

Ultrasmooth Gold as a Top Metal Electrode for Molecular Electronic Devices

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In the emerging area of molecular electronics, fabrication of reliable metallic contacts remains one of the most critical challenges. Nanotransfer printing (nTP) is an attractive low-cost non-destructive technique to provide contact to organic monolayers. This work introduces the use of ultrasmooth gold on polymeric substrates, fabricated by using an nTP-based method, as a novel means to form metal-molecule-silicon molecular electronic test structures. We have used self-assembly to fabricate high-quality COOH-terminated alkanethiols on ultrasmooth gold. Covalent bonding to the H-Si(111) substrate was achieved through the application of moderate pressure and temperature. Because of the critical role of molecular conformation on electrical properties, infrared spectroscopy was used to explore the influence of these two parameters (P,T) on molecular ordering. Moderate conditions effectively fabricate high-quality reproducible molecular electronic test structures preserving molecular conformation with molecules bonded to both electrodes. This work proves a useful strategy for the development of hybrid nanoelectronic devices.

Introduction

Utilizing molecule-semiconductor hybrid devices has been identified by the semiconductor industry as an emerging research area for potential next-generation memory and logic devices. Molecules offer advanced functionality since they have the potential to store charge by altering their molecular conformation or alter polarization within the realm of spintronics. Moreover, molecular electronic devices based on silicon can capitalize on the extensive Si-device technology fabrication expertise to fabricate molecule-based devices that are embedded on the chip along with conventional electronic devices. This advantage reduces development time and also speeds integration of molecule-based devices with conventional CMOS technology.

Advances in the field of molecular electronics depend not only on the discovery of novel chemical species with interesting electronic properties but also on their connection

to the electrodes in molecular devices. Actually, this is the greatest challenge to molecular state electronics. Instead of the idealized metal-molecule-substrate sandwich structure, often conventional metal evaporation methods will damage, penetrate through, or even displace the molecular monolayers directly attached to Si resulting in the metal artifacts dominating the electrical response (1-4). Nanotransfer printing (nTP) is a soft-lithography technique which is attracting attention as a low cost method for printing nanometer-scale geometries. This technique is especially promising for fabrication requirements involving nonplanar substrate patterning, invasive processing, or large area patterning (5, 6). Briefly, nTP consists of transferring material from one substrate to another utilizing differential adhesion as a driving force. To contact organic molecular materials, surface chemistry provides a means for promoting a strong interaction between the metal and the monolayer. Because of the high affinity between Au and sulfur, thiols are commonly utilized to attach thiol-terminated molecules to a Au surface (7, 8).

Thiol-containing molecules have been demonstrated to create high-quality monolayers bonded to gold, due in part to the ability of the molecules to diffuse on the surface maximizing intermolecular interactions. In contrast, the silicon surface forms quite strong covalent bonds, essentially cutting off surface diffusion of bonded molecules, making the formation of high quality monolayers challenging (9). During the nTP formation of Si/molecule/metal molecular junctions, substrate surface quality (10, 11) and external factors such as pressure (12, 13) or temperature (14-16) could modify the conformation of the monolayer and therefore can be critical for the consequent electrical properties of molecular electronic test structures. Thus, it is important to develop effective methods to prepare and characterize monolayers on the electrode surfaces. Polarized backside-reflection absorption infrared spectroscopy (pb-RAIRS) has been shown as an effective technique to characterize the organic monolayers directly bonded to silicon under thick metal electrodes (1, 17).

In this study we demonstrate the use of ultra-smooth nanolaminated gold films on plastic substrates (uS-Au/PET) as top metal electrodes for molecular electronic devices in which the organic monolayer is bonded to both Au and Si. High-quality self-assembled monolayers are first formed on ultrasmooth gold films and then bonding to the H-terminated silicon surface is achieved through applied pressure and temperature. We demonstrate that the formation of molecular junctions only occurs when bifunctional monolayers are utilized. In particular, we have investigated 16-mercaptohexadecanoic acid (MHDA), a long-chain alkane thiol containing a carboxylic acid head group capable of bonding to the H-Si(111) surface. The effects of temperature and mechanical compression on molecular conformation were examined. The monolayers were characterized prior to formation of the sandwich structure by using infrared spectroscopy (IRS), spectroscopic ellipsometry (SE), and atomic force microscopy (AFM). Following formation of the nanolaminated metal-molecule-silicon structure, pb-RAIRS was used to characterize molecular conformation within these molecular electronic test structures.

