Probing Occupied States of the Molecular Layer in Au−Alkanedithiol−GaAs Diodes

Julia W. P. Hsu,*,† David V. Lang,‡ Kenneth W. West,‡ Yueh-Lin Loo,§ Mathew D. Halls,‖ and Krishnan Raghavachari‖

Sandia National Laboratories, Albuquerque, New Mexico 87185, Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974, Department of Chemical Engineering, University of Texas, Austin, Texas, and Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received: December 17, 2004; In Final Form: February 1, 2005

Internal photoemission (IPE) studies were performed on molecular diodes in which the alkanedithiol [$HS(CH_2)_nSH$, $n = 8, 10$] molecular layer is sandwiched between Au and GaAs electrodes. The results are compared to those from Au−GaAs Schottky diodes. An exponential energy dependence in the IPE yield was observed for the molecular diodes, in contrast to the quadratic energy dependence characteristic of metal−semiconductor Schottky diodes, indicating that Au is not the source of electrons in the IPE process in the molecular diodes. From the GaAs dopant density dependence, we also can rule out GaAs being the source of these electrons. Compared with the results of cluster electronic structure calculations, we suggest that IPE is probing the occupied levels of GaAs−molecular interfacial states.

Introduction

Integrating organic molecules with semiconductors opens up opportunities for new applications, e.g., bioengineering and sensing, which are difficult to achieve by either one alone.[1] On the fundamental side, the molecular layer could modify surface electronic properties of the semiconductor through inducing reconstruction[2] or creating an interfacial dipole layer.[3] Vice versa, the coupling with an electrode can broaden the molecular levels as well as create new interfacial states. The alignment between molecular levels in the organics and the bands in the semiconductor is an important question because it governs the electrical transport through the organic−inorganic interface. However, few techniques are able to probe a molecular layer when it is sandwiched between electrodes, as in real devices. In this paper, we report the results from internal photoemission experiments to probe the occupied levels of an alkanedithiol molecular layer sandwiched between metal (Au) and semiconductor (GaAs) electrodes. The results are referenced to Au−GaAs Schottky diodes and discussed in the framework of electronic structure calculations using a cluster model.

Internal photoemission (IPE) refers to absorption of photons that results in electronic transitions from the occupied states of a material (emitter) to the empty states of another (collector). The most common example is the excitation of an electron near the Fermi energy of a metal to the (unoccupied) conduction band of an adjacent semiconductor by absorbing a visible or infrared photon to overcome the energy barrier. This process is termed internal photoemission in analogy to standard photoemission where the transition is between occupied states of a material and the vacuum level. IPE is a powerful method to measure barrier heights (Φ) in metal−semiconductor Schottky diodes,[4] complementing the more commonly used current−voltage ($I-V$) and capacitance−voltage ($C-V$) techniques.

* Corresponding author. Phone: 1-505-284-1173. Fax: 1−505-844-1197. E-mail: jwhsu@sandia.gov.
† Sandia National Laboratories.
‡ Lucent Technologies.
§ University of Texas.
‖ Indiana University.

Compared to $I-V$, IPE signals are not dominated by the presence of a small fraction of low barrier regions so that the measured IPE barrier is more representative of the average barrier height across the diode. In $C-V$, the barrier height is obtained by extrapolating the band bending of the depletion layer to the junction interface and, therefore, can be overestimated.[5] In contrast, IPE directly measures the barrier height seen by the electrons when transporting across the metal−semiconductor interface. Furthermore, the energy distribution of the density of states (DOS) of the emitter is reflected in the energy dependence of the IPE spectrum.[6] In addition to measuring metal−semiconductor barrier heights, IPE has been used measure band alignment between metal or semiconductor electrodes and insulators[7] or organics.[8,9] In the current work, we have applied IPE on Au−alkanedithiol−GaAs diodes, with different dopant levels of GaAs substrates to distinguish the contribution of the molecular layer from that of the GaAs.

