Theoretical Simulation of Monochromatic Photoemission Peak in Diamondoid Monolayers

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Recent photoemission experiments have discovered a highly monochromatized secondary electron peak emitted from diamondoid self-assembled monolayers on metal substrates. New experimental data and simulation results are presented to show that a combination of negative electron affinity and strong electron-phonon scattering is responsible for this behavior. The simulation results are generated using a simple Monte Carlo transport algorithm. The simulated spectra contain the main spectral features of the measured ones.

The recent isolation of previously inaccessible quantities of nanometer-sized hydrogen terminated diamond clusters[1], also known as diamondoids, has led to renewed interest in these unique molecular systems. In a recent paper[2], photoemission spectra were collected for self-assembled monolayers (SAMs) of a functionalized diamondoid compound, [121]tetramantane-6-thiol, deposited on metal substrates. It was shown that the electrons emitted from the diamondoid SAMs are largely monochromatized, with as many as 68% of the electrons emitted in a single low-energy peak with a FWHM of about .3 eV (see figure 1). This is an unusual property and may have applications in a number of fields ranging from photocathodes to flat-panel displays[3].

This work explores the mechanism for this process, and our results show that this unusual property could be explained by negative electron affinity (NEA) in conjunction with strong electron-phonon scatting within the monolayer. We observe NEA effects and measure the mean free path for scattering by analyzing photoemission spectroscopy data. The mean free path measurement demonstrates that there is an unusually short interaction length in the material. Using these measurements as well as measurements of the phonon spectrum[4], we created a reasonable model for the scattering process. We created a transport Monte Carlo algorithm to test this model which uses a realistic secondary electron tail as a starting point and creates output spectra which match experimental results quite closely. We discuss the limitations of our algorithm and possible ways to improve it.

The experimental results of the original diamondoid self-assembled monolayer photoemission spectroscopy experiments are discussed in our previous work[2]. Figure 1 shows a characteristic spectrum taken of a tetramantanethiol SAM. The most striking feature of the spectrum is the large, narrow peak at low energy. This peak is similar to that seen in semiconductor NEA photocathodes[5] as well as the more closely related di-

amond NEA systems[6–8].

The sharp, low-energy peak is indicative of negative electron affinity. However, NEA alone is not sufficient to explain the intensity of the peak. There must also be an efficient energy loss mechanism which thermalizes many of the electrons. To verify the existence of this energy loss mechanism, additional photoemission data was taken for this work. [121]tetramantane-6-thiol self-assembled monolayers were prepared on silver and gold substrates using established techniques[2,9]. Photoemission experiments were performed at Stanford Synchrotron Radia-
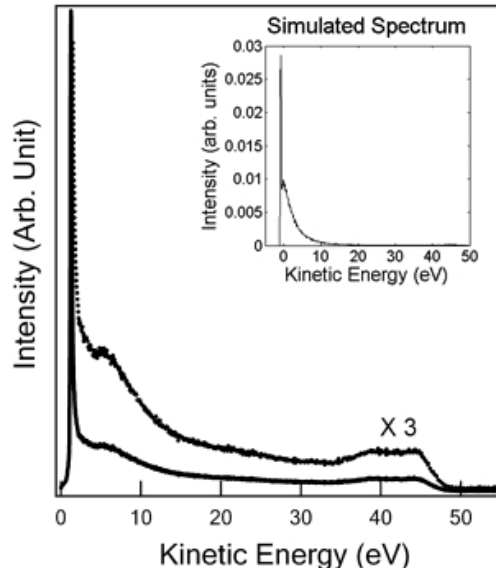

FIG. 1: Experimental photoemission spectrum of a tetramantanethiol SAM on gold surface with 55 eV incident photons, from Ref[2]. Dotted line is a magnification of this spectrum which shows the detail of the secondary electron tail and valence band electrons. Inset shows our simulated spectrum (see text).

tion Laboratory beamline 8-1 using synchrotron radiation with a monochromator which has an energy range of 20-180 eV. Photoemission spectra were measured using a PHI model 10-360 hemispheric capacitor electron analyzer. To detect the lowest energy photoelectrons, a sample to detector voltage bias of -9 Volts was applied.

The mean free path was measured by observing the gold $4f$ peak with the film present and then again after the film has been removed by annealing at 200 °C for 20 minutes. The kinetic energy of the emitted $4f$ electrons was modified by altering the energy of incident photons. By comparing the total counts in the $4f$ peak with and without the film we can measure how many electrons either back-scatter in the film or lose enough energy to no longer be counted in the peak.

The total photoelectron yield was measured for 50, 75, and 100 eV photon energies. The sample was placed perpendicular to the incident photons and biased with a voltage of -9 V. The photoelectrons were collected on the chamber body, which is grounded, and the photocurrent was measured. To get the yield relative to the bare gold surface, the total yield was measured with the film present and then again after the film had been removed by annealing at 200 °C.

