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# Gold surface with sub-nm roughness realized by evaporation on a molecular adhesion monolayer

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This letter describes a technique for realizing a gold (Au) surface with roughness at the atomic scale using techniques compatible with integrated device fabrication. The Au layer is electron-beam evaporated on a self-assembled monolayer of (3-Mercaptopropyl) trimethoxysilane on an oxidized silicon substrate and shows a root-mean-square surface roughness of ~2 Å over a 1 $\mu m^2$ area. The physical stability of the Au film toward commonly used chemicals and processes for photolithography and self-assembly, and its suitability for formation of well-ordered organic monolayers indicate that the films are well suited as substrates for future device fabrication in molecular electronics or other devices involving self-assembled monolayers. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2183820]

Gold surfaces have been commonly used substrates for the formation of well-ordered self-assembled monolayers (SAMs),[1] which can be used for molecular electronic studies down to the single-molecule level,[2] chemical interface layers, and selective binding sites for sensing or biological devices. Since typical organic molecules for SAMs are 1–2 nm long, the surface roughness of the Au is an important factor in the quality of the SAM as well as the ability to characterize the film properties. Efforts[3] to produce ultraflat gold layers with a surface roughness at the atomic scale include template-stripped Au surfaces[4–6] over Si substrates, and vapor deposited Au thin films on substrates of mica,[7] silicon,[8] glass,[9] highly oriented pyrolytic graphite,[10] as well as flame-annealing procedures to reduce the roughness of "as-deposited" Au layers. Many of these techniques employ substrate layers or preparation procedures[5] that are not compatible with typical device fabrication approaches. The use of organic SAMs on $SiO_2$ and $Al_2O_3$ in order to assist nucleation during noble metal evaporation[11] has also been reported. In that report, the formation of discontinuous metal islands and a surface roughness of approximately 7 nm were inferred for Au films on a monolayer of an organic disulphide on $SiO_2$. The tendency for siloxane solutions to polymerize may give rise to the surface roughness. In this letter, we present a method to achieve atomically flat gold thin films on $SiO_2$ substrates using a SAM of (3-Mercaptopropyl) trimethoxysilane (MPTMS) as a molecular adhesive (Au/MPTMS structure).

To achieve the atomically flat Au surfaces, the $SiO_2$ substrates were silanized with MPTMS and coated with Au. The 5000 Å thermal oxide-coated Si substrate from Silicon Quest International, Inc., was cleaned with piranha solution [a 1:1 mixture of sulfuric acid ($H_2SO_4$) and hydrogen peroxide ($H_2O_2$)] by dipping the wafer for 10 min followed by rinsing in deionized (DI) water and blowing dry with $N_2$. Next, we performed a plasma etch in argon and oxygen with a radio-frequency power of 100 W and a base pressure of 1000 mTorr for 10 min, which results in a modified $SiO_2$ surface with an excess of oxygen molecules sitting on the top [Fig. 1(a)]. In the hydroxylation process, the sample was immersed in a 6:1:1 solution of DI water, hydrochloric acid (HCl), and $H_2O_2$ at 85 °C for 10 min. This process leaves -OH groups on the surface [Fig. 1(b)]. The sample was exposed to vapor-phase MPTMS for 4 h inside a desiccator containing an open vial of MPTMS ($C_6H_{16}O_3SSi$, from Aldrich and Co., USA) and evacuated to $\sim 10^{-3}$ Torr. Reactions occur between the $SiO_2$ surface silanols and silanol group $-Si(OCH_3)_3$ of MPTMS with formation of hydrogen bonded intermediates followed by the elimination of $H_2O$ and $CH_3OH$ to form covalent Si–O–Si bonds to the $SiO_2$ surface [Fig. 1(c)], leaving the thiol (–SH) functional group on top. A thin layer (20 nm) of Au was e-beam evaporated at a chamber pressure of $2-3\times 10^{-7}$ Torr and a deposition rate around 0.5 Å/s. The substrate was kept nominally at room temperature. Figure 1(d) shows a schematic diagram of a thin Au layer deposited on the MPTMS-capped $SiO_2$ sub-