Experimental Section

Au−alkanedithiol−GaAs molecular diodes were fabricated by first forming a molecular layer (by vapor or solution deposition) on oxide stripped (using NH_4OH) GaAs wafers. While there is probably no in-plane order for these short-chain dithiol molecules, we have established that a substantial fraction of the molecules bonded to the GaAs surface have free thiol end groups pointing away from the GaAs surface to facilitate nanotransfer printing (nTP).[10] Surface treatment experiments as well as Fourier transform infrared spectroscopy and atomic force microscopy have been used to characterize the molecule-treated surfaces, and the results have been reported previously.[10,11] For the molecular diodes used in this experiment, the top Au electrodes were deposited using nTP. We have previously established that electrical shorting between Au and GaAs is minimized in nTP diodes compared to diodes with top Au contacts made by electron beam deposition.[11,12]

Molecular diodes are compared to control samples of Au−GaAs Schottky diodes, which were made by electron beam evaporation of Au on the same GaAs wafers (with native oxide

stripped using NH_4OH) as the molecular diodes. The electron beam deposition was performed in a vacuum chamber that has been evacuated to $(2-5) \times 10^{-7}$ Torr prior to deposition. For both types of diodes, the Au films were deposited at a rate of 10 Å/s and have a thickness of 15−20 nm. The top Au contact was kept thin to allow visible and infrared light to penetrate through. The samples (either PDMS or GaAs chips) were ∼30 cm away from the source in a direct line-of-sight configuration. The samples were not cooled and the temperature did not increase by more than 1 °C during the short deposition time.

Degenerately doped n^+ (001) GaAs wafers (Si-doped, 1.65×10^{18} cm^{-3}) were used directly for the 1E18 samples. For the lighter doped samples, a 1 μm epilayer of GaAs (10^{16} or 10^{17} cm^{-3}) was grown by molecular beam epitaxy onto the n^+ wafers. Dopant densities given here were measured by $C-V$ on Au−GaAs control diodes. The reason for using epilayers on n^+ substrates for lower dopant density samples is to minimize the resistance in the ohmic contact. The light source used in the IPE experiment was a tungsten halogen lamp through a grating monochromator (Jobin TRIAX 180) that was chopped at 250 Hz. The resulting photocurrent, measured between the Au and GaAs contacts of the sample at zero applied bias was first amplified by a current preamp and then detected with a lock-in amplifier to reduce noise and dark current. The monochromator output was calibrated using silicon and germanium photodiodes, and the measured photocurrent spectra were normalized by the incident photon flux to give the IPE yield.

Results and Discussion

The difference in IPE spectra between the Au−GaAs and the Au−octanedithol−GaAs diodes for GaAs with 10^{16} cm^{-3} Si concentration are depicted in Figure 1a, where the photo-response yield (Y), photocurrent per incident photon, is plotted in log scale as a function of photon energy (E_{ph}). The Au−GaAs control diodes (blue dotted curve in Figure 1a) show a quadratic energy dependence, i.e., Y is proportional to $(E_{ph} - \Phi)^2$, characteristic of metal−semiconductor Schottky diodes. This quadratic energy dependence is the direct consequence of the metal DOS being independent of energy[6] and is made explicit in Figure 1b, in which $\sqrt{Y}$ is plotted vs E_{ph} (Fowler plot). The 1E16 control diode displays a linear energy dependence in this plot (blue line in Figure 1b) with extrapolating $\sqrt{Y}$ to zero at $\Phi = 0.86$ eV, comparable to literature values of barrier heights for Au−GaAs Schottky diodes.[4] This value is also in excellent agreement with barrier height values obtained from $I-V$ (0.85 eV) and $C-V$ (0.82 eV). The barrier heights determined from IPE by extrapolating $\sqrt{Y}$ to zero are 0.82 and 0.76 eV for 1E17 and 1E18 control diodes, respectively, consistent with reduction of apparent barrier height due to image potential in highly doped semiconductors.[13] Another way to analyze the data and to see more explicitly whether there are more than one barrier height is to plot the first derivative of yield, dY/dE_{ph} vs E_{ph} (Figure 1c).[14] Our data show a linear dependence (blue line in Figure 1c) with a fitted value of $\Phi = 0.9$ eV. We do not observe any additional barrier height that might signal a heterogeneous interface.[14]