The results of the mean free path measurements and an example of the $4f$ peak with and without the film are shown in figure 2. This measurement finds that even at 3.5 eV, 49% of the counts in the peak are lost in the film, far more than the 9% that would be anticipated using the universal curve[10] for the 1 nm thick film. Thus we see that diamondoids do have a much shorter interaction length than most materials, indicating a strong scattering process.

Surprisingly, the electrons continue to strongly interact with the monolayer even at energies which are well below 5.6 eV, a measured lower-bound for the band gap of tetramantane[11]. This means that it is unlikely that electron-electron interactions play a significant role in the scattering process, as many of the electrons observed in these experiments have too little energy to promote an electron from the valence band of the diamondoid to the conduction band. It is clear, however, that there is a strong interaction at low energy as most of the electrons in this energy range are effected as they pass through the film. Given that electron-electron interactions seem unlikely, the best candidate is electron-phonon scattering which can occur at much lower energy.

We measured the quantum yield relative to gold at a number of photon energies. Our measurement finds that the addition of the diamondoid SAM increases the quantum yield significantly. The relative yield was found to be 1.27, 1.29, and 1.37 for 50, 75, and 100 eV incident photons, respectively. Because the diamondoid monolayer is too thin to interact with the photons significantly, this effect is likely caused by negative electron affinity effects. NEA systems have reduced work functions[5] and this results in an increase in the total photoelectron yield. Upon further measurement, the onset energy for the spectrum

appears to shift by about 1 eV when the SAM is present, and we take this to be the value of the work function reduction caused by the film.

We developed a Monte Carlo algorithm to probe the effectiveness of a phonon-scattering model as an explanation for the monochromatic peak seen in diamondoid SAMs. As initial assumptions, we asserted that the only relevant processes were inelastic electron-phonon scatting events and boundary processes such as reflection and refraction at the gold-diamondoid border. We assumed that the electrons had a free electron-like dispersion. We used the work function of gold as the band minimum energy for electrons in the gold. We used the measured measured value of -1.0 eV as the band minimum for the SAM. We assumed that all scattering events occurred at the same phonon energy, which was selected to be the most energetic phonon observed in the [121]tetramantane phonon spectrum, .36 eV[4]. The assumption that there is only one relevant phonon is almost certainly inaccurate, but the simulation results were found to be fairly insensitive to the exact value of the phonon energy so a single phonon was used for simplicity. Additionally, we made the assertion that once an electron's energy had fallen beneath this phonon energy, it was no longer capable of interacting at all. Finally, we assumed that the electron mean free path was constant at all electron energies, and we treated this as a free parameter.

The algorithm used to test this model used simple Monte Carlo transport techniques. The initial electrons were created with a random direction and a random energy, weighted by a realistic electron spectrum. This spectrum consisted of a secondary electron tail as described in Ref[12,13] and a valence electron peak. We simulated 50 eV incident photons in order to compare with our quantum yield data as well as with data from previous work[2].

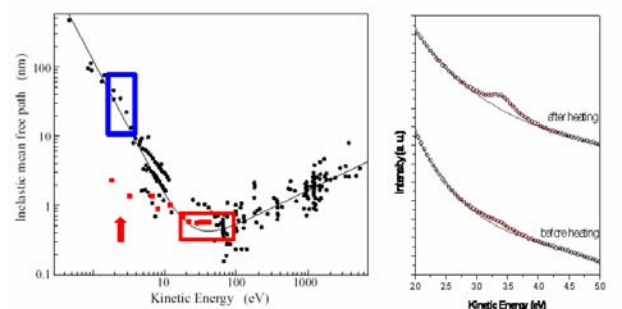The electrons were transported in steps through the

FIG. 2: Left panel: measured mean free path of electrons in Diamondoid SAMs (red squares) plotted against universal curve[10]. Right panel: spectrum of gold $4f7/2$ peak plotted before and after the SAM is removed by heating. The reduction in the peak intensity was used to determine the mean free path in the monolayer.

materials. Two basic processes were then taken into account: boundary processes and phonon scattering. Boundary processes were considered at the gold-SAM boundary. These included refraction, reflection off the gold back into the monolayer, and total internal reflection back into the gold. The angles and probabilities involved in these processes were solved by using a free electron wave function with the relevant band minima.

The scattering process was treated as simply as possible. The interaction length was determined using the mean free path and the Poisson distribution. When a scattering occurred, the direction of the electron was randomized, and the process was restarted. Electron tracks were terminated once it was determined that the electron had either escaped into the vacuum or returned into the gold. Electrons that escaped were counted and a virtual spectrum was created.

To place some reasonable constraints on the mean free path (λ) of the phonon-electron scattering, we simulated the gold $4f$ peak traveling through the film. We found that λ=.8 nm yielded approximately the same reduction in the $4f$ peak integral as was observed experimentally, so we believe this to be the optimum value. We believe that this parameter is strongly dependent on the quality of the individual film, however, so we performed the simulation with a number of different values of λ ranging from .4 nm to 1.3 nm.

