Formation of Alkanethiol Monolayer on Ge(111)

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Abstract: Alkanethiols, $CH_3(CH_2)_{n-1}SH$, are shown to react readily with HF-treated Ge(111) surface at room temperature to form a high-quality monolayer. The resulting films are characterized by using contact angle analysis (CAA), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and high-resolution electron energy loss spectroscopy (HREELS). The octanethiol and octadecanethiol films on Ge(111) both exhibit 101° and 40° water and hexadecane contact angles, respectively. These values indicate that the thiol surface coverage is relatively high, and that the films possess a high degree of orientational ordering. The angle-resolved XPS analysis supports that thiols are bound to the Ge surface by Ge−S bonds at the monolayer/Ge interface. The film thickness values obtained by XPS and SE agree well with the earlier reported values on alkyl monolayers on Ge(111) prepared by Grignard reaction. On the basis of HREEL spectra taken after thermal annealing steps, the monolayers are found to be thermally stable up to 450 K. The thermal stability provides further evidence that thiols are covalently bonded to Ge(111).

Introduction

Self-assembled monolayers (SAMs) of organic molecules provide means to modify chemical and physical properties of metal, semiconductor, and insulator surfaces. The surface modification lends itself to a variety of applications such as microtribological lubrication,[1,2] metal corrosion barrier,[3−5] biosensor,[6,7] and lithographical mask.[8−10] The success of these applications relies on robust heterogeneous chemistry between self-assembling organic molecules and underlying substrate. For instance, a number of chemistries have been reported to form tightly packed monolayers on Si.[11−13] The alkyl-terminated hydrophobic SAM surfaces are proven to be effective for safe structural release and durable operation of microelectromechanical systems (MEMS) made from polycrystalline Si.[2]

For a similar purpose, the latest advent of MEMS that interlace electronic devices with mechanical actuators has prompted a new interest in a robust chemistry to passivate Ge surfaces.[14−16] He et al. reported self-assembly of alkyl monolayers on Ge(111) surface by Grignard reaction.[17,18] Grignard reagents such as $CH_3(CH_2)_{n-1}MgX$ (X = Cl and Br) react with Cl-terminated Ge(111) surface at 60 to 80 °C under inert Ar ambient. The resulting alkyl monolayer is covalently bonded to Ge. However, long reaction times are required to form such a monolayer (e.g., 7 days to form an octadecyl layer, $n = 18$). In search of a simpler approach, we have encountered a reported result that $(NH_4)_2S$ reacts with Ge in an aqueous solution.[19] It is argued that S atoms adsorb onto Ge bridge sites and provide