

## Interaction of vapor-deposited Ti and Au with molecular wires

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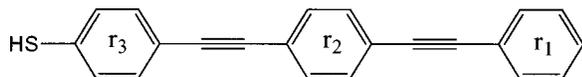
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We have investigated the interaction of vapor-deposited titanium and gold with a self-assembled monolayer (SAM) of 4-[4'-(phenylethynyl)-phenylethynyl]-benzethiol, an unsubstituted oligo(phenylene-ethynylene), chemisorbed on a gold substrate, a typical SAM of interest for molecular electronics. Deposited titanium atoms are observed to react in a top-down fashion with the SAM molecules to form Ti–C bonds, destroying the monolayer structure. In contrast, deposited Au atoms undergo continuous penetration through the monolayer, even at high coverages, leaving the SAM “floating” on the Au substrate surface. © 2004 American Institute of Physics.

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The use of molecules as active components in electronic devices has become of considerable experimental and theoretical interest recently.<sup>1,2</sup> Many molecule-based device behaviors have been demonstrated.<sup>3–9</sup> Significant device-to-device variation, however, has been observed<sup>7</sup> and general issues have arisen related to the critical details of the molecule–electrode integrity and bonding, and their relationship to device behavior.<sup>10</sup> A typical size-scalable device is prepared by self-assembling molecules on a lithographically fabricated bottom contact, typically gold, and then depositing a top metal contact using thermal evaporation.<sup>7</sup> The top contact metal can vary widely from reactive metals, such as titanium, to inert metals, such as gold, but given the current lack of fundamental data on the complexities of the interfacial chemistry and nucleated metal morphologies the choices of metal and related deposition conditions for optimizing a given type of molecule and device remain highly problematic.

This letter reports on a study of the interaction of vapor-deposited titanium and gold with well-ordered self-assembled monolayers (SAMs) of 4-[4'-(phenylethynyl)-phenylethynyl]-benzethiol (OPE; chart 1, note labels for ring identification), the three ring member of the oligo-phenylene-ethynylene family of “molecular wires,” chemisorbed on Au.



OPE monolayers have been demonstrated to have rectifying behavior<sup>5</sup> and also to form the backbone of molecules that demonstrate negative differential resistance behavior.<sup>7,8</sup>

Titanium is used in microelectronics as an adhesion-promoting layer<sup>11</sup> and in ohmic contacts,<sup>12</sup> and also in molecular electronics.<sup>3,4</sup> Studies of the interaction of vapor-deposited titanium with both polymeric films and SAMs<sup>11–15</sup> have demonstrated that Ti reacts with both the carbon backbone and the functional groups of these molecules. Gold is

also used as an ohmic contact in microelectronics<sup>16</sup> and molecular electronics.<sup>6–8</sup> Many studies of the interaction of vapor-deposited gold with polymeric films and functionalized alkanethiolate/Au SAMs have indicated that the Au atoms diffuse through these layers,<sup>17–21</sup> although deposited Au forms a sharp interface with the organic semiconductor 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA).<sup>22</sup>

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) analyses were performed on a custom instrument as described previously.<sup>23</sup> The primary Ga<sup>+</sup> ions were accelerated to 15 keV and contained in a 100 nm diameter probe beam rastered over a (106×106) μm<sup>2</sup> area during data acquisition. All spectra were acquired using a total ion dose of less than 10<sup>11</sup> ions cm<sup>-2</sup>. Relative peak intensities are reproducible to within ±8% from sample to sample and scan to scan. Infrared reflection spectroscopy (IRS) was performed on a Fourier transform instrument (Mattson Research Series 1000) modified for grazing incidence reflection from samples under vacuum.<sup>24</sup> A liquid nitrogen cooled MCT detector was used with an effective low frequency cutoff of ~750 cm<sup>-1</sup>.