The simulation was run for a range of λ values using 10^7 primary electrons. Figure 3 shows several simulated spectra. The simulation has successfully recreated the major feature of the observed spectrum shown in figure 1: a sharp, low energy peak with a FWHM of roughly .3 eV. Several different values of λ are shown. As the interaction length gets smaller, we see that the height of the peak increases dramatically. Assuming that λ is a function of the film quality, this explains why some films exhibited much stronger peaks than others. Specifically, it may explain why the effect appears much stronger in films grown on silver than in films grown on gold. The ratio of the peak integral to the total integral is listed in table I.

The quantum yield results are also shown in table I. The quantum yield is reduced as the mean free path is shortened because the increase in quantum yield is assumed to be caused entirely by work function reduction, which was assumed to be the same for all samples. Scattering within in the film can only reduce the yield, as no new electrons are generated. The 1 eV change in work function alone (without any scattering) produces a relative quantum yield of 2.00. Shorter values of λ result in more electrons being back-scattered into the gold, reducing the total observed yield. At the optimum value of λ, 0.8 nm, we found the quantum yield to be 1.25. This is in excellent agreement with the measured value of 1.27 at 50 eV photon energy. The discrepancy could easily be caused by a small inaccuracy in the measurement of the work function reduction, as the simulation is very sensitive to this value.

Mean Free Path (λ)	Peak Fraction	Rel. Quantum Yield
0.4	0.59	1.07
0.5	0.48	1.12
0.6	0.41	1.17
0.7	0.35	1.22
0.8	0.30	1.25
0.9	0.27	1.29
1.0	0.24	1.32
1.1	0.21	1.36
1.2	0.19	1.39
1.3	0.17	1.41

TABLE I: The fraction of the total counts found in the peak and the quantum yield relative to gold for the simulation at several different value of λ

Although the low energy peak is recreated successfully in the simulation, there are several noticeable differences between the measured and the simulated spectrum. First, the measured peak is quite a bit higher in intensity than the simulated one. This is probably because the experiments were performed with a sample to detector bias which increased the low-energy counts. Second, the shape of the electron tail at intermediate energies is noticeably different than the measured one. In the measured spectrum, the secondary electron peak is more heavily suppressed relative to the valence peak and appears broader than the simulation predicts. These differences are most likely due to the oversimplification of the model used in the simulation. The mean free path for phonon scattering was treated as constant, and electron-electron scattering was not considered at all. Both of these approximations would have an effect on the shape
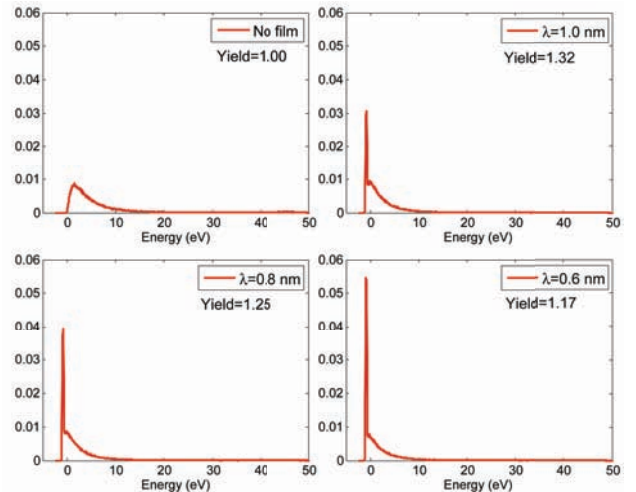

FIG. 3: Simulated photoemission spectra of tetramantanethiol SAMs on gold substrates for several values of mean free path (λ), along with total quantum yield for the spectrum relative to the bare gold surface.

of the spectrum at higher kinetic energies. Using a more accurate mean free path model and including electron-electron scattering will improve the simulation.

Despite these minor problems, however, the simulation successfully reproduced the major feature of the observed spectrum. The peak has the correct FWHM and is nearly the correct intensity in terms of integral counts. This demonstrates that phonon scattering with a short mean free path is sufficient to produce the strongly thermalized peak present in the data. Considering that the simulation models only a small number of highly simplified processes, the qualitative and quantitative agreement with experimental data are quite reasonable. This is a good indication that the assumptions made for the model are generally sound, and other processes do not contribute significantly to the generation of the sharp peak, which is the most interesting feature in the spectra.

In summary, through further analysis of the photoemission spectra of diamondoid SAMs we have been able to find several interesting new properties, including greater than unity quantum yield and an unusually short electron interaction length. Using these measurements we were able to create a simple phonon scattering model capable of reproducing the most interesting feature in the measured spectrum. While it would be better to include a more detailed description of the electron-phonon scattering process, even a simplified model was sufficient to reproduce the large, narrow, low energy peak which is observed in the data, as well as the increase in quantum yield. We therefore conclude that electron-phonon scattering combined with negative electron affinity is a feasible mechanism for producing the unusual spectra seen in these samples.

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