Experimental

Preparation and characterization of MHDA monolayers

MHDA monolayers were prepared on an ultrasmooth gold film that was previously transfer printed onto a polyethylene terephthalate (PET) substrate. These uS-Au/PET substrates were first fabricated by vapor-evaporation of 200 nm of Au on a silicon substrate previously treated with a fluorinated-release layer. This Au thin film was then transfer printed onto a PET substrate by applying pressure and temperature resulting in the ultrasmooth gold substrate (Au/PET). Detailed description of the preparation of these substrates is described elsewhere (18, 19). Immediately prior to immersion, the substrates were first cleaned by using a 10-min UV-ozone cleaner (UVO) and subsequently rinsed with anhydrous ethanol. MHDA was deposited by immersion in a 1 mmol/L anhydrous ethanol solution overnight. Upon removal, samples were rinsed with 2 mol/L HCl to remove physisorbed contaminants and ensure the formation of an acid-terminated single monolayer. Reference samples were created by fabricating octadecanethiol (ODT) monolayers on nanolaminated gold substrates.

Surface morphology of the ultrasmooth gold substrate was examined by using a commercial AFM instrument with a deflection-type scanning head. Tapping mode images were acquired in air using Si ultrasharp tips. The hydrophobicity of the terminal group of alkanethiol was measured by water contact angle (CA) at 20 °C under ambient atmosphere. A drop of deionized water (18 M Ω cm) was put on each monolayer. All contact angles reported are the contact angle of an advancing water drop. The reported value is the average of three measurements of at least triplicate measurements taken at different positions of the substrate. The thickness of the molecular film was obtained by means of SE at an angle of incidence of 75°. The dielectric constant of Au was determined by assuming the ODT film thickness was 2.3 nm. The thickness of MHDA was determined by using a simple three phase Air/organic($n=1.5$)/Au model.

Reflection absorption infrared spectra (RAIRS) were recorded by using a commercial Fourier transform (FT) instrument with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector (600 cm⁻¹ to 4000 cm⁻¹) set to 8 cm⁻¹ resolution. The angle of incidence was 69° from the surface normal. Spectra were referenced to the corresponding Au/Si for bare SAMs on Au and Si/gold/Si for the case of sandwich samples.

Results and Discussion

Bifunctional Monolayers on Ultrasmooth Gold Substrates

Ultrasmooth Gold on Plastic Substrate. Gold substrate topography has a strong impact on the resulting organic molecular monolayer structure. Large and flat Au grains are commonly preferred to obtain densely packed monolayers (11). Thus, we tested the quality of the uS-Au/PET surface by means of AFM, see Figure 1. The surface exhibits a homogeneous morphology described by large, flat gold grains with amorphous regions extending several hundreds of nanometers. The surface roughness (rms) was ≈ 0.4 nm \pm 0.1 nm, as expected from a template stripped surface (20). We would like to note that these surface characteristics strongly differ from the surface quality usually reported from

traditional evaporated gold films which typically exhibit small rounded gold grains with $\text{rms} \approx 3 \text{ nm}$ (21). Therefore, nanolaminated gold on PET substrates hold great potential for fabricating Au-molecule-semiconductor structures because the reduced gold surface roughness ensures high-quality monolayers and the substrate flexibility ensures conformal contact to both ends of the molecule. This fabrication route avoids metal filament formation, monolayer degradation and other detrimental aspects observed for traditional vapor-phase deposition on molecular layers.