In contrast, the IPE spectra of molecular diodes cannot be described by a quadratic energy dependence. This can be explicitly seen in the $\sqrt{Y}$ vs E_{ph} plot in Figure 1b. Instead, the molecular diode (red curve in Figure 1a) shows an exponential E dependence (black line), $\exp(E/E_0)$, in the IPE yield, where E_0 is the characteristic energy. This E dependence is drastically different from that observed in Au−GaAs control diodes, indicating that Au is not the emitter in these molecular diodes.
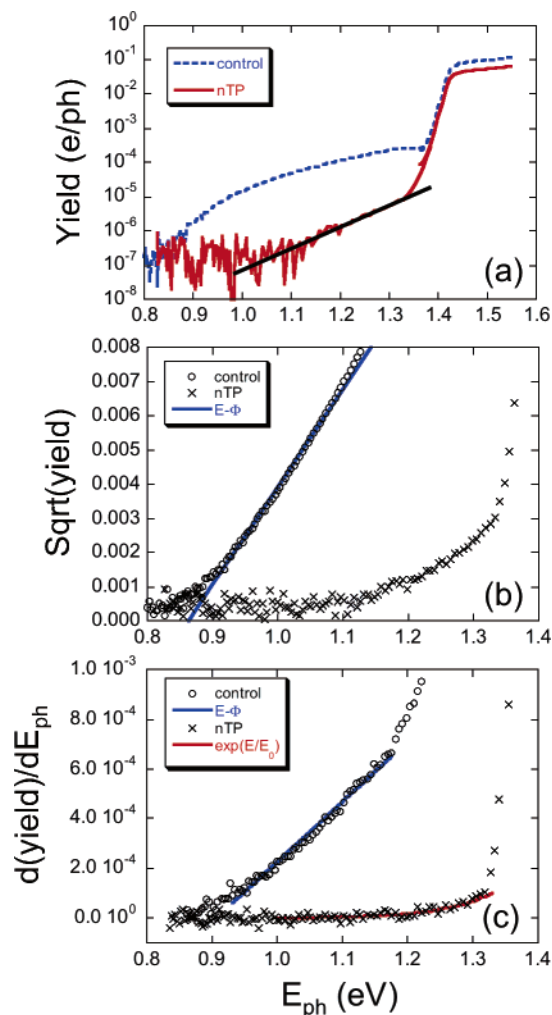

Figure 1. (a) Internal photoemission yield (Y), defined as electron per incident photon, plotted in logarithmic scale as a function of photon energy (E_{ph}). The solid red curve represents a Au−octandithol−GaAs molecular diode with nanotransfer printed Au contacts. The dotted blue curve represents a Au−GaAs Schottky diode. The dopant density of the GaAs was 1×10^{16} cm^{-3}. The black line is an exponential fit to the molecular diode. (b) The $\sqrt{Y}$ data (same data as in a) are plotted vs E_{ph} to explicitly show the quadratic energy dependence characteristic of the metal−semiconductor Schottky diode and that the molecular diode does not display this energy dependence. The barrier height obtained by extrapolating $\sqrt{Y}$ to zero (blue line) is 0.86 eV. (c) dY/dE are plotted vs E_{ph} as suggested in ref 14. The data have been smoothed to reduce noise in the dY/dE plot. The blue line is a linear of fit to the control diode near threshold, yielding 0.9 eV barrier height. The red line is the derivative of the exponential fit to the molecular diode data in a (see text).

