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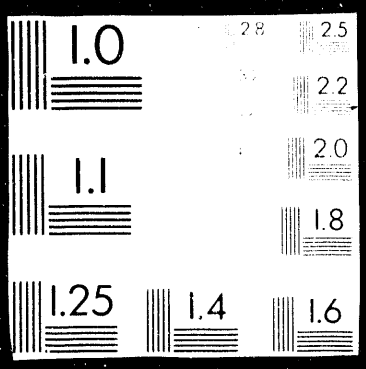

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ELECTRON EMISSION FROM NANOMETER-SIZE METALLIC CLUSTERS: ELECTRONIC STATES AND STRUCTURAL STABILITY OF SUPPORTED Au CLUSTERS

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ABSTRACT. Techniques developed to measure the thermodynamic and electronic properties of a single metallic cluster with nanometer-size dimensions are described. Using these techniques, experiments that resolve the quantized energy spectrum of electrons in a nanometer-size cluster of metallic atoms at room temperature have been performed. Studies on the stability of the electron emission current from an individual nanometer-size cluster supported on a tungsten tip have been performed to learn more about the intrinsic stability of these nanometer-size objects. The data show abrupt jumps between different emission states that are revisited as time progresses. This phenomenon is attributed to a rearrangement of the cluster structure and/or orientation on the substrate and provides new evidence of multiple 'isomeric' structures for small clusters of metallic atoms.

1. Introduction

The manipulation of atoms to fabricate nanometer-scale structures ultimately requires an understanding of the size-dependent thermodynamic, electronic, and structural properties of discrete aggregates of atoms. The properties of these aggregates differ from bulk properties and these differences will set limits on the stability and performance of structures fabricated at the nanometer length scale. In order to provide experimental information about these limits, techniques recently developed to measure the size-dependent properties of clusters of atoms supported on substrates will be reviewed. Using these techniques, the thermodynamic,[1–3] electronic, and electron emission properties of an individual nanometer-size aggregate of atoms can now be probed.

A unique feature of the structures under study is that the influence of high applied electric fields on the electronic conduction process can be performed in a natural way. This is because the techniques rely on the study of electrons field emitted from an individual cluster. To produce field emission, electric fields of order 10^9 V/m are required. In the following paper, we describe a series of experiments conducted on the electronic properties of small nanometer-size metallic clusters that provide information relevant to the above stated goals. The studies summarized below provide a unique window into the electronic structure that is important at this length scale.

2. Cluster growth and sample preparation

A description of the construction and operation of the multiple expansion cluster source (MECS) used in this study can be found in the literature.[4–6] The clusters are grown as aerosol particles in an inert gas and introduced into a vacuum chamber (10^{-6} Torr) to form a cluster beam. In previous studies, cluster samples have been captured on amorphous carbon substrates and analyzed by TEM. The isolated clusters studied in this way confirm the ability of the MECS to produce metal clusters having an approximately spherical shape, a controlled mean size, and a narrow size distribution.[4,5] This TEM size-determination method has been used in conjunction with field emission studies to determine the mean diameter and variance of the cluster-size distribution from which the clusters of interest are sampled.

To study field emission from a single cluster, a tungsten tip is exposed to the cluster beam and then transferred to a field emission chamber in a vacuum transfer cell at pressures of $\sim 5 \times 10^{-8}$ Torr.[6] Experiments are performed in the field emission chamber at typical pressures of $\sim 2 \times 10^{-10}$ Torr. A schematic of the retardation/127° energy analyzer used in these experiments is shown in Figure 1. The characterization and performance of this analyzer is described elsewhere.[7,8]

3. Size-dependent field emission spectra from supported Au clusters

The ability to measure the energy distribution of electrons emitted from a single supported Au cluster with a diameter of $\sim$ 1 nm was reported previously.[9] The observed emission spectra provided good evidence that the quantized electronic states in an individual 1 nm diameter Au cluster can survive when the cluster is supported on a W surface. A resonant-tunneling model based on first-order perturbation by the applied electric field was used to provide an estimate for the position in energy of the peaks observed in the field emission spectrum. A reasonable account for the experimental observations was obtained and a tentative identification of the cluster shell-levels responsible for the observed structure was proposed.[9,10]

As the size of the cluster increases, a number of difficulties arise in applying this resonant tunneling analysis. First, the effect of electric field penetration becomes less important since the surface to volume ratio of the cluster decreases. If the electric field does not penetrate the cluster significantly, the cluster-substrate interaction becomes the dominant perturbation. This implies that as the cluster diameter increases, the field-dependent downward shift in the electron energy spectra diminishs. Second, as the cluster size increases, increased coupling between the cluster and substrate can be anticipated since the number of cluster atoms in close proximity to the substrate increases. Since these effects are difficult to include in the resonant-tunneling model, a detailed comparison between the measured emission spectra and the model outlined in Refs. 9 and 10 has not been attempted. Rather, data on the size-dependent structure are presented to illustrate the capabilities of the technique and to illustrate any size-dependent trends that they reveal.