The preparation and characterization of the SAMs used has been described in detail in Ref. 24. All metals used were

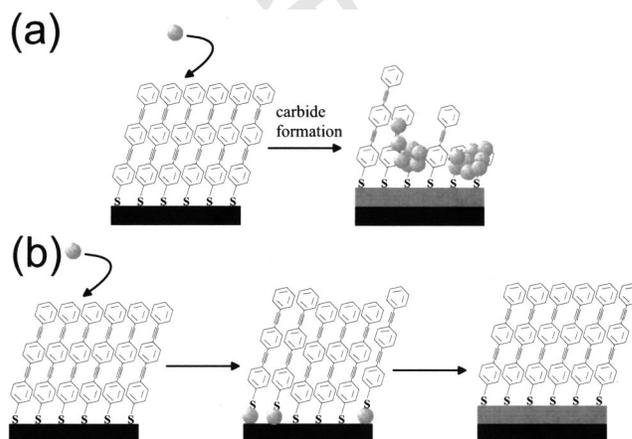


FIG. 1. Schematic diagrams of the interaction of the vapor deposited (a) Ti and (b) Au with the OPE monolayer.

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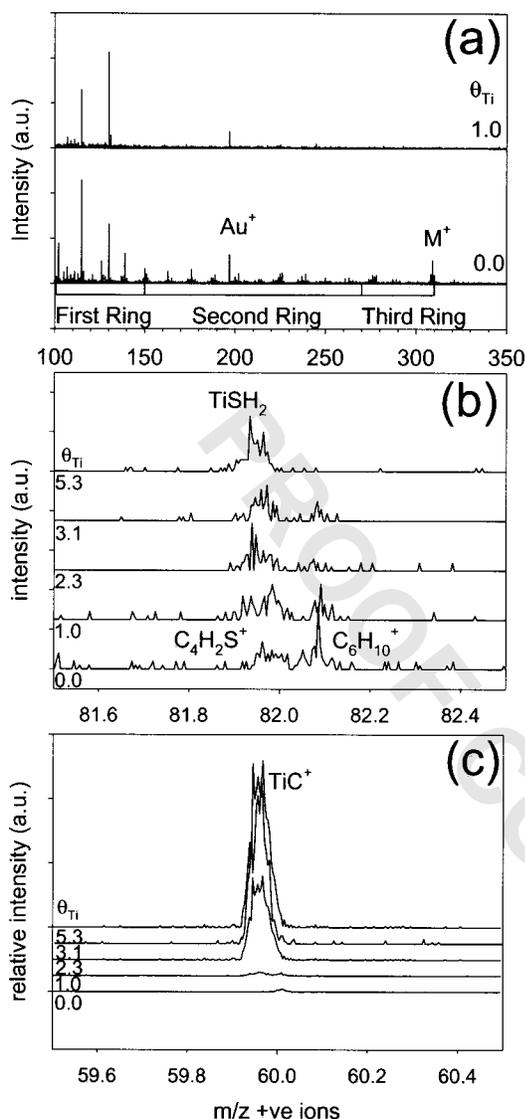


FIG. 2. TOF SIMS positive ion mass spectra: (a) 100–350 Da, of the bare OPE monolayer and upon deposition of  $\theta_{\text{Ti}}=1.2$  Ti atoms/SAM monolayer; and high resolution mass spectra of (b)  $\text{TiSH}_2^+$ , nominal mass 82, and (c)  $\text{TiC}^+$ , nominal mass 60.

of  $\geq 99.99\%$  purity (Goodfellow, Alfa Aesar, Sigma Aldrich). The metals were evaporated *in situ* from a W-wire basket at a rate of  $\sim 0.15$  atoms  $\text{nm}^{-2} \text{s}^{-1}$  onto a room temperature sample and monitored by a quartz crystal microbalance. The deposited amounts were converted to metal atom coverage per SAM molecule,  $\theta_M$  ( $M=\text{Ti}$  and  $\text{Au}$ ), assuming a sticking probability of unity. The SAM molecular density is  $4.5$  molecules  $\text{nm}^{-2}$  in a well-formed arenethiolate/Au SAM.<sup>24–26</sup>