If the emitter were Au, the IPE yield would have a quadratic energy dependence with a lower yield due to the reduced transmission from tunneling through the insulating molecular layer. dY/dE of the molecular diode data show a very small energy dependence below the GaAs band gap. To show that this dependence is consistent with the exponential yield, the red line in Figure 1c is the derivative of the fitted values to the molecular diode data (black line in Figure 1a). Thus, the E dependence of the molecular diode yield is exponential; however, the prefactor is small so that dY/dE does not show a strong energy dependence in this energy range. Our results are distinctly different from a recent report of two barrier heights observed in Au−dicarboxylic molecules−GaAs diodes on 1E16 GaAs.[15] We did not observe any obvious indication of multiple barrier heights in either control or nTP diodes.
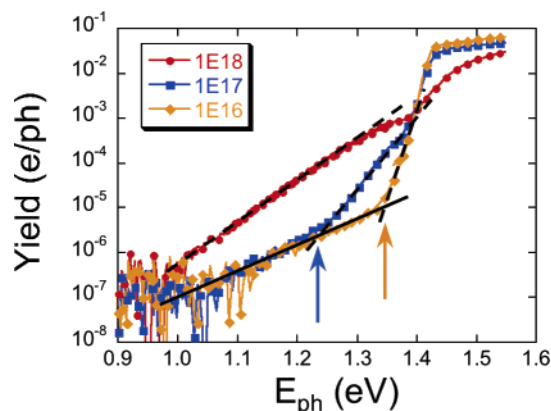
Figure 2. Dopant density dependence of IPE yield. The red curve represents the 1.65×10^{18} cm^{-3} (1E18) sample, the blue curve represents the 1×10^{17} cm^{-3} (1E17) sample, and the orange curve represents the 1×10^{16} cm^{-3} (1E16) sample. All three samples show an exponential behavior (dahsed lines), $\exp(E/E_0)$, below band gap (1.4 eV). For the 1E18 sample, the exponential energy dependence of IPE yield has $E_0 = 47$ meV. For the 1E17 and 1E16 samples, a second exponential energy dependence (solid line) of IPE yield occurs at lower energy (marked by arrows) with $E_0 = 67$ meV.
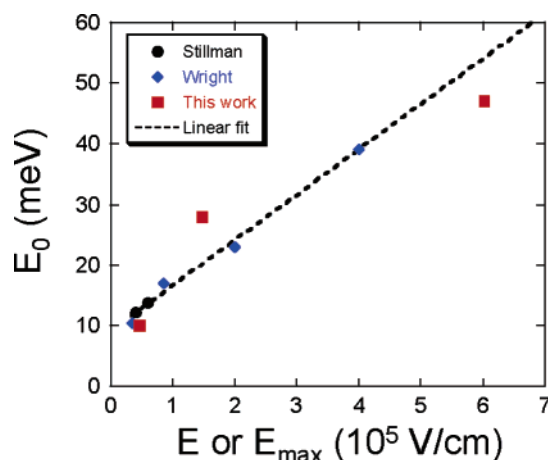
Figure 3. E_0 as a function of applied electric field (E, from refs 18 and 19) or maximum electric field (E_{max}) in the depletion region (this work). The dotted line is a linear fit to all data.

Exponential tails below band gap have been observed in the optical absorption spectra of semiconductors. This tail is more pronounced in higher dopant density materials[16] and when the semiconductor is subjected to a high electric field.[17] Since the electric field could be high in the depletion region and be the source of the exponential dependence of IPE yield, we made molecular diodes on GaAs with different dopant densities to separate the contribution of the molecular layer from that of the GaAs. Figure 2 shows Y vs E_{ph} for molecular electrodes with 1.65×10^{18} cm^{-3} (red circles), 10^{17} cm^{-3} (blue squares), and 10^{16} cm^{-3} (orange diamonds) Si dopant densities. As the dopant density decreases, the slope of the exponential dependence (dashed lines) near the GaAs band gap (1.42 eV) increases; i.e., E_0 decreases. Taking the built-in voltage to be 1 V, we can calculate the maximum electric field (E_{max}) in the depletion region for the three samples. In Figure 3, the values of E_0 determined from the dashed lines in Figure 2 are plotted as a function of E_{max}, along with E_0 reported in the literature for GaAs in electric fields.[18,19] The agreement between our results and those reported in the literature establishes that the broadening of the IPE spectra just below the GaAs band gap arises from the band tailing effect of the GaAs valence band.[16] In particular, this effect dominates the IPE spectrum over the
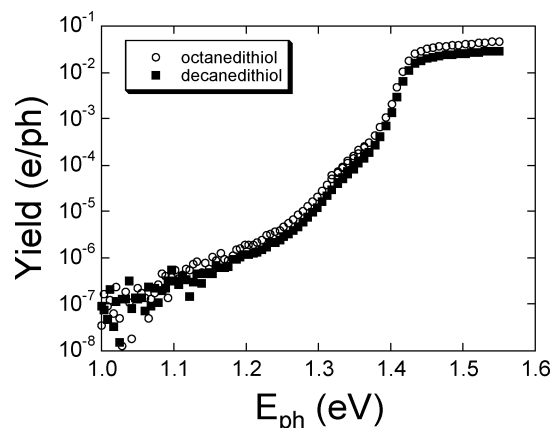
Figure 4. Y vs E_{ph} for octanedithiol and decanedithiol molecular diodes made on 1E17 GaAs.