The emission spectra for several different cluster sizes are summarized in Figure 2.[11] The data show that the electron energy distribution shifts toward the substrate E_F with

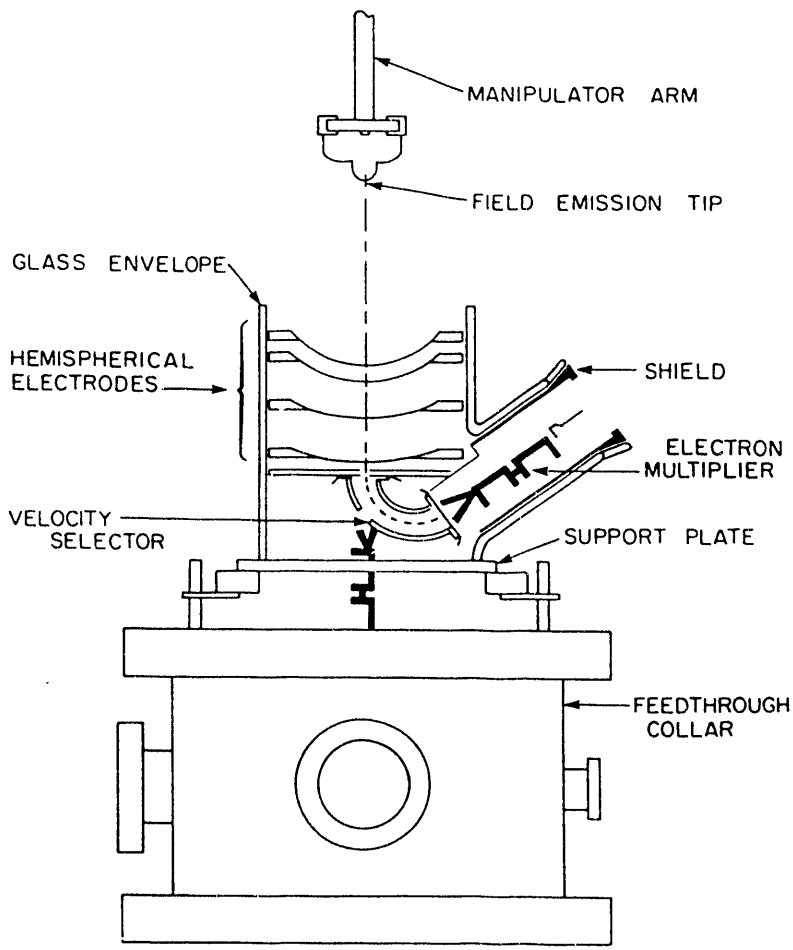

Figure 1: A schematic of the energy analyzer used in these studies. Electrons emitted from a cluster deposited on the apex of the tip are accelerated toward the first hemispherical electrode which is coated with a fluorescent screen. Those electrons passing through the probe hole in this electrode are subsequently decelerated until they reach the entrance slit of the 127° velocity selector. This analyzer has an energy resolution of 0.07 eV. Figure reproduced from Ref. 7

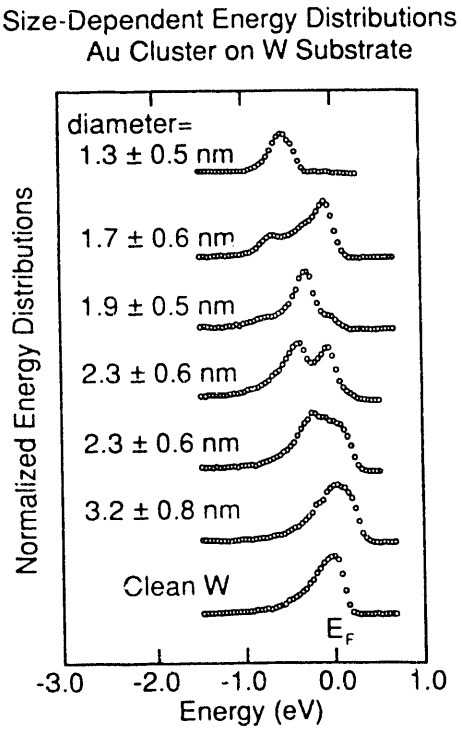

Figure 2: The size-dependent energy distribution of electrons emitted from a Au cluster supported on a W tip at room temperature. The observable features in the energy distribution mirror the quantized electronic structure of the supported Au cluster. The energy distribution obtained from a clean W tip provides a convenient method to determine the Fermi energy of the underlying substrate. Figure reproduced from Ref. 11

