we went to 4 K and did the same. Some speed runs were done on Sept. 20. On Sept. 27 IR spectra were taken in the SPEX spectrophotometer (700-2000 nm) (Chemla group) at 77 K. On Sept. 28, more spectra were taken at 4 K. On Oct. 9, we took UV/VIS spectra at 9 K in the Cary 2093 spectrophotometer. At the end of this run, we took activation energy data. Starting on Oct. 19 Neil Greenham in Paul Alivisatos group made measurements (they are in his lab book) from 400 to 1000 nm

In the end we discovered that this device was Si. We had bonded through the oxide barrier and measured the transport through the Si substrate. Discussed in section 6.4.2.

A5 - The Bare Device

Made April 9, 1995. SEM's appear on p137 of Lab book 2. It was wired and measured w/o nanocrystals. 1 device was very dramatic and likely had nearly touching leads. All leads were blown in subsequent processing. Discussed in section 6.4.3.

A6 - 5.8 nm Diameter Au Device

Made May 14, 1995, has 5.8 nm Au nanocrystals deposited. Data taken on 4d ("40 nm", pin 11). Most of the data is in the beginning of lab book 3. May 19 - 22: RT and 77 K data. 4 K data taken on May 24-30 then removed from can. Tried to measure again on June 7. pin 5 (used as gnd.) seemed dead at RT, used pin 2 (2a, "<10 nm", measured as a short) as a ground. At RT pin 11 conducted a bit, but died after ~4 hrs of RT sweeping at ± 0.2 V. Discussed in section 6.2.2

A64d: $C_1 = 2.1$ aF, $C_2 = 1.5$ aF, $e/C = 44$ mV, $R_1 = 32$ M Ω , $R_2 = 2$ G Ω .

B3 - 2 nm Diameter Au Device

Made June 14, 1995, has 2 nm Au nanocrystals deposited. Data taken on 3c ("over", pin 7). Data starts on p38 of lab book 3. 77 K and 4 K taken on Aug. 17-18. RT data Aug. 18-19 then cool to 77 K and take more data. Large voltages were applied to put the device in several states. Discussed in section 6.2.2.

B33d: $e/C_{\text{tot}} \sim 250$ mV, $R_1 \sim 40$ M Ω , $R_2 \sim 120$ M Ω in one state

$e/C_{\text{tot}} \sim 50$ mV, $R_1 \sim 10$ M Ω , $R_2 \sim 15$ M Ω in another state

B8 - 5.8 nm Au + aminothiols phenol

e-beam lithography on June 21, 1995, processed on Aug. 17, 1995. Data taken on 1e ("20 nm", pin 15). See page 62 of lab book 3. August 18: RT, 77 K. Aug. 18-21: 4 K. Aug. 25-Sept. 3: in fridge. Discussed in Section 6.4.4

B81e: $e/C \sim 50$ mV (?), $R \sim 3$ G Ω

B10 - 5.8 nm CdSe

Made October 19, 1995. Data taken on leads 4b ("10 nm", pin 7), 6c ("over", pin 3), 2a ("kiss", pin 13), 5e (10 nm, pin 2). Starts on page 117 of lab book 3. Oct. 25: 77 K. Oct. 26: RT, 77 K. Oct. 26-31: 4 K. Oct. 31: RT. Nov. 9 - 14: fridge. Pin 7 showed great data at 4 K, then was boring in the fridge. Pin 3 died suddenly in the fridge. Discussed in section 6.2.3.

B10-5e: $e/C_1 = 160$ mV, $e/C \sim 80$ mV (?), $R \sim 50$ M Ω .

B10-6c: $e/C_1 \sim 200$ mV, $e/C \sim 30$ mV, $R \sim 10$ M Ω

B10-4b: $e/C_1 = 110$ mV, $e/C_2 = 60$ mV, $e/C \sim 40$ mV, $R \sim 100$ M Ω

B16 - 5.8 nm CdSe

Made Dec. 18, 1995. Data taken on leads 1b ("kiss", pin 12) and 1d ("20 nm", pin 11). Data starts on page 5 of lab book 4. Dec. 21: 77 K. Dec. 22-23: 4 K. Dec. 23: RT. Dec. 23-24 4 K. Left sitting at RT (6 days in vac., 7 days at atmosphere) for 2 weeks. Jan. 8: 77 K. Jan. 9-23: 4 K (+ some variable T). Discussed in section 6.4.5.

