FINAL REPORT

Quantum Confinement, Carrier Dynamics and Interfacial Processes in Nanostructured Direct/Indirect-Gap Semiconductor-Glass Composites

DOE Grant Number
DE-FG05-91-ER45462

Joseph H. Simmons
Department of Materials Science & Engineering
University of Arizona
Tucson, AZ 85721
1-352-392-6679
simmons@aml.arizona.edu

August 13, 2002

ABSTRACT

The behavior of semiconductor clusters precipitated in an insulated matrix was investigated. Semiconductor compositions of CdTe, Si and Ge were studies and the insulating matrix was amorphous SiO_2. As a function of size, quantum confinement effects were observed in all three composite systems. However significant differences were observed between the direct-gap column 2-6 semiconductors and the indirect-gap column 4 semiconductors.

As observed by others, the direct-gap 2-6 semiconductors showed a distinct saturation in the energy-gap blue shift with decreasing size. Theoretical studies using a 20-band k dot p calculation of the electronic and valence bands for a 3-dimensionally confined CdTe semiconductor showed that mixing of the conduction band states leads to a flattening of the central valley. This increases the electron mass drastically and saturates the size dependent blue shift in the bandgap.

In contrast, the blue shift in the Si and Ge nanocrystals showed no sign of saturation and increased drastically with decreasing size. In fact, Si and Ge crystals were formed with blue shift values that moved the bandgap to the near UV region. We examined the absorption curves to determine whether the bandgap was direct or indirect in the quantum dots. The results are that the absorption shows an indirect gap for all but the smallest Si crystals and an indirect gap for all Ge crystals.

Raman studies showed negligible size dependence due to a lack of phonon confinement in the matrix embedded clusters. Exciton saturation and recovery times were found to be very short (of the order of 400fs) and are the fastest reported for any quantum dot system.

Work to examine the type of confinement obtained in a matrix that consists of a transparent conductor is under way.

Studies of the photoinduced absorption change in GeSe glasses showed a significant effect of photodarkening, regardless of composition. The photodarkening effect appears to be composed of permanent and transient effects, presumed to be associated with photo-induced structural changes in the glass. The transient effects appear to have recovery times in at least two different time scales – one in minutes and one in less than a microsecond. Time-resolved studies are under way to determine the structural origin of each photodarkening effect.

REVIEW OF OBJECTIVES AND PROGRESS OF RESEARCH

INTRODUCTION

Composite structures consisting of quantum confined semiconductor clusters embedded in a transparent matrix have posed interesting and puzzling fundamental physics and materials science problems as well as offering a number of potential high value applications. Regarding the fundamental issues, we have observed changes in bandgap energy with cluster size which do not adhere to conventional models at small crystal sizes [1] and appear to depend strongly on whether the semiconductor is a 2-6 direct-gap type or a column 4 indirect-gap type. Here, we have observed that composites doped with CdTe, CdS and CdSe in a silica matrix exhibit a pronounced saturation of the predicted blue shift in bandgap energy with decreasing size [2]. By contrast, composites with Si and Ge doped in a silica matrix which exhibit indirect-gap transitions, continued to exhibit a large blue shift in bandgap energy with decreasing size. This effect was so pronounced that Si- and Ge-doped composites have been fabricated that exhibit bandgap energy transitions from the IR (corresponding to the bulk values) to the UV for crystal sizes of the order of 4 D [3].

Time-resolved pump-probe studies have revealed very fast (100-400 fs) recovery of exciton bleaching times in CdTe-glass composite thin films [2], contrary to times of 400 ps observed by numerous investigators in CdSe melt-derived composites [4]. This effect was coupled with a difference in the presence of multivalent ions at the semiconductor-glass interface between the films (no ions) and the melt-derived glasses (high concentration of Fe interface impurities [5]).

Materials science issues involved fabrication processes which lead to a variety of cluster sizes and size distributions [1], and interface structures. Potential applications range from very highly efficient solar cells [6] to fast optical switches.

As a consequence of this work, the original objectives of the current research effort were as follows:

(1) To combine experimental and theoretical studies to build an understanding and a model of the quantum confinement mechanism that differentiates the behavior of direct-gap and indirect-gap semiconductor clusters.

(2) To investigate the time-dependent behavior of quantum dots to determine the effect of the interface and matrix on exciton-biexciton formation, carrier coupling/decoupling, charge trapping and the formation of bound image charges.

(3) To develop a theoretical basis for the examination of carrier dynamics in quantum confined structures with support from experimental studies.

(4) To determine the role of the cluster-matrix interface on quantum confinement and carrier lifetimes, and to examine methods of tailoring such interface, including the formation of an interface layer.