increasing cluster size until all structure in the distribution becomes unresolvable for clusters with diameters greater than ~3 nm.

The position in energy of the peaks in the energy distribution from an individual cluster were reproducible over a period of time spanning a few weeks. The height of the peaks changed when measured on a time scale of a few hours, a fact attributed to the time-dependent coupling of the cluster states to the substrate.[10] Different clusters with the same nominal size did not necessarily exhibit identical emission spectra, a fact which indicates the need to more accurately determine the number of atoms comprising each cluster in future studies. Similar variations in the tunneling spectra of single clusters have been reported for Si clusters supported on Au substrates.[12]

For a 1.3 ± 0.5 nm diameter cluster, a single electron emission peak was observed ~ 0.2 eV below the substrate Fermi level, indicating that the highest occupied cluster state was not pinned to the Fermi energy of the substrate. As the applied field increased, the peak moved further below the Fermi level of the substrate.

Two distinct peaks appear in the energy distribution from a 1.7 ± 0.6 nm diameter cluster and both shift to lower energies with increasing field. This shift with applied field

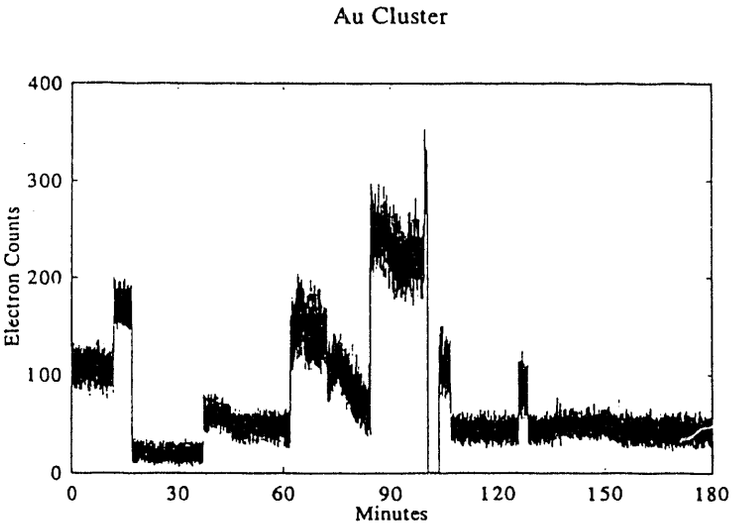

Figure 3: A typical plot of electron counts vs. time from a nominal 2.6 nm diameter Au cluster supported on the apex of a W tip. The abrupt changes in the field emitted current is found to take place only between well-defined emission states.

provides a useful way to identify cluster states[9] and indicates whether the discrete energy states are related to the supported cluster or to surface states of the substrate.

For a 1.9 ± 0.5 nm diameter cluster, three peaks are observed in the energy distribution. One peak is located at the Fermi level of the substrate and does not shift with applied field. The two other peaks are $\sim$ 0.16 eV and $\sim$ 0.40 eV below the Fermi level respectively. These two latter peaks were field dependent and are therefore interpreted as a signature of the cluster states. Thus, for this cluster, we evidently observe not only ballistic emission of electrons from the substrate through the cluster but also emission from the two highest-lying cluster states.

When a cluster with 2.3 ± 0.6 nm diameter was deposited on the W tip two peaks were again resolved. During this deposition, two well-separated clusters were observed on the apex of the field emission tip. The two-peaked structure observed for both clusters are similar as shown in Figure 2. Both peaks are cluster-related states because their position depends on the applied electric field. The data shows that the peak at lower energy is larger than the one nearer the Fermi level, a result indicative of a partially filled upper energy shell.