B16-1d: 2 dots, $e/C_1^a = 40$ mV, $e/C_1^b = 146$ mV, $e/C^a \sim 70$ mV, $R \sim 1$ G Ω .

B24 - 5.8 nm CdSe

Made March 2, 1996. Note this is a side gate structure. Data starts on p38 of lab book 4. Data taken on 3b("over", pin 10), 2b ("over", pin 12), 3f ("sl over", pin 8), 3c/3e ("sl over", pins 15/16 (shorted together)), 6b ("sl. over", pin 7). Discussed in section 6.4.6.

B24-2b: $e/C_1 = 120$ mV, $e/C = 60$ mV, $R \sim 2$ G Ω . Metallic looking

B24-3c/3e: $e/C \sim 10$ mV, $R \sim 2$ G Ω

B24-6b: $e/C_1 \sim 170$ mV $e/C \sim 100$ mV (?) $R \sim 800$ M Ω . A bit odd.

B24-3d: $e/C_1 \sim 100$ mV, $R \sim 10$ G Ω . Metallic looking.

B24-3f: $e/C_1 \sim 55 \text{ mV}$, $e/C \sim 25 \text{ mV}$, $R \sim 1 \text{ G}\Omega$.

B24-3b: $e/C_1 \sim 80 \text{ mV}$, $e/C \sim 40 \text{ mV}$, $R \sim 1 \text{ G}\Omega$.

C6 - 5.8 nm CdSe

Made ~ May 29. Data taken on 1e ("10 nm", pin 14). Data starts on page 85 of lab book 4. June 5: 77 K. June 6-12: 4 K. Killed on June 12, as a result of the accidental removing of a grounding plug from a 1/100 box (and the subsequent application of $V_{sd} = 4 \text{ V}$). Discussed in section **.

C6-1e: $e/C \sim 35 \text{ meV}$, $R \sim 1 \text{ G}\Omega$.

G3 - 5.8 nm CdSe

Made December 2, 1996. Data mostly taken on 5d (" $<10 \text{ nm}$ ", pin 15). Data starts on page 61 of lab book 5. Dec. 9: RT, 4 K. Dec. 10-13: 4 K. Dec. 14: Attempt at VTI, blew device up in the process.

G3-5d: $e/C \sim 35 \text{ meV}$, $R \sim 1 \text{ G}\Omega$

G11 - 5.8 nm CdSe

Made January 28, 1996. Data taken on 2a (no SEM, pin 13) and 4a (no SEM, pin 15). Data starts on page 92 of lab book 5. Feb. 3: 4 K (2a only). Feb. 5: 4 K (4a only). Feb. 6-9 in VTI. 2a was killed when the 4 K cryostat was knocked (probably coupled V from the gate wire. 4a was killed by the VTI's resident poltergeist.

References

Alivisatos A P, J. Phys. Chem. **100**, 13226 (1996a).

Alivisatos A P, Science **271**, 933 (1996b).

Alivisatos A P, Johnsson K P, Peng X, Wilson T E, Loweth C J, Bruchez M P Jr, Schultz P G, Nature **382**, 609 (1996).

Alperson B, Cohen S, Rubinstein I, and Hodes G, Phys. Rev. B **52**, 17017 (1995).

Amman M, Mullen K, and Ben-Jacob E, J. Appl. Phys. **65**, 339 (1989).

Amman M *et al.* Phys. Rev. B. **43**, 1146 (1991).

Anderson P W and Rowell J M, Phys. Rev. Lett. **10**, 230 (1963).

Andres R P, Bein T, Dorogi M, Feng S, Henderson J I, Kubiak C P, Mahoney W, Osifchin R G, and Reifenberger R, Science **272**, 1323 (1996).