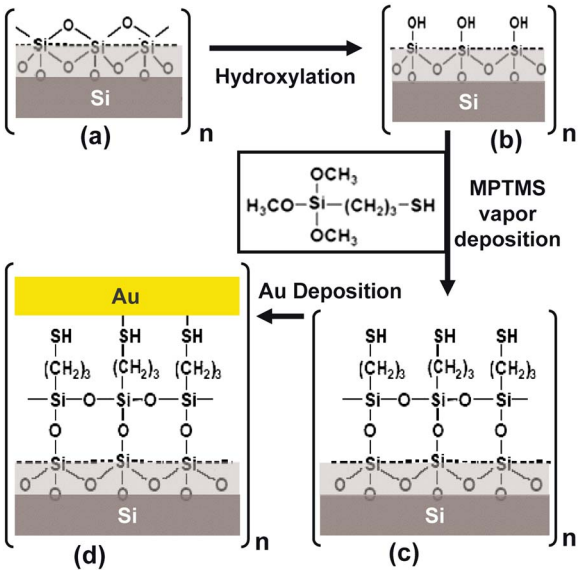


FIG. 1. (Color online) A schematic diagram showing the chemical processes involved during silanization procedure [(a)–(d)] for the formation of a MPTMS (inset) monolayer over $SiO_2$ substrate, (a) plasma exposure, (b) hydroxylation, and (c) Si–O–Si covalent bond after exposure to MPTMS gaseous molecules inside a vacuum desiccator, and (d) a cartoon of the Au thin film e-beam evaporated on $SiO_2$ with MPTMS adhesive monolayer.

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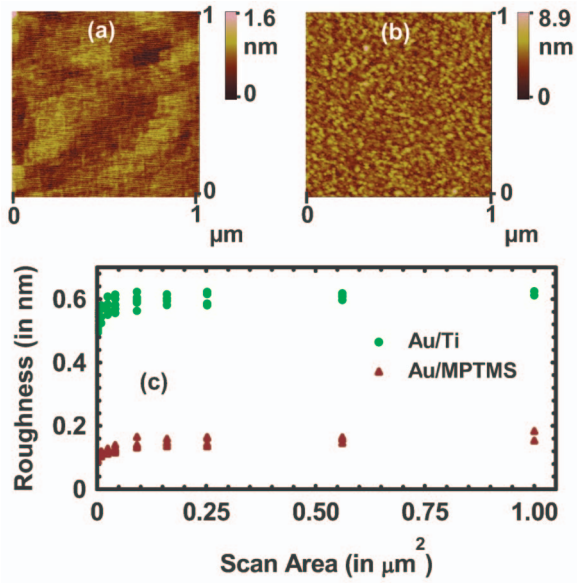


FIG. 2. (Color) AFM image of Au surface for (a) $Si/SiO_2/MPTMS/Au(200\ Å)$ structure and (b) $Si/SiO_2/Ti(32\ Å)/Au(200\ Å)$ structure. (c) Plots of rms surface roughness vs scan area for representative samples from the two types of structures.

strate. A Si/SiO2/Ti/Au structure was also fabricated using the same Au evaporation parameters as the MPTMS sample and without breaking the vacuum between Ti and Au depositions.