As cluster size increases, the discrete states should become more closely spaced until their separation is smaller than the energy resolution of our apparatus. This behavior is observed in the spectrum obtained for a 3.2 ± 0.8 nm diameter cluster where only one broad peak was observed. This peak is broader than the W field emission energy distribution from the substrate. It is not clear what mechanism is responsible for this broadening, but it is likely a signature of electron emission from many closely spaced cluster states that can not be resolved by the energy analyzer used in this study. The disappearance of structure at

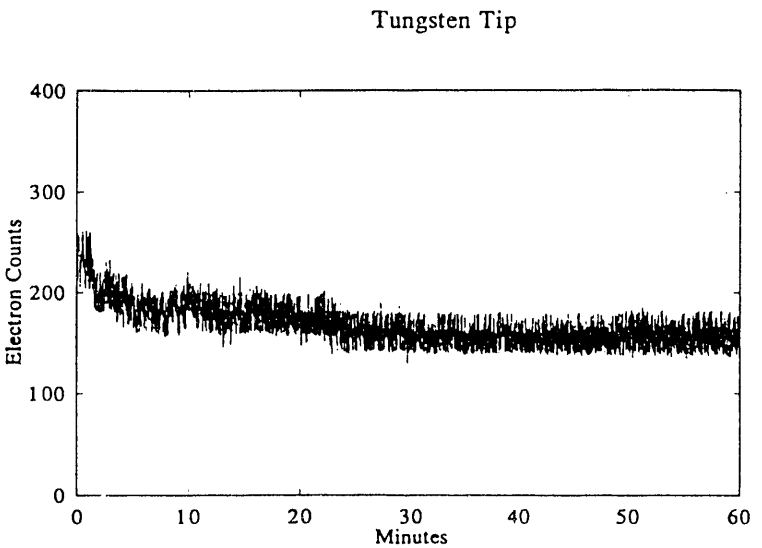

Figure 4: A typical plot of electron counts vs. time for field-emitted electrons from a tungsten tip after desorption of the Au cluster.

the $\sim$ 3 nm cluster size is in good qualitative agreement with model calculations presented elsewhere.[10,11,13]

Finally, a representative energy spectrum is shown from a clean tungsten tip. This spectrum was obtained after a supported cluster was thermally desorbed from the tip. A fit to this data using the standard theory of field emission[14,15] locates the Fermi level of the substrate and provides a convenient reference curve for intercomparison of the cluster emission spectra.

4. Structural Stability

The structural stability of a supported cluster in the nanometer size range is a question that is still under considerable debate. It has been established from computer simulations that a nanometer-size cluster has many structural configurations that are closely separated in energy from the true ground state. These calculations predict structures that deviate from the cluster shape given by the classical Winterbottom criterion[16] which dictates that minimization of the surface free-energy determines the final cluster shape.

In contrast to these theoretical calculations which attempt to predict a well-defined structural state for a nanometer-size cluster, other investigations have postulated the presence of a new state, often referred to as the 'quasi-molten' state, as the equilibrium state for a small nanometer-size cluster.[17–20] However, the high-resolution transmission electron microscope (TEM) studies of this proposed cluster state requires electron-beam irradiation of the clusters, producing effects by the high-energy incident electron beam which are difficult to characterize. Despite arguments to the contrary, concerns regarding the role of the incident electron beam in producing the observed 'quasi-molten' state have not been

conclusively eliminated.

As discussed in the previous section, we have performed a number of experiments utilizing electron emission from a nanometer-size cluster supported on the apex of a sharp field emission tip. While it is not possible to achieve the spatial resolution necessary to determine structural changes directly from field emission microscopy, fluctuations in the field emission current do provide information about this important question. For instance, it is well established that fluctuations in the field emission current from a sharp tip can give useful information about the diffusion of intentionally adsorbed gaseous species.[21-23] We take advantage of this technique to study the stability of a nanometer-size object to determine the inherent stability of a supported nanometer-size cluster. By following this approach, we can obtain results without resorting to the bombardment of the supported cluster by a flux of energetic electrons.

A priori, any instability in the cluster structure should cause abrupt changes in the total field emission current. This follows because of the exponential dependence of the emission current on the local value of both the work function and the applied electric field. Field emission can therefore serve as a very sensitive monitor to structural changes in cluster shape and/or orientation on a substrate. It is important to realize that because of the small radius of curvature of the cluster with respect to the field emission tip, electrons emitted from one cluster only can be directed through the probe-hole of our energy analyzer, thereby permitting a study of the structural stability of a single supported cluster.