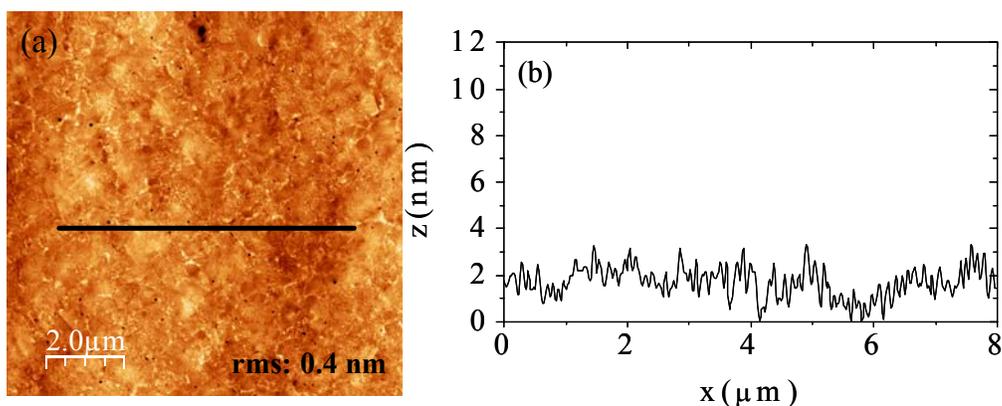


Figure 1. (a) $10 \mu\text{m} \times 10 \mu\text{m}$ AFM topographic image of 200 nm of ultrasmooth gold on polyethylene terephthalate (PET) substrate. (b) Height profile of the region denoted by the black line shown in (a).

Monolayers on ultrasmooth gold on PET. MHDA monolayers present an ellipsometric thickness of $2.5 \text{ nm} \pm 0.2 \text{ nm}$. This value is consistent with a $\approx 0.12 \text{ nm}$ per methylene unit scaling reported in the literature (22). Water contact angle measurements of $12^\circ \pm 1^\circ$ are consistent with hydrophilic acid-terminated monolayers. Thus, we can confirm that this bifunctional monolayer exposes the COOH group at the surface forming a dense packed structure. A vibrational spectrum of the C-H region of MHDA at room temperature is shown in Figure 2 (green trace, 25°C). Vibrational peak position and peak intensity can be correlated with the degree of conformational defects (*gauche*) and degree of chain tilt, respectively (23). The two main peaks at 2919 cm^{-1} (d-) and 2850 cm^{-1} (d+), identified as asymmetric(d-) and symmetric(d+) methylene stretches, reflect the high degree of conformational order within the MHDA monolayer, similar to that of crystalline n-alkanes (24, 23). The monolayer exhibits an all-trans zig-zag molecular chain orientation. Peak absorbance agrees with a single monolayer thickness slightly tilted to increase the three-dimensional density of the monolayer. It is reported that the chains are initially tilted $\approx 23^\circ$ from the surface normal because sulfur atom packing on the gold substrate is less dense than the packing of the chains optimized by van der Waals interchain interactions (25). Therefore, we have obtained all-trans oriented MHDA monolayers on ultrasmooth gold substrates exposing the carboxylic acid end group. This configuration is ideal for adhesion to H-Si(111) to fabricate Au-molecule-silicon test structures.