The surface morphology of the samples was determined by imaging using a Veeco Dimension 3100 atomic force microscope (AFM) in tapping mode. An AFM image of the gold surface in a $Si/SiO_2/MPTMS/Au$ (200 Å) structure [Fig. 2(a)] shows a root-mean-square (rms) surface roughness of 1.5 Å over a scan area of 1 $\mu m^2$. The topography of a $Si/SiO_2/Ti/Au$ (200 Å) structure formed using the same gold deposition parameters indicates a surface roughness of 6.4 Å over 1 $\mu m^2$ area [Fig. 2(b)]. Figure 2(c) shows the measured rms roughness versus the scan area for multiple areas within a representative region of samples using the two adhesion layers. In both types of samples, the roughness is observed to be relatively constant for scan areas above 0.1 $\mu m^2$, indicating that there are not significant surface features in this size range. Different studies show a consistent surface roughness of 1.0–2.0 Å for MPTMS/Au samples compared to 6.0–40 Å for Au/Ti samples, each consisting of 20 nm Au films. Note that the observed rms roughness values in the Au/Ti samples are lower than those observed for typical evaporations, consistent with reports of surface roughness of 1 nm or less for thin Au films (20 nm) with a slow evaporation rate. A roughness of 1.6–4.0 nm is observed for thick Au (200 nm)/Ti films when evaporated at a rate of 1–2 Å/s, which increases to 10–15 nm by deposition at a higher rate (~10 Å/s). MPTMS/Au shows an overall roughness (of 1–2 Å) comparable to that of the best available techniques for the formation of ultraflat Au (Refs. 4 and 6) (a surface roughness of 1.0–3.0 Å is observed for template stripping[4,5] and flame annealing[6] methods). A conductivity of $2.7\times10^5\ \Omega^{-1}\ cm^{-1}$ is measured for the Au (200 Å)/MPTMS films, which is comparable to the value $4.1\times10^5\ \Omega^{-1}\ cm^{-1}$ for bulk Au.[11]

The advantages of this process include the ease of fabrication, the absence of postevaporation processing, and the potential for realizing patterned regions. Although Au surfaces with flatness in the same range have been observed through template stripping (Ref. 4) (also observed for platinum)[5] and flame- annealing,[6] patterned layers required for most device applications are difficult to achieve with these techniques. The current technique should result in little Au contamination, which can occur during thermal deposition or flame annealing.[6]

It is believed that the evaporated Au atoms are anchored to the top–S atoms of the MPTMS SAM. Au–S is known to be a strong bond and is frequently used in molecular electronics.[12] This Au–S bond is strong enough to hold the Au thin film tightly. The oxane–siloxane–silsesqueoxan bond at the $SiO_2$ surface and the sulphur–gold (S–Au) bond at the top evaporated Au contact, makes MPTMS an efficient adhesive monolayer [Fig. 1(d)].

Among the expected growth mechanisms of layer-by-layer (LL), mound formation (MF),[13] downward funneling (DF),[14] and restricted downward funneling (RDF) (Ref. 15) that control the roughness of metal thin film surfaces, LL and DF are known to be smooth growth compared to MF and RDF. In this case, LL growth can be eliminated because it may be impossible to make a pure single layer through physical deposition techniques. Here, the secondary adatoms prefer to slide to the nearest possible gaps on the substrate with thiolated functional groups, rather than nucleating at the first adatom sites, hence DF is the expected growth mechanism for achieving such a smooth surface.

Physical stability of the MPTMS/Au layer has been tested by rinsing the sample in commonly used chemicals during surface cleaning and SAM formation (including tolune, acetone, methanol, ethyl alcohol, and dichloromethane), and by photolithographic patterning using several photoresists. The layer is resistant to all the above chemicals and lithography processes, leaving the Au layer unaffected (no delamination or crack is observed through high-resolution microscopy) even after a 30 min ultrasonification, heating to ~130 °C or ultraviolet light. The physical stability indicates that the atomically flat Au surfaces are generally suitable for molecular characterization and electronic devices.

In order to verify that the $Si/SiO_2/MPTMS/Au$ structure yields a suitable substrate for the formation of well-ordered SAMs, a 1-hexadecanethiol (HDT, $C_{16}-SH$) monolayer was deposited by immersing the Au substrate into a 2 mM solution in ethanol. Figure 3 represents the absorbance Fourier transform infrared (FTIR) spectroscopy of an HDT SAM formed over the flat Au surface. Peaks at wave numbers 2926.25 and 2853.56 $cm^{-1}$ are characteristic vibrational modes for C–H stretches in the $C_{16}$–alkane chain,[16] indicating the presence of a well-ordered SAM.