Ashcroft N. W. and Mermin N. D., *Solid State Physics* (Saunders College, Philadelphia 1976).

Ashoori R C, Störmer H L, Weiner J S, Pfeiffer L N, Baldwin K W, West K W, Phys. Rev. Lett. **68**, 3088 (1992).

Ashoori R C, Störmer H L, Weiner J S, Pfeiffer L N, Pearton S J, Baldwin K W, West K W, Phys. Rev. Lett. **71**, 613 (1993).

Averin D V and Odintsov A A, Phys. Lett. A **140**, 251 (1989).

Averin D V and Nazarov Y V, Phys. Rev. Lett **65**, 2446 (1990).

Averin D V and Likharev K K, in *Mesoscopic Phenomena in Solids*, ed. by Al'tshuler B L, Lee P A, and Webb R A (Elsevier, Amsterdam, 1991).

Averin D V and Nazarov Y V, in *Single Charge Tunneling*, ed. by Grabert H and Devoret M H (Plenum Press, New York, 1992).

Bain C D, Troughton E B, Tao Y-T, Evall J, Whitesides G M, and Nuzzo R G, J. Am. Chem. Soc. **111**, 321 (1989).

Bawendi M G, Steigerwald M L, Brus L E, Ann. Rev. Phys. Chem. **41**, 477 (1990a).

Bawendi M G, Wilson W L, Rothberg L, Carroll P J, Jedju T M, Steigerwald M L, and Brus L E, Phys. Rev. Lett. **65**, 1623 (1990).

Beale S C, Hsieh Y-Z, Wiesler D, and Novotny M, J. Chromatogr. **499**, 579 (1990).

Baranger H and Westervelt R, in *Nano-Science and Technology*, ed. by Timp G (AIP Press, New York, 1997).

Beenakker C W J, Phys. Rev. B **44**, 1646 (1991).

Betzig E, Finn P L, Weiner J S, Appl. Phys. Lett. **60**, 2484 (1992).

Bezryadin A and Dekker C, presented at APS March Meeting, March 17-21 (1997).

Binggeli M and Nate C M, Appl. Phys. Lett. **65**, 415 (1994).

Binnig G, Rohrer H, Gerber Ch, and Weibel E, Appl. Phys. Lett. **40**, 178 (1982a).

Binnig G, Rohrer H, Gerber Ch, and Weibel E, Phys. Rev. Lett. **49**, 57 (1982b).

Binnig G, Quate C F, and Gerber Ch, Phys. Rev. Lett **56**, 930 (1986).

Bishop D J, Licini J C, and Dolan G J, Appl. Phys. Lett. **46**, 1000 (1985).

Black C T, Ralph D C, and Tinkham M, Phys. Rev. Lett. **76**, 688 (1996).

Blanton S, Leheny R, Hines M, Nagal S, Guyot-Sionnest P, presentation at the APS March meeting, March 17-21 (1997).

Bockrath *et al.*, Science **275**, 1922 (1997).

Böer K W, *Survey of Semiconductor Physics* (Van Nostrand Reinhold, New York 1990).

Borelli N R, Hall D W, Holland H J, Smith D W, J. Appl. Phys. **61**, 5399 (1987).

Boulas C, Davidovits J V, Rondelez F, and Vuillamueme D, Phys. Rev. Lett. **76**, 4797 (1996)

Bowen Katari J E, Colvin V L, Alivisatos A P, J. Phys. Chem. **98** 4109 (1994).

Bowen Katari J E, *Electron Spectroscopy of Semiconductor Nanocrystals* (UC Berkeley, 1994).

Brus L, Appl. Phys. A **53**, 465 (1991).

Buchanan R C, *Ceramic Materials for Electronics : Processing, Properties, and Applications* (M. Dekker, New York 1986).

Chang A M, Hallen H D, Harriott L, Hess H F, Kao H L, Kwo J, Miller R E, Wolfe R, and van der Ziel J, Appl. Phys. Lett. **61**, 1974 (1992).