Temperature effects on molecular conformation. Thermal stability of alkanethiols on gold has been widely studied as model systems for numerous potential applications (26). In our case, we are interested in evaluating the influence of temperature on molecular conformation to ensure monolayer integrity during the adhesion process where moderate temperature is used to form the Au-molecule-Si sandwich structures. We performed a systematic study of the influence of temperature on MHDA molecular conformation by placing the monolayer on a hot plate at different target temperatures, from 25°C to 120°C for 5 minutes. All IR spectra were measured at room temperature and ambient atmosphere, after a post-anneal rinse of the sample with ethanol. Changes observed in peak position and shape of the vibrational spectrum (Figure 2) indicate irreversible changes occurred for the range of temperatures studied here. In particular, we observed that by increasing temperature, the peak position shifts to higher wavenumbers while the full-width at half-maximum (FWHM) remains almost constant. The peak absorbance increases up to 100 °C and then decreases to 120 °C. Based on previously reported temperature studies of SAMs on evaporated gold, we can identify this behavior as two types of thermal-induced defects (27, 28). From 25 °C to 100 °C, *gauche* defects are incorporated into the alkyl chain. These defects start at the end group and migrate to mid-chain with increasing temperature producing a liquid-like state, which is in complete agreement with the trend observed in the peak frequency and peak absorbance of Figure 2. Above 100 °C partial desorption starts, evidenced by the decrease in peak intensity. Previous thermal studies of carboxylic acid-terminated monolayers show similar behavior (14), although, the onset of desorption was reported to be around 120 °C. Our observation of desorption occurring at a slightly lower temperature is likely due to different cycles of heating and cooling used. As a result, it is essential to form the Au-monolayer-Si sandwich structure at moderate temperatures to avoid monolayer degradation.

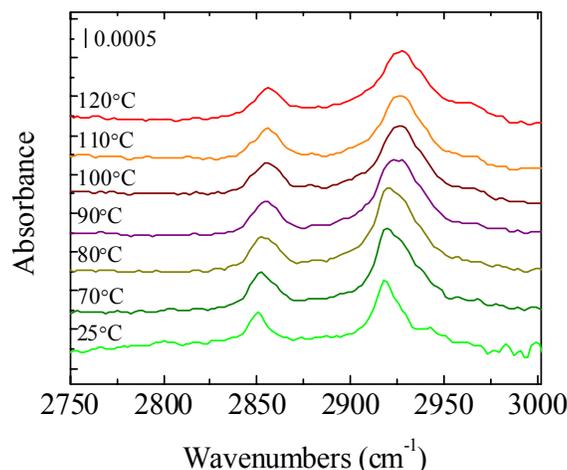


Figure 2. Vibrational spectra of MHDA on uS-Au/PET substrates after 5 minutes exposure to temperatures between 25 °C and 120 °C.

Influence of pressure on the adhesion of monolayers to H-Si(111). Preliminary work performed to fabricate Au-monolayer-Si molecular electronic junctions found that applying heat alone was not sufficient for the two electrodes to adhere, indicating that

mechanical compression is also needed. Therefore, we evaluated the effect of applied pressure on ODT and MHDA monolayers within the structure H-Si(111)-monolayer-uS-Au to identify changes in the monolayer structure and evaluate the role of the COOH end group in Si adhesion. This study was performed at 25 °C by applying pressure ranging from 0.5 MPa to 2 MPa, for 5 minutes (18). In this work, we focused on the effect of 0.8 MPa, the minimum pressure needed for adhesion to H-Si(111). For ODT films on uS-Au/PET, we did not observe adhesion to the H-Si(111) substrate. However, MHDA, containing a reactive COOH end group adheres to H-Si(111) at pressures above 0.5 MPa.

Similar to applied temperature (discussed above), applied pressure can induce modifications in molecular chain tilt resulting in changes in the IR spectra. By means of pb-RAIRS, we analyzed the conformational changes in the monolayer due to pressure. Figure 3 shows vibrational spectra of the C-H region for monolayers on Au and Si-monolayer-Au structures after 0.8 MPa was applied. In the case of the Au-ODT-Si structure, where the H-Si(111) substrate did not adhere to the methyl-terminated monolayer, pb-RAIRS data was acquired with a freshly prepared H-Si(111) in physical contact to the ODT-Au substrate. In addition to the two methylene features at 2919 cm^{-1} (d-) and 2850 cm^{-1} (d+), observed in the MHDA monolayers, the vibrational spectra of ODT monolayers contain peaks at 2965 cm^{-1} , 2937 cm^{-1} , and 2879 cm^{-1} assigned to the CH_3 - asymmetric and Fermi resonance split symmetric stretching modes, respectively. ODT monolayers do not show changes in their vibrational peak position and peak shape indicating the all-trans zig-zag molecular conformation is preserved. This behavior is not unexpected since adhesion between silicon and ODT did not occur and the onset of chain tilting has been reported to occur at much larger (≈ 50 MPa) pressures (12, 29). The MHDA pb-RAIRS spectra exhibit constant peak positions but peak intensity increases after adhesion to silicon (see Figure 3 (d)). We attribute the increased intensity in IR spectra to changes in molecular tilt of the MHDA molecules. Carboxylic acid-terminated monolayers exhibit lower coverage compared to ODT monolayers due to steric effects between carboxylic acid groups (18, 30). Thus, MHDA molecules have more room to tilt under compressive effects, yet still retain a high degree of conformation with no major structural changes.