RESULTS OF RESEARCH

1. Si and Ge films:
Films produced under various preparation conditions were analyzed by absorption spectroscopy, Raman scattering and high resolution transmission electron microscopy (TEM). The results of TEM analysis showed that the films, as produced by RF sputtering, were amorphous. This was supported by Raman measurements that show phonon peaks characteristic of an amorphous Si and Ge structure. Variations in fabrication conditions could produce thin cluster films or discs, as well as spherical cluster structures. Progressive structural changes of the cluster during heat treatment were followed in Raman studies that showed the development of crystals with time. This crystallization process led to an expected sharpening of the band-edge absorption and an unexpected shift in bandgap energy. Composites containing Si and Ge clusters were developed with different size crystalline and amorphous structures in a silica glass matrix. The variations in bandgap energies with cluster size and structure were examined. The absorption edge of these composites was also examined to determine any shift from indirect-gap to direct-gap behavior. The results show that the bandgaps of Ge clusters increase drastically with decreasing cluster size, but the transition remains indirect at all sizes studied between 4 and 150 D. Silicon clusters exhibited the same pronounced shift in bandgap energy, however, the transition was indirect between 18 and 162 D, and became direct at sizes between 4.5 and 9 D. The latter is consistent with a previous theoretical paper by Stanton and co-workers [8] that shows a distinct change to direct behavior in Si wires at small and large sizes, however, this change is not experimentally observable until very small cluster sizes due to the comparatively weak oscillator strength in the direct-gap transition.

2. Investigation of carrier injection into conducting matrices:
Prompted by the potential for solar cell applications of the Si and Ge quantum dots, we began to examine the effect of lowering the potential barrier causing the quantum confinement effect. By varying the bandgap energy of the matrix and its electron affinity with suitable choice of composition, we sought to investigate quantum confinement and carrier tunnelling in composites where the matrix only effectively confines either only the electron or the hole. This study would reveal, for the first time, how each carrier can be independently confined by a suitable potential well. As a physics problem it offers a study of the effect of the potential well on the electron-hole interaction. As a materials science problem, it provides a possible means of controlling carrier injection between the semiconductor and the matrix and the investigation of a tailored p-n junction system.

Toward this goal, we have modified the sputtering system to produce Si and Ge quantum dots in different glass matrices than silica. This objective has brought back fabrication as an important issue in the study, as we must control the oxidation energy of the various matrix components so as to avoid oxidizing the Si or Ge semiconductors. So far, we have been unable to control the oxidation of Si during the deposition of an ITO matrix. (The latter is a film of indium and tin oxide, widely used as transparent n-type conductor.) We have found that indium oxide readily gives up its oxygen to Si. However, the transfer is slow enough that we are investigating conditions that may produce a partial transfer only, as this will produce Si clusters with an SiO_2 coating in an ITO matrix. Such a composite would provide a complex p-i-n junction interface. Studies with Ge show a better resistance to oxidation and we are currently preparing films of Ge clusters in an ITO matrix to study the effect of hole-only confinement on the optical and carrier transport properties of the composite.

3. Studies of ultrafast carrier dynamics in quantum wells:
Most photo-induced carrier dynamic processes in semiconductors occur in very short time scales. For example, nanoscale semiconductor devices are exposed to electric field strengths over a shorter time period than carrier scattering rates, causing significant changes in carrier transport. Our studies have examined these changes theoretically and fitted the results to experimental studies. We have solved the exact quantum mechanics of a model semiconductor system in which an electron excited to coherent superposition is subjected to self-interference. Our results show that phonon emission is isolated to bursts in time (e.g. a phonon staircase effect) if the electron starts from an initial broad correlated state. This work was followed by an examination of the ultrafast decoherence of an electronic wave packet in a semiconductor quantum well exposed to a strong magnetic field. Results were obtained for magnetic $Cd_{1-x}Mn_xTe$ and CdTe quantum wells.

4. Investigations of new chalcogenide semiconductors and glasses:
It is known that as one reduces the bandgap energy of semiconductors the exciton Bohr radius increases and the quantum confinement behavior occurs in larger crystals. We showed this effect in going from CdS and CdSe to CdTe. We decided to continue in this direction with Ge_xSe_y crystals. Such materials provide convenient low bandgap energy semiconductor crystals and IR transparent glass matrices with possibilities for carrier conduction due to the easily formed mid-gap states. We have begun studies of optical absorption edge and photosensitivity in Ge_xSe_y materials. Our results so far point to the fact that midgap states formed by the defect structure and exposure to light play an important role in photostructural effects and a potentially important role in carrier transport.