Chen W, Ahmed H, Nakazoto K, Appl. Phys. Lett. **66**, 3383 (1995).

C. E. D. Chidsey, J. Am. Chem. Soc. **114**, 5221 (1992).

Christenson H K, Gruen D W R, Horn R G, and Israelachvili J N, J. Chem. Phys. **87**, 1834 (1987).

Cohen-Tannoudji C, Diu B, and Laloë F, *Quantum Mechanics Volumes One and Two* a translation of *Mecanique Quantique* (John Wiley & Sons, Inc., New York and Herman, Paris, France, 1977).

Colvin V L, Schlamp M C, and Alivisatos A P, *Nature* **370**, 354 (1994).

Dabbousi B O, Bawendi M G, Onitsuka O, and Rubner M F, *Appl. Phys. Lett.* **66**, 1316 (1996).

Dai H, Hafner J H, Rinzler A G, Colbert D T, and Smalley R E, *Nature* **384**, 147 (1996).

Delsing P, Likharev K K, Kuzmin L S, Claeson T, *Phys. Rev. Lett.* **63**, 1861 (1989).

Denek M, Jensen K F, Murray C B, Bawendi M G, *Appl. Phys. Lett.* **65**, 2795 (1994).

Dixon D, Kouwenhoven L P, McEuen P L, Nagamune Y, Motohisa J, and Sakaki H, *Phys. Rev. B* **53**, 12625 (1996).

Dobisz E A and Marrian C R K, *Appl. Phys. Lett.* **58**, 2526 (1991).

Dolan G J, *Appl. Phys. Lett.* **31**, 337 (1977).

Dolan G J, Miller R E, Linke R A, Phillips T G, and Woody D P, *IEEE Trans. Mag.* **17**, 684 (1981).

Dorogi M, Gomez J, Osifchin R, Andres R P, and Reifenberger R, *Phys. Rev. B* **52**, 9071 (1995).

Drexler H *et al.*, *Phys. Rev. Lett.* **73**, 2252 (1994).

Efros A L and Rodina A V, *Phys. Rev. B* **47**, 10005 (1993).

Efros A L, Rosen M, Kuno M, Nirmal M, Norris D J, and Bawendi M G, Phys. Rev. B **54**, 4843 (1996).

Eigler D M, Schweizer E K, Nature **344**, 524 (1990).

Ekimov A I, Hache F, Schanne-Klein M C, Ricard D, Flyzanis C, Kurdryavtsev I A, Yazeva T V, Rodina A V, and Efros A L, J. Opt. Soc. Am. B **10**, 100 (1993).

Elbel N, Günther E, and von Seggern H, Appl. Phys. Lett **65**, 642 (1994).

Empedocles S A, Norris D J, and Bawendi M G, Phys. Rev. Lett. **77**, 3873 (1996).

Esteve D, in *Single Charge Tunneling*, ed. by Grabert H and Devoret M H (Plenum Press, New York, 1992).

Faraday, Phil. Trans. **147**, 145 (1857).

Foxman *et al.*, Phys. Rev. B **47**, 10020 (1992).

Frenkel J, Phys. Rev. **36**, 1604 (1930).

Fulton T A and Dolan G J, Phys. Rev. Lett. **59**, 109 (1987).

Fulton T A, Gammel P L, Bishop D J, Dunkleberger L N, Phys. Rev. Lett. **63**, 1307 (1989).

Galkin A A and Ignat'ev O M, Ukr. Fiz. Zh. **15**, 438 (1970).

Geerligs L J, Averin D V, Mooij J E, Phys. Rev. Lett. **65**, 3037 (1990a).

Geerligs L J, Anderegg V F, Holweg P A M, Mooij J E, Pothier H, Esteve D, Urbina C, and Devoret M H, Phys. Rev. Lett. **64**, 2691 (1990b).

Gelb L D and Lynden-Bell R M, Phys. Rev. B **49**, 2058 (1994).

Giaever I and Zeller H R, Phys. Rev. Lett. **20**, 1504 (1968).