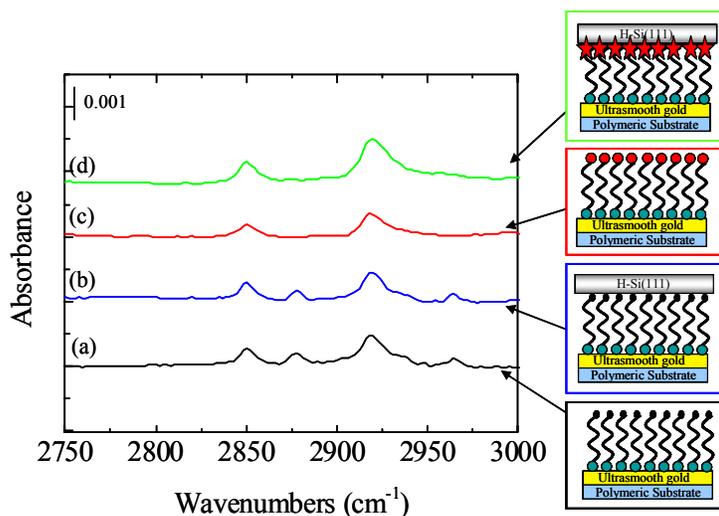


Figure 3. Vibrational spectra of the C-H region from (a) ODT on uS-Au/PET, (b) H-Si(111) physically placed on ODT / uS-Au/PET, (c) MHDA on uS-Au/PET and (d) H-Si(111) adhered on MHDA / uS-Au/PET.

Conclusions

We demonstrated that monolayers formed on ultrasMOOTH gold surfaces on plastic substrates are optimal for fabrication of molecular electronic test devices. Highly ordered MHDA monolayers were assembled with an all-trans molecular chain conformation and the terminal COOH group exposed on this ultrasMOOTH Au substrate. These monolayers degrade irreversibly when heated due to the incorporation of gauche defects (at temperatures below 100 °C) with the onset of desorption occurring above 100 °C. The formation of the Au-monolayer-Si structure was achieved through application of moderate pressures (≥ 0.5 MPa), where the H-Si(111) substrate adheres to the carboxylic-acid terminated monolayer (MHDA) and the molecular order is preserved within this structure. Thus, the combination of a nanotransfer printing-based technique under moderate conditions of pressure and temperature offers a promising approach to obtain high quality and reproducible molecular electronic junctions.

By first forming dense monolayers on ultrasMOOTH Au-PET surfaces and applying pressure we can form dense monolayers adhered between silicon and gold electrodes. This approach has several advantages over the inverse route of formation of monolayers on silicon followed by conventional metal evaporation. First, self-assembly is not possible on the semiconductor substrate due to the strong covalent bonding while Au-S bonding is ideal for formation of well-ordered bifunctional monolayers. Second, conventional evaporation of Au has been shown to completely displace molecular monolayers directly attached to Si (1-4). Instead, this strategy allows us to preserve the integrity of the molecules within the Au-molecule-Si sandwich structure. Finally, by assembling monolayers on gold instead of on silicon we have the advantage of having dense monolayers adhered to both electrodes. This strategy will facilitate a wide range of fundamental studies to provide the characterization basis necessary for the realization of semiconductor-based molecular electronics.

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