BIBLIOGRAPHY

[1] B. G. Potter, Jr., J. H. Simmons, P. Kumar and C. J. Stanton, "Quantum-Size Effects on the Band Edge of CdTe Clusters in Glass," J. Appl. Phys. 75, 8039-8045 (1994).
[2] J. H. Simmons, “What is so exciting about non-linear viscous flow in glass, molecular dynamics simulations of brittle fracture and semiconductor-glass quantum composites -- G. W. Morey Award Lecture,” J. Non-Crystalline Solids 239, 1-15 (1998).
[3] T. J. Bukowski, T. Varghese, R. Ochoa and J. H. Simmons, “Absorption and Raman Scattering Spectroscopies from Semiconductor-Glass Composites,” J. Non-Crystalline Solids, (accepted for publication).
[4] N. Peyghambarian, B. Fluegel, D. Hulin, A. Mingus, M. Joffre, A. Antonetti, S. Koch and M. Lindberg, “Femtosecond Optical Nonlinearities in CdSe Quantum dots,”IEEE J. Quant. Electron. 25, 2516-22 (1989).
[5] J. Malhotra, D. J. Hagan and B. J. Potter, “Laser-induced Darkening in Semiconductor-Doped Glasses,” J. Opt. Soc. Am. B8, 1531-6 (1991).
[6] Joseph H. Simmons, "Novel Design for the Fabrication of High Efficiency Solar Cells," US Patent 5,720,827 February 24, 1998.
[7] J. H. Simmons, B. G. Potter and O. R. Ochoa, “Nonlinear Optical Materials – Cluster-Insulator Composites” in Handbook of Laser Science and Technology – Suppl. 2: Optical Materials, CRC Press (Boca Raton, 1995).
[8] G. J. Sanders, C. J. Stanton and C. Chang, Phys. Rev. B48, 11067 (1993).

PUBLICATIONS

Published papers:

“Interaction Induced Electron Self-Interference in a Semiconductor: The Phonon Staircase Effect,” Phys. Rev. Lett. 78, 4873 (1997).

"Raman Characterization of CdTe Nanocrystallites embedded in a Glass Matrix," J. Mater. Science Lett. 16, 613-16 (1997).

“Femtosecond Relaxation Kinetics of Highly Excited Electronic WavePackets in Semiconductors,” Phys. Rev. B57, 12369 (1998).

Morey Award Paper: “What is so exciting about non-linear viscous flow in glass, molecular dynamics simulations of brittle fracture and semiconductor-glass quantum composites,” J. Non-Crystalline Solids 239, 1-15 (1998).

“Probing Semiconductor Carrier Kinetics with Ultrafast Nonlinear Faraday Rotation,” Phys. Rev. B58, 13399 (1998).

“Absorption and Raman Scattering Spectroscopies from Semiconductor-Glass Composites,” T. J. Bbukowski, T. M. Neidt, R. Ochoa and J. H. Simmons, J. Non-Crystalline Solids 274, 87-92 (2000).

“Photodarkening in Ge_3Se_{17} Glass,” C. R. Schardt, J. H. Simmons, P. Lucas, L. Le Neindre and J. Lucas, J. Non-Crystalline Solids 274, 23-29 (2000).

Dissertation:
“Electronic, Optical and Transport Properties of Widegap II-VI Semiconductors” Janzhong Li, PhD Dissertation, University of Florida, Gainesville, FL, December 1997.

Patent Issued:
"Novel Design for the Fabrication of High Efficiency Solar Cells," US Patent 5,720,827 February 24, 1998.

Papers accepted for publication:

“Using Ultrafast Coherent Phonons as a Novel Spectroscopy Tool to Probe Semiconductor Surfaces and Interfaces,” C. J. Stanton, C. K. Sun, D. S. Kim, J. C. Liang, J. H. Simmons and S. P. DenBaars, Superlattices and Microstructures (accepted for publication).

“Raman Temperature Measurement During Photodarkening of Ge_xSe_{1-x} Glass,” Craig R. Schardt, Joseph H. Simmons and Pierre Lucas, Appl. Phys. Lett. *(Submitted).*

PERSONNEL

Principal investigators:
Joseph Simmons (MSE Dept.)
Christopher Stanton (Physics Dept., University of Florida)

Research Personnel (University of Florida):
Catherine J. Simmons - Scientist (MSE Dept.) Partial support
Tansen Varghese - Graduate student (MSE) – Graduated MS degree
Craig R. Schardt - Graduate student (MSE)
Tracie Bukowski - Graduate student (MSE)
Christophe Juncker - Graduate student (MSE)