Golan Y, Margulis L, Rubinstein I, Hodes G, Langmuir **8**, 749 (1992).

Golan Y, Margulis L, Hodes G, Rubinstein I, Hutchison J L, Surf. Sci. **311**, L633 (1994).

Gorter C J, Physica **17**, 777 (1951).

Grabert H and Devoret M H eds. *Single Charge Tunneling* (Plenum Press, New York, 1992).

Guo L, Leobandug E, Chou S, Science **275**, 649 (1997).

Haller I, J. Am. Chem. Soc. **100**, 8050 (1978).

Hines M A, Guyot-Sionnest P J, J. Phys. Chem. **100**, 468 (1996).

- Hofmann F *et al.*, Phys. Rev. B **51**, 13872 (1995).
- Holm R and Meißner W, Z. Phys. **74** (1932).
- Holm R and Meißner W, Z. Phys. **86** (1933).
- Horinti I and Polanyi M, Trans. Faraday Soc. **30**, 1164 (1934).
- Horn R G and Israelachvili J N, J. Chem. Phys. **75**, 1400 (1981).
- Hosaka S, Koyanagi H, Hasogawa T, Hosoki S, and Hiraiwa A, J. Appl. Phys. **72**, 688 (1992).
- Iafrante G J, Hess K, Krieger J B, Macucci M, Phys. Rev. B **52**, 10737 (1995).
- Israelachvili J N, Surf. Sci. Reports **14**, 109 (1992a).
- Israelachvili J N, *Intermolecular and Surface Forces* (Academic, New York, 1992b).
- Jaklevic R C and Lambe J, Phys. Rev. Lett. **17**, 1139 (1966).
- Johnson A T, Kouwenhoven L P, de Jong W, van der Vaart N C, Harmans C J P M, and Foxon C T, Phys. Rev. Lett. **69**, 1592 (1992).
- Josephson B D, Phys. Lett. **1**, 251 (1962).
- Junno T, Deppert K, Montelius L, and Samuelson L, Appl. Phys. Lett **66**, 3627 (1995).

Keller D J, Chih-Chung C, Surf. Sci. **268**, 333 (1992).

Kim Y and Lieber C M, Science **257**, 375 (1992).

Kirton M J and Uren M J, Adv. in Phys. **38**, 367 (1988).

Kittel C, *Introduction to Solid State Physics*, 7th ed. (John Wiley and Sons, New York 1996).

Klein D L, McEuen P L, Roth R, Lim A, and Alivisatos A P, *in preparation* (1997).

Klein D L, McEuen P L, Bowen-Katari J E, Roth R, and Alivisatos A P, Appl. Phys. Lett. **68**, 2574 (1996a).

Klein D L, McEuen P L, Bowen-Katari J E, and Alivisatos A P, Nanotechnology **7**, 397 (1996b).

Klein D L and McEuen P L, Appl. Phys. Lett. **66**, 2478 (1995).

Kortan A R, Hull R, Oplia R L, Bawendi M G, Steigerwald M L, Carroll P J, and Brus L E, J. Am. Chem. Soc. **112**, 1322 (1990).

Kouwenhoven L P, Johnson A T, van der Vaart N C, van der Enden, Harmans C J P M, and Foxon C T, Z. Phys. B **85**, 381 (1991).

Kouwenhoven L P, Johnson A T, van der Vaart N C, Harmans C J P M, and Foxon C T, Phys. Rev. Lett. **67**, 1626 (1991b).

Kouwenhoven L P *et al.*, Phys. Rev. B **50**, 2019 (1994a).

Kouwenhoven L P *et al.*, Phys. Rev. Lett. **73**, 3443 (1994b).

Kouwenhoven L P and McEuen P L, in *Nano-Science and Technology*, ed. by Timp G (AIP Press, New York, 1997).

Kouwenhoven L P, Marcus C M, McEuen P L, Tarucha S, Westervelt R M, and Wingreen N S, in *Mesoscopic Electron Transport*, ed. by Kouwenhoven L P, Schön G, and Sohn L L (Kluwer, 1997).