entire photon energy range covered in this experiment for the 1E18 sample, which shows the exponential behavior over $3^1/_2$ decades in IPE yield with $E_0 = 47$ meV.

However, for the lower dopant density samples, at lower photon energies (<1.35 eV for the 1E16 sample and <1.23 eV for the 1E17 sample), an abrupt change in slope was observed (marked with arrows in Figure 2). Below this energy, another exponential IPE behavior is observed with $E_0 = 67 \pm 4$ meV (solid line in Figure 2). Most significantly, this exponential behavior is independent of GaAs dopant density, indicating that the source of electrons in this IPE regime is not GaAs. We already know that Au is not the emitter in these molecular diodes. Thus, the source of these IPE electrons must be the occupied levels of the molecules or the GaAs−molecular interfacial states.[20] In this case, the exponential dependence would indicate that these interfacial states have an exponential distribution, with E_0 reflecting the width of the distribution.[6] In the self-assembly of alkanethiol on Au, it is known that monolayers of molecules with less than 12 methylene units are highly disordered.[21] Given that octanedithiol has only eight methylene units and two reactive ends, it is reasonable that the octanedithiol layer contains a lot of disorder, resulting in DOS with an exponential distribution. The molecular contribution in the 1E18 sample is masked by the band tailing contribution from the high field space-charge region.

We have studied the length dependence by performing IPE experiments on two commercially available dithiol molecules: octanedithiol and decanedithiol.[22] Figure 4 shows the Y vs E_{ph} dependence for molecular diodes made from the two molecules on 1E17 GaAs. They show the same energy dependence with decanedithiol displaying a yield smaller by approximately a factor of 2. This result suggests the disorder still dominates in decanedithiol molecular diodes. The reduction in the yield probably arises from the longer tunneling length across the molecular layer in longer chain molecular diodes.

Quantum Chemical Calculations

Since the emitter DOS has an exponential distribution, the absolute position of these states cannot be obtained from IPE, unlike the case of Schottky diodes where a barrier height can be determined.[6] However, because an appreciable signal is measured for photon energy of ∼1 eV, there exist occupied states within 1 eV below the GaAs conduction band. To lend critical insight for the interpretation of our IPE observations, quantum chemical calculations were carried out using the B3LYP hybrid density functional,[23,24] along with the 6-31+G* basis set.[25] The calculations were carried out using the Gaussian