The experimental procedures are similar to those described earlier. The major modification occurs in the way data is acquired. The experiment was performed by first depositing a Au cluster on the W tip from the cluster beam. Subsequent TEM images of a carbon grid exposed to the same cluster beam showed a size-distribution that was characterized by a nominal diameter of 2.6 ± 0.8 nm. After deposition, the electrons emitted from the supported cluster were directed into the probe hole of the energy analyzer. After measuring the energy distribution of the electrons from the supported cluster, the bias voltage on the fourth plate of the retardation section of the energy analyzer was fixed at a value that maximized the electron count rate. This procedure minimized the effect of any small drifts in bias voltage that may have occurred during the course of data acquisition.

A computer was programmed to accumulate the number of electrons emitted from the cluster in time intervals of 0.5 seconds. Due to the large amount of data, an IBM 386 25MHz lap-top computer with 4Mb RAM was used as an auxiliary computer to store the experimental data. The zero of time was set by adjusting the total field emission current from the cluster to approximately 2 nA for a brief period of time followed by a return to its nominal value of $\sim$0.5 nA.

In Figure 3, the field emission current striking the electron multiplier from the nominal 2.6 nm gold cluster during a time span of three hours is presented. At the beginning, the rate of electron emission per 0.5 second time interval is maintained at $\sim$110 electrons. After $\sim$ 12 minutes, the emission rate jumps to $\sim$ 160 electrons per half second and remains stable for about 4 minutes. A discontinuity of emission rate occurs between these two stages. Similar discontinuities can be observed during the first two hours of field emission and seem to occur less frequently as the experiment progresses. Besides the discrete levels observed in this spectrum, the emission rate was found to decrease in a somewhat continuous way

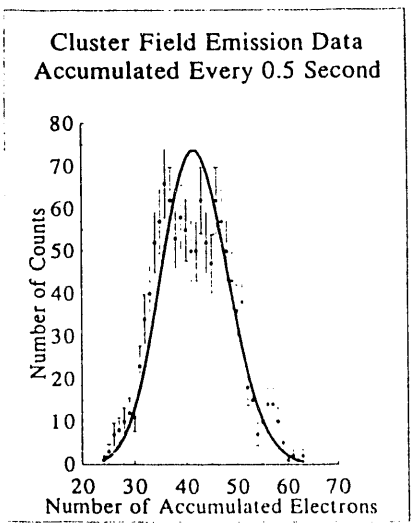

Figure 5: The experimental distribution in count rate during the last 1200 $\frac{1}{2}$-second time intervals for field emission from the Au cluster shown in Fig. 3. The solid curve is the best least-squares fit to a Poisson distribution with mean value of 42.

on one occasion (see Figure 3). For example, the emission rate of field-emitted electrons is decreasing continuously from ~150 electrons to ~80 electrons per half second between the ~ 62nd minute and the ~ 85th minute of the data record. On only one occasion did the emission rate drop to zero at ~ 100 minutes after the experiment had begun.

From this data it is evident that abrupt changes are a characteristic of electron emission from a supported cluster in a high electric field. These abrupt changes occur between ~ 5 distinct emission states that have steady electron emission characteristics. Examination of this data also shows that the time dependence of the field-emitted electrons can be classified into a number of well-defined levels. It is likely that each level is associated with a different configuration between the cluster and substrate. The electron emission, when studied in this way, suggests that the cluster sequentially visits the same five configurations during the three hour period of data acquisition.

A possible explanation which might account for the abrupt changes in the electron emission rate is related to sudden contamination by gas atoms in the ultra-high vacuum (UHV) environment. In order to eliminate this possibility, the cluster was thermally desorbed from the tip apex and an electron emission stability experiment was performed on electrons emitted from a small region of the W tip alone. The results of this experiment are shown in Figure 4, and demonstrate that the emission rate is quite stable with time. No abrupt change in the emission rate is observed and the time dependence of the emission current is consistent with a gradual increase in the tip's work function due to slow contamination by residual gas in the UHV chamber. On the basis of this data, contamination and diffusion effects can be ruled out as a possible explanation of the data shown in Figure 3.

Probable explanations for the instabilities observed in this experiment can be suggested.