Kulik I O and Shekhter R I, Zh. Eksp. Teor. Fiz. **68**, 623 (1975). Translated in Sov. Phys. JETP **41**, 308 (1975).

Kumar A and Whitesides G M, Appl. Phys. Lett. **63**, 2002 (1993).

Kuramochi H, Uchida H, and Aono M, Phys. Rev. Lett **72**, 932 (1994).

Lafarge P, Pothier H, Williams E R, Esteve D, Urbina C, and Devoret M H, Z. Phys. B **85**, 327 (1991).

Lambe J and Jaklevic R C, Phys. Rev. Lett. **22**, 1371 (1969).

Lantz M A, O'Shea S J, and Welland M E, Appl. Phys. Lett **65**, 409 (1994).

Levene P A and Kuna M, J. Biol. Chem. **115**, 275 (1936)

Levene P A and Kuna M, J. Biol. Chem. **121**, 747 (1937).

Levinstein H J and Kunzler J E, Phys. Lett. **20**, 581 (1966).

Lide D, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, USA 1992).

Likharev K K, IEEE Trans. Magn. **23**, 1142 (1987).

Likharev K K IBM J. Res. Dev. **32**, 144 (1988).

4. Livermore C *et al.*, Science **274**, 1332 (1996).

Luo K, Shi Z, Lai J, and Majumdar A, Appl. Phys. Lett. **68**, 325 (1996).

Macucci M, Hess K, Iafrate G W, J. Appl. Phys. **77**, 3267 (1995).

Madelung O ed., *Landolt-Börnstein Group III, Volume 17b: Semiconductors; Physics of II-VI and I-VII Compounds* (Springer-Verlag, New York 1982).

Magonov S N, Wawkuszewski A, Cantow H-J, Liang W, and Wangbo M-H. Appl. Phys. A **59**, 119 (1994).

Majumdar A, Oden P I, Carrejo J P, Nagahara L A, Graham J J, and Alexander J, Appl. Phys. Lett. **61**, 2293 (1992).

Mamin H J, Guethner P H, and Rugar D, Phys. Rev. Lett. **65**, 2418 (1990).

Martin Y and Wickramasinghe H K, Appl. Phys. Lett. **50**, 1455 (1987).

March J, *Advanced Organic Chemistry* (Wiley, New York, ed. 3, 1985).

Martin Y, Abraham D W, and Wickramasinghe H K, Appl. Phys. Lett **52**, 1103 (1988).

Matsumoto *et al.*, Appl. Phys. Lett. **68**, 34 (1996).

Matsuoka H, Ichiguchi T, Yoshimura T, Takeda E, Appl. Phys. Lett **64**, 586 (1994).

Matsuoka H and Kimura S, Appl. Phys. Lett. **66**, 613 (1995).

McCord M A and Awschalom D D, Appl. Phys. Lett **57**, 2153 (1990).

McEuen P L, Foxman E B, Meirav U, Kastner M A, Meir Y, Wingreen N S, and Wind S J, Phys. Rev. Lett. **66**, 1926 (1991).

McEuen P L, Foxman E B, Kinaret J, Meirav U, Kastner M A, Wingreen N S, and Wind S J, Phys. Rev. B **45**, 11419 (1992).

McEuen P L, Wingreen N S, Foxman E B, Kinaret J, Meirav U, Kastner M A, Meir Y, and Wind S J, Physica B **189**, 70 (1993).

McGonigal G C, Bernhardt R H, Yeo Y H, and Thomson D J, *J. Vac. Sci. Technol. B* **9**, 1107 (1991).

McIntyre B J, Salmeron M, and Somorjai G A, *Science* **265**, 1415 (1994).

Meirav *et al.*, *Z. Phys. B* **85** 357 (1991).

Meyer G and Amer N M, *Appl. Phys. Lett* **57**, 2089 (1990).

Mittleman D M, Schoenlein R W, Shiang J J, Colvin V L, Alivisatos A P, Shank C V, *Phys. Rev. B* **49**, 14435 (1994).