Most of the information in the SIMS spectra is found in the positive ion mass spectrum. The molecular adsorbate ions,  $M^+$  and  $(\text{Au}+M)^+$  ( $M=\text{OPE}$ ), are observed at  $m/z=309$  and  $506$ , respectively. Other common fragments observed include  $\text{C}_2\text{H}_2^+$ ,  $\text{C}_4\text{H}_4^+$ , and other hydrocarbon ions directly related to the OPE molecule. The IR modes of the bare OPE monolayer have been characterized previously.<sup>24</sup>

A schematic diagram of the reaction of Ti with the OPE monolayer is shown in Fig. 1(a). Upon deposition of titanium, there are marked changes in both the positive ion mass [Fig. 2(a)] and IR spectra (Fig. 3) that indicate strong chemical reactions with ring degradation. At  $\theta_{\text{Ti}}\sim 1$  the ions that

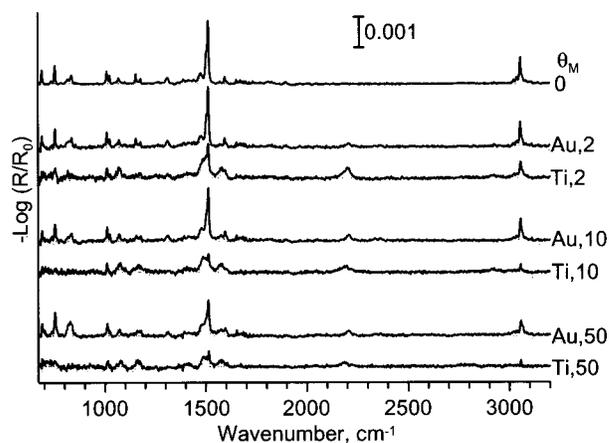


FIG. 3. Low and high frequency region IRS of the bare OPE monolayer and upon Ti and Au deposition.

are chiefly observed are  $\text{C}_4\text{H}_4^+$  ( $m/z=52$  Da) and those associated with a single phenyl ring [Fig. 2(a)] indicating degradation of the SAM molecules, while the appearance of  $\text{TiC}^+$  ions [Fig. 2(c)] indicates that titanium carbide forms.<sup>14</sup> This agrees with the IR observation of rapid attenuation with increasing  $\theta_{\text{Ti}}$  of the C–H and C=C stretching mode intensities ( $\sim 1500$  and  $3050$   $\text{cm}^{-1}$ , respectively). Note that the intensities of the out-of-plane bending modes of phenyl rings  $r_1$  and  $r_2$  ( $690$ ,  $837$ ,  $1026$ , and  $1150$   $\text{cm}^{-1}$ ) decrease faster relative to the  $r_3$  modes ( $1011$  and  $1179$   $\text{cm}^{-1}$ ) showing that Ti initially attacks the rings nearest the vacuum interface. By  $\theta_{\text{Ti}}=50$ , the  $r_1$  and  $r_2$  C–H bending intensities are reduced to background level; in contrast the modes associated with  $r_3$  remain discernable. Finally, the activation of the C $\equiv$ C stretch modes at  $\sim 2200$   $\text{cm}^{-1}$ , which are optically inactive in the pure SAM because of the high local symmetry, with the onset of Ti deposition confirms strong OPE-Ti interactions.

Furthermore, we observe the formation of  $\text{TiSH}_2^+$  fragment ions, which indicates that Ti atoms penetrate to the Au/S interface [Fig. 2(b)]. We note that while the masses of  $\text{TiSH}_2^+$  ( $81.936$  Da) and  $\text{C}_4\text{H}_2\text{S}^+$  ( $81.988$  Da) are very close [Fig. 2(b)] they are fully resolved by our ToF SIMS instrument. Furthermore, we observe that the ion intensity increases relative to that of  $\text{C}_6\text{H}_{10}^+$  upon deposition of Ti; this would not be the case if the ion were  $\text{C}_4\text{H}_2\text{S}^+$ . Given the vigorous reaction of the Ti with the OPE molecules, particularly at the topmost ring ( $r_1$ ), the penetration appears to be the result of partial etching away of portions of the monolayer.