Lateral metal-molecule-metal (M-M-M) devices[17] were fabricated using an electromigration-induced break junction (EBJ) technique. EBJs formed from the Au/MPTMS structures exhibited minimum gaps in the range of 2–5 nm (as observed by field emission scanning electron microscopy), while comparable EBJs using Au/Ti structures showed gaps of 10–15 nm. An increase in the conductivity of the Au/MPTMS nano gaps following the solution-based deposition of both aromatic dithiol molecules and double-stranded deoxyribonucleic acid (15-base pairs) indicates that molecular-scale gaps can be achieved. Details of the EBJ and electrical characteristics of few molecule devices have been reported elsewhere.[17]

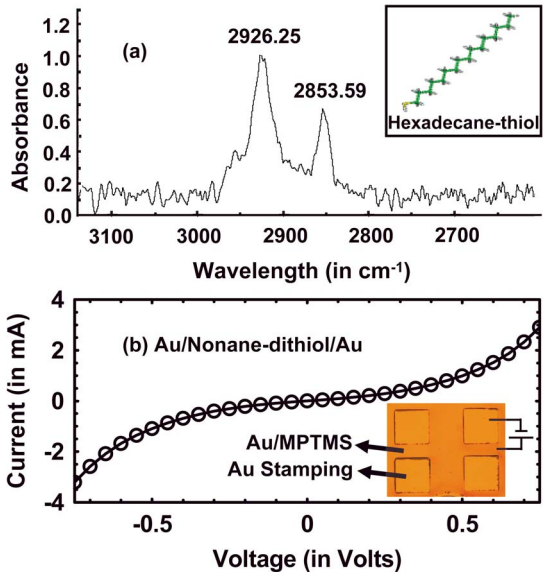


FIG. 3. (Color online) (a) Transmittance FTIR spectroscopy of a SAM of 1-hexadecanethiol on the ultraflat Au surface, which shows a well ordered SAM. Inset in (a) shows the schematic of the $C_{16}$–SH molecule. (b) A representative current-voltage characteristics of nonane-dithiol in a M-M-M vertical device structure (microscopic image is shown in the inset).

We have also used the flat Au thin film as the bottom contact in vertical M-M-M device structures. A nonane–dithiol ($HS-C_9-SH$) SAM was formed on the Au surface by immersing the substrate into a 2 mM solution in ethanol, for 24 h. A patterned ($20\times 20\ \mu m^2$ area) top Au contact was transferred on to the device using a stamping technique (Au deposition over a patterned polydimethylsiloxane (PDMS) pad followed by making a physical contact with the SAM).[18] All of the patterns were successfully transferred and a nonlinear current-voltage characteristic was observed [Fig. 3(c)]. In comparable structures made using Au/Ti bottom contacts, the roughness of the Au surface impedes the formation of a well-ordered monolayer and also makes the transfer of preformed contacts difficult, presumably due to limited areas over which intimate contact can be achieved. The current density in this experiment ($\sim 10^5\ A/cm^2$ for $Au/HS-C_9-SH/Au$) is significantly higher than that reported in Au-molecule-GaAs devices,[18,19] presumably due to much stronger coupling between the molecular states and Au. This value is comparable to the reported value of $3-6\times 10^5\ A/cm^2$ for alkanedithiol molecules in M-M-M structures.[20] M-M-M devices with evaporated top contacts must generally be below 100 nm in order to avoid shorts.[21] The stamping technique using Au/MPTMS allows the study of large devices without shorts. The demonstration of high yield (>95%) M-M-M vertical device structures illustrates the suitability of the films as substrates in molecular electronic devices.

In conclusion, a technique has been developed to realize Au films with surface roughness comparable to the best available techniques, and suitable for formation of patterned device structures. The Au/MPTMS structure shows a rms surface roughness of ~1.5 Å over a 1 $\mu m^2$ area, and ~2 Å over a 10 $\mu m^2$ area, compared to ~6 Å–40 Å for Au/Ti structures. A SAM of a alkanethiol molecule was formed on the surface and characterized. The resulting ultraflat Au layers remain physically unaffected by chemical processing during photolithography and self-assembly. Lateral and vertical moledular devices were successfully fabricated. This study indicates that the atomically flat Au films prepared in this technique will be useful as substrates for molecular monolayer characterization and for M-M-M vertical devices.

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