Montelius L, Junno T, Carlsson S B, Samuelson L, *Microelectronic Engineering* **35**, 281 (1997).

Mooij J E and Schön G, in *Single Charge Tunneling*, ed. by Grabert H and Devoret M H (Plenum Press, New York, 1992).

Moulson A J and Herbert J M, *Electroceramics*, (Chapman and Hall, New York, 1990).

Mullen K, Ben Jacob E, Jaklevic R C, and Schuss Z, *Phys. Rev. B* **37**, 98 (1988).

Muller C J, van Ruitenbeek J M, de Jongh L J, *Phys. Rev. Lett.* **69**, 140 (1992).

Müller W T, Klein D L, Lee T, Clarke J, McEuen P L, and Schultz P G, *Science* **268**, 272 (1995).

- Murray C B, Norris D B, Bawendi M G, J. Am. Chem. Soc. **115**, 8706 (1993).
- Murray CB, Kagan C R, and Bawendi M G, Science **270**, 1335 (1995).
- Musselman I H and Russel P E, J. Vac. Sci. Technol. A **8**, 3558 (1990).
- Nakamura Y, Klein D L, and Tsai J S, Appl. Phys. Lett. **68**, 275 (1996a).
- Nakamura Y, Chen C D, and Tsai J S, Jap. J. Appl. Phys. **35**, 1465 (1996b).
- Nirmal M, Norris D J, Kuno M, Bawendi M G, Efros A L, and Rosen M, Phys. Rev. Lett. **75**, 3728 (1995).
- Norris D J and Bawendi M G, Phys. Rev. B **53**, 16338 (1995a).
- Norris D J, Efros A L, Rosen M, and Bawendi M G, Phys. Rev. B **53**, 16347 (1995b).
- Odinstov A A, Appl. Phys. Lett. **58**, 2695 (1991).
- Oosterkamp *et al.*, Phys. Rev. Lett. **78**, 1536 (1997).
- O'Shea S J, Welland M E, and Rayment T, Appl. Phys. Lett. **60**, 2356 (1992).
- Ogawa S, Fan F-R F, and Bard A J, J. Phys. Chem. **99** 11182 (1995).
- Peng X, Schlamp M C, Kadavanich A V, and Alivisatos A P, *submitted to J. Am. Chem. Soc.* (1997).

Porter M D, Bright T B, Allara D L, and Chidsey C E D, J. Am. Chem. Soc. **109**, 3559 (1987).

Pothier H, Lafarge P, Orfila P F, Urbina C, Esteve D, and Devoret M H, Physica B **169**, 573 (1991).

Pothier H, Lafarge P, Orfila P F, Urbina C, Esteve D, and Devoret M H, Europhys. Lett. **17**, 249 (1992).

Ralph D C, Black C T, and Tinkham M, Phys. Rev. Lett. **74**, 3241 (1995).

Ralph D C, Black C T, and Tinkham M, submitted to Phys. Rev. Lett. (1997).

Reed M A, presentation at APS March Meeting, March 17-21 (1997).

Reed M A, Randall J N, Aggarwall R J, Matyi R J, Moore T M, and Wetsel A E, Phys. Rev. Lett. **60**, 535 (1988).

Rugar D, Züger O, Hoen S, Yannoni C S, Vieth H M, Kendrick R D, Science **264** 1560 (1994).

Rylander P N, *Organic Synthesis with Noble Metal Catalysts* (Academic Press, New York, 1973).

Sacara A, Norris D J, Murray C B, and Bawendi M G, J. Chem. Phys. **103**, 5236 (1995).

Salmeron M, Ogletree D F, Ocal C, Wang H-C, Neubauer G, and Kolbe W, J. Vac. Sci. Technol. B **9**, 1347 (1991).

Sarid D, *Scanning Force Microscopy* (Oxford University Press, New York, 1991)

Schleicher B, Jung T, and Burtscher H, J. Col. Int. Sci. **161**, 271 (1993).

Schmid G, Chem. Rev. **92**, 1709 (1992).

Schmidt ME, Blanton SA, Hines MA, Guyot-Sionnest P, J Chem. Phys. **106**, 5254 (1997).