5722 *J. Phys. Chem. B, Vol. 109, No. 12, 2005*

Hsu et al.
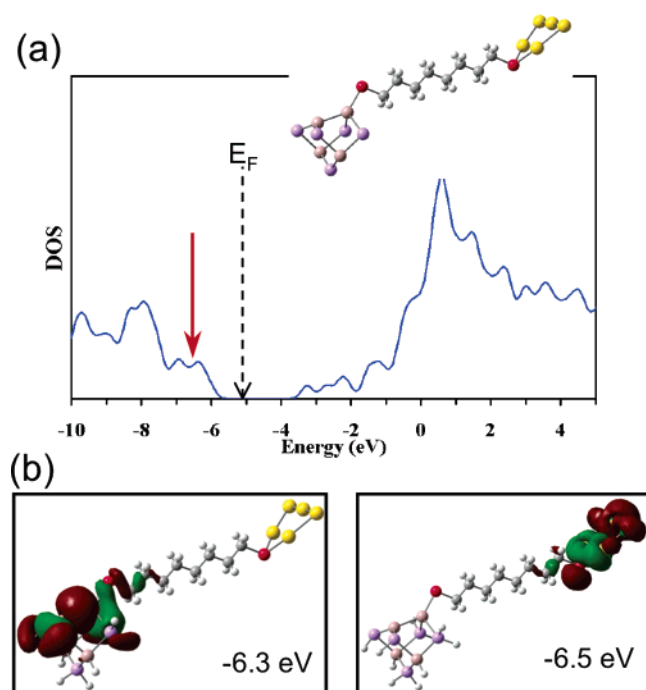
Figure 5. (a) Electronic DOS vs *E*. The Au work function is marked as E_F by the dashed arrow. Also shown is the $Au_5-C_8H_{16}S_2-Ga_4As_5H_{10}$ cluster model used in this work. Red balls denote S. (The DOS plot was generated from the electronic structure using a Gaussian line shape with a full width at half-maximum of 0.4 eV.) (b) Isoelectronic density surfaces (0.02 e au^{-3}) at the energy position marked by the red arrow in *a* for representative interface coupling orbitals at −6.3 eV (left) and −6.5 eV (right). Green and red represent regions of positive and negative amplitude, respectively.

suite of programs.[26] A model of the Au−octanedithiol−GaAs interface was used, representing the Au and GaAs surfaces as truncated clusters. Dangling bonds that would have been generated by excision of the cluster model from the extended interface were terminated using hydrogen atoms, giving a final stoichiometry of $Au_5-C_8H_{16}S_2-Ga_4As_5H_{10}$.[27] Though small, the cluster model used contains a proper balance between covalent and dative bonds appropriate for a compound semiconductor such as GaAs.[28,29] The interface cluster model is illustrated in the Figure 5a inset. Various binding modes to gold were explored,[27] with the minimum energy configuration having a S bonded to two Au atoms at a bridge site, consistent with other studies.[30]

At the optimized geometry, the electronic structure was calculated. The electronic DOS is shown in Figure 5a. Using our model, the lowest unoccupied molecular orbital (LUMO) is found at −3.2 eV and is mostly localized on the Au cluster with a small component extending onto the alkanethiol layer, and similarly the highest occupied molecular orbital (HOMO) is at −6.1 eV and is mostly localized on the GaAs cluster, again with a minor amplitude on the molecular bridge. Although these localized orbitals most likely contribute little to electric transport and may show some sensitivity to cluster model size, more delocalized orbitals which extend across the interface are calculated to lie just slightly below the HOMO (indicated by the red arrow in Figure 5a) composed of contributions from the alkanethiol and surface cluster models, which are more physically characteristic of the molecular bridge/surface interface giving rise to transport. Figure 5b shows the orbital at −6.3 eV which covers part of the GaAs cluster and extends into the alkane backbone. Similarly, the one at −6.5 eV overlaps the Au and the molecule. We take the Fermi level (EF) as the Au

work function at −5.2 eV. For a 0.9 eV Schottky barrier height (as obtained from experimental data), the GaAs conduction band is at −4.3 eV. The difference between the calculated occupied levels at −6.1 to −6.5 eV and the GaAs conduction band is ∼2 eV. It is then possible for an electron to transition to the GaAs conduction band from the high-energy tails of the occupied orbitals by absorbing a photon. In particular, we believe that most of the contribution would come from GaAs− molecular interfacial states because electrons originating from the Au−molecular interfacial states would have to tunnel through the molecules and thus would have a much smaller contribution to the IPE yield.

Conclusions

We have performed IPE measurements on Au−alkanedithiol− GaAs diodes and compared them to Au−GaAs Schottky diodes. The dopant density of the GaAs electrode has been varied to separate out the contribution of the molecular interface from that of the GaAs band tail. The molecular diodes show an exponential dependence in the IPE yield that does not come from Au or GaAs. The most likely origin of these electrons is the occupied levels of the GaAs−molecular interfacial states.