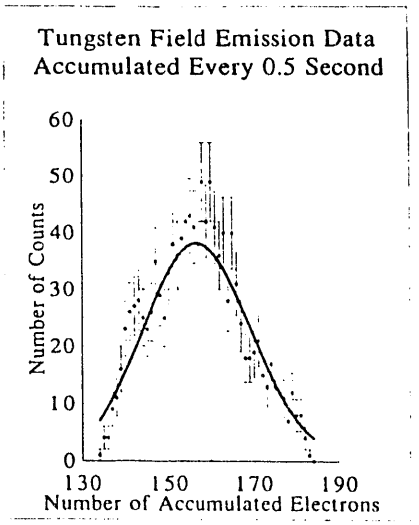

Figure 6: The experimental distribution in count rate during the last 1200 $\frac{1}{2}$-second time intervals for field emission from the W tip shown in Fig. 4. The solid curve is the best least-squares fit to a Poisson distribution with mean value of 157.

For instance, electron tunneling resonance effects are known to influence field emission from clusters.[10] These effects determine the current enhancement factor for cluster field emission and are strongly dependent on the coupling between the cluster and substrate. As a result, the field emission rate will vary, accounting for the discontinuities in Figure 3. The resonance tunneling enhancement factor can also be changed by rotating the cluster. One mechanism that can be discounted is a diffusion of the cluster across the substrate. This would be readily observed due to the high spatial resolution of the field emission microscope.

5. Statistical Analysis of Emission Rate

Further insight into each emission state can be gained by further analyzing the data from one emission state using Poisson statistics. These statistics describe the probability $P(x, \mu)$ of observing x events separated in time by a mean value τ over a time interval t. This distribution, which describes the fluctuation in the count rate for a process in which emission occurs at random intervals, is given by

$$P(x, \mu) = \frac{\mu^x}{x!} e^{-\mu} \tag{1}$$

where $\mu = t/\tau$ is the average number of events observed in the time interval t. It is useful to compare our experimental data from the individual cluster to the predictions based on Poisson statistics.

Typical results of this comparison are shown in Figure 5 for emission from the Au cluster and in Figure 6 for emission from the W tip. The solid lines in these Figures are the

least-squares fit to the count rate distribution based on Poisson statistics. It is difficult to determine the quality of these fits to the experimental data by eye. Therefore, we use the reduced χ^2 test[24] to check the agreement between the experimental distributions and the Poisson fits. The results are given in Table 1 and clearly indicate that while the likelihood of fitting the Poisson distribution to the tungsten field emission data is better than 20%, the two cases of electron emission analyzed from the cluster are fit with a likelihood of less than 0.5%.

Table 1: Table comparing the experimental data to a fitted Poisson distribution using reduced χ^2 analysis. (a) The first 1415 samples of the count rate for field emission from the Au cluster, (b) the last 1200 samples of the count rate for field emission from the Au cluster, (c) the last 1200 samples of the count rate for field emission from the W tip after the cluster was thermally desorbed, (d) the same as in (b), but assuming two closely spaced emission channels (hence two mean values) characterize electron emission from a supported cluster.

	Number of Samples	Bins	Mean Value	Reduced χ^2	Probabilities
(a)	1415	61	107	2.0	less than 0.5%
(b)	1200	40	42	3.0	less than 0.5%
(c)	1200	50	157	1.15	~21%
(d)	1200	40	38,46	1.4	~5%

Improvements in the fit of the cluster data occurs if the mean value of the Poisson distribution is split into two well defined values. Using the *ad-hoc* approach that emission from one cluster state is actually fluctuating between two closely-spaced levels, a least squares fit shows that a combined Poisson fit to the data acquires a 5% significance level (see Table 1(d)). This result suggests that the emitted current from the cluster is fluctuating between two different emission channels at a rate comparable to the sampling time of 0.5 seconds employed in these preliminary studies. By further exploiting this technique, non-obtrusive information about the stability of nanometer-size objects supported on substrates will be possible.

6. Summary and Conclusions

Experiments that measure the properties of individual nanometer-size clusters of atoms have been described. By combining the Multiple Expansion Cluster Source and field emission techniques, the distribution in energy of electrons emitted from single Au clusters has been studied as a function of cluster size. This data provides evidence that the quantized cluster states survive the deposition process and can now be studied in a systematic way

at room temperature.

We also summarize the evidence for the structural stability of a supported cluster obtained by studying the electron emission current from a supported nanometer-size cluster as a function of time. The data are interesting because they were taken without the need for irradiation by a high-energy flux of incident electrons produced by a TEM electron gun. Abrupt changes in the electron emission current suggest that a change in cluster shape or orientation on a substrate occurs as a function of time. It is found that the electron emission level revisits values previously measured, indicating that changes in electron current are due to structural fluctuations between well-defined cluster-substrate configurations.

Acknowledgements

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