In contrast to Ti, deposited Au has almost no effect except penetration through the SAM with an accompanying roughening of the substrate, as depicted in Fig. 1(b). The lack of metal overlayer formation is indicated by the approximately constant intensity of the OPE molecular ion signal, even up to  $\theta_{\text{Au}}\sim 14$  (Fig. 4). Even after depositing  $\sim 214$  Au atoms/SAM molecule, the molecular ion,  $M^+$ , is still observed indicating that there is little or no metallic overlayer formation. In agreement with the TOF SIMS data, significant deposition is required before noticeable changes arise in the IR spectra (Fig. 3). The main changes of note are an intensity increase in the C–H ring out-of-plane deformation ( $\sim 828$   $\text{cm}^{-1}$ )<sup>24</sup> at high coverages, the onset of slight

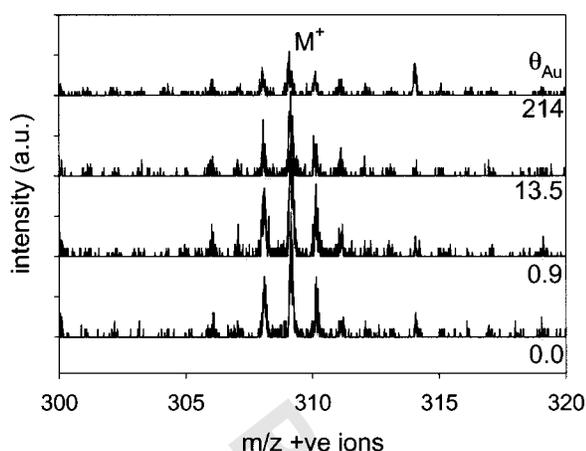


FIG. 4. High resolution SIMS spectral overlays of the molecular ion  $M^+$ , nominal mass 309.

optical activity for the  $C\equiv C$  stretch ( $\sim 2200\text{ cm}^{-1}$ ) approaching  $\theta_{Au}=10$  (indicating some breaking of local  $C\equiv C$  symmetry) and a slow decline of the  $C-H$  aryl stretching mode peak intensity. From these combined observations we conclude that the OPE monolayer coverage is intact but the molecules undergo some degree of orientational and translational disordering, consistent with the roughening of the growing Au underlayer as Au atom penetration continues. It should be noted that the metal atom penetration occurs despite the fact that the initial monolayers are highly self-organized and exhibit a well-ordered molecular superlattice.<sup>24</sup>

The present results show that the use of vapor-deposited titanium and gold contacts, even on well ordered SAMs, is highly problematic for formation of *reliable* device contacts. Titanium reacts top down with the organic film to form progressively thicker carbidic layers, degrading the molecule to produce complex interfaces. Experiments are underway to perform depositions onto SAMs cooled to cryogenic temperatures to check for temperature thresholds for carbide formation. While low temperatures should initially suppress degradation, it is of interest to see if upon warming reaction the Ti starts to degrade the interface. In contrast, while room temperature vapor-deposited Au does not react, it does penetrate readily through the well-packed OPE monolayer. This result could lead to a highly incomplete and nonoperational top contact as well as shorting paths to the bottom electrode. At sufficiently high deposition rates ( $\gg 1\text{ \AA s}^{-1}$ ) it is possible to deposit a Au molecular overlayer, but over time, and especially under electrical bias, this layer is likely unstable with respect to transport of gold atoms through the SAM, as evidenced, for example, by the formation of Au “stalagmites”<sup>6</sup> and preliminary results in our laboratories.

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