References and Notes

(1) Likharev, K. *Ind. Phys.* **2003**, *9*, 20.
(2) See for example: Bent, S. F. *J Phys. Chem B* **2002**, *106*, 2830.
(3) Vilan, A.; Shanzer, A.; Cahen, D. *Nature* **2000**, *404,* 166.
(4) Sze, S. M. Metal-Semiconductor Contacts. *Physics of Semiconductor Devices,* 2nd ed.; Wiley: New York, 1981; Ch. 5, p 288.
(5) Chen, L. C.; Caldwell, D. A.; Finstad, T. G.; Palmstrom, C. J. *J. Vac. Sci. Technol., A* **1999**, *17*, 1307.
(6) Powell, R. J. *J. Appl. Phys.* **1970**, *41*, 2424.
(7) Afanas'ev, V. V.; Houssa, M.; Stesmans, A.; Heyns, M. M. *Appl. Phys. Lett.* **2001**, *78*, 3073.
(8) Campbell, I. H.; Smith, D. L. *Appl. Phys. Lett.* **1999**, *74*, 561.
(9) Vuillaume, D.; Boulas, C.; Collet, J.; Allan, G.; Delerue, C. *Phys. Rev. B* **1998**, *58*, 16491.
(10) Loo, Y.-L.; Hsu, J. W. P.; Willett, R. L.; Baldwin, K. W.; West, K. W.; Rogers, J. A. *J. Vac. Sci. Technol., B* **2002**, *20*, 2853.
(11) Hsu, J. W. P.; Loo, Y.-L.; Lang, D. V.; Rogers, J. A. *J. Vac. Sci. Technol., B* **2003**, *21*, 1928.
(12) Loo, Y.-L.; Lang, D. V.; Rogers, J. A.; Hsu, J. W. P. *Nano Lett.* **2003**, *3*, 913.
(13) Anderson, C. L.; Crowell, C. R.; Kao, T. W. *Solid-State Electron.* **1975**, *18*, 705.
(14) Okumura, T.; Tu, K. N. *J. Appl. Phys.* **1983**, *54*, 922.
(15) Haick, H.; Ambrico, M.; Ligonzo, T.; Cahen, D. *Adv. Mater.* **2004**, *16*, 2146.
(16) Pankove, J. I. *Phys. Rev.* **1965**, *140*, A2059.
(17) Paige, E. G. S.; Rees, H. D. *Phys. Rev. Lett.* **1966**, *16*, 444.
(18) Stillman, G. E.; Wolfe, C. M.; Bozler, C. O.; Rossi, J. A. *Appl Phys. Lett.* **1976**, *28*, 544.
(19) Wright, D. R.; Heaton, J. M.; Keir, A. M.; Norcross, R. J.; Pryce, G. J.; Wright, P. J.; Birbeck, J. C. H. *IEE Proc.* **1988**, *135*, 39.
(20) We note that the values of this exponential tail are large for a molecular layer of 10−30 Å.
(21) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
(22) Nonadithiol was not compared to avoid the complication of "odd− even" effect.
(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(24) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(25) Hehre, W. J.; Ditchfield, R.; Pople, J. *J. Chem. Phys.* **1972**, *56*, 2257.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *Gaussian 03*, Revision B.2; Gaussian, Inc.: Pittsburgh, PA, 2003.

(27) Calculations were carried out representing the Au surface with clusters of varying stoichiometry to determine the local bonding characteristics of the interface. In particular, the bonding between S and the corner, edge, and face sites of the gold surface was investigated for Au_n, $n = 5-13$. For all clusters considered, edge sites corresponding to a dicoordinate bridging attachment of S to two Au atoms were found to be the most stable geometrical arrangement. The electronic structure depends only weakly on the size of the gold cluster, though substantially larger clusters will be needed to get the full metallic band structure of gold.

(28) Fu, Q.; Negro, E.; Chen, G.; Law, D. C.; Li, C. H.; Hicks, R. F.; Raghavachari, K. *Phys. Rev. B* **2002**, *65*, 075318.

(29) Raghavachari, K.; Hicks, R. F.; Fu, Q.; Chen, G.; Li, L.; Li , C. H.; Law, D. C. *J. Am. Chem. Soc.* **2002**, *124*, 15119.

(30) See for example: Basch, H.; Ratner, M. A. *J. Chem. Phys.* **2003**, *119*, 11926.