Schönenberger C, van Houten H, and Donkersloot H C, Europhysics Letters **20**, 249 (1992).

Schumm J S *et al.*, Nanotechnology **7**, 430 (1996).

Shiang J J, Kadavanich A V, Grubbs R K, and Alivisatos A P, J. Phys. Chem. **99**, 17417 (1995).

Simmons J G, J. Appl. Phys. **34**, 1793 (1963).

Soldatov *et al.* JETP letters **64**, 556 (1996).

Soldatov *et al.* submitted to Phys. Rev. Lett. (1997).

Steigerwald M L, Alivisatos A P, Gibson J M, Harris T D, Kortan R, Muller A J, Thayer A M, Duncan T M, Douglass L E, and Brus L E, J. Am. Chem. Soc. **110**, 3046 (1990).

Su B, Goldman V J, Santos M, and Shayegan M, Appl. Phys. Lett. **58**, 747 (1991)

Su B, Goldman V J, Cunningham J E, Science **255**, 313 (1992a).

Su B, Goldman V J, Cunningham J E, Phys. Rev. B **46**, 7644 (1992b).

Su B, Goldman V J, Cunningham J E, Surface Science **305**, 566 (1994).

Tanaka A, Onari S, and Arai T, Phys. Rev. B **45**, 6587 (1992).

Tanaka Y and Akera H, Phys. Rev. B **53**, 3901 (1997)

Tanaka Y and Akera H, J. Phys. Soc. Japan **66**, 15 (1997).

Tans *et al.*, Nature **386**, 474 (1997).

Tarucha S, Austing D G, Honda T, van der Hage R J, and Kouwenhoven L P, Phys. Rev. Lett. **77** 3613 (1996).

Tolbert S H and Alivisatos A P, Science **265**, 373 (1994).

Tortonese M, Barrett R C, and Quate C F, Appl. Phys. Lett. **62**, 834 (1993).

Tsukruk V V, Lander L M, and Brittain W J, Langmuir **10**, 996 (1994).

Turkevich J, Cooper Stevenson P, and Hillier J, *J. Disc. Faraday Soc.* **11**, 55 (1951).

van Bentum P J M, Smokers R T M, and van Kempen H, *Phys. Rev. Lett.* **60**, 2543 (1988).

van der Vaart N C *et al.*, *Phys. Rev. Lett.* **73**, 320 (1994).

van der Vaart N C *et al.*, *Phys. Rev. Lett.* **74**, 4702 (1995).

van Houten H, Beenakker C W J, and Staring A A M, in *Single Charge Tunneling*, ed. by Grabert H and Devoret M H (Plenum Press, New York, 1992).

van de Leemput L E C and van Kempen H, *Rep. Prog. Phys.* **55**, 1165 (1992).

Wang Y R and Duke C B, *Phys. Rev. B* **37**, 6417 (1987).

Weisenhorn A L, Mac Dougall J E, Gould S A C, Cox S D, Wise W S, Massie J, Maivald P, Elings V B, Stucky G D, and Hansma P K **247**, 1330 (1990).

Wienhaus H and Ziehl H, *Chem. Ber.* **65**, 1461 (1932).

Wiesendanger R, *Scanning Probe Microscopy and Spectroscopy : Methods and Applications*, (Cambridge University Press, Cambridge, Great Britain, 1994).

Wolter O, Bayer Th, Greschner J, *J. Vac. Sci. Technol. B* **9**, 1353 (1991).

Womelsdorf J F, Ermler W C, Sandroff C J, J. Phys. Chem. **95**, 503 (1991).

Yanson I K and Vlasenko A A, JETP Lett. **9**, 407 (1969).

Yanson I K and Vlasenko A A, JETP Lett. **13**, 294 (1971).

Yazdani A, Eigler D M, Land N D, Science **272**, 1921 (1996).

Zeller H R and Giaver I, Phys. Rev. **181**, 789 (1969).

Zhou *et al.*, Appl. Phys. Lett. **67**, 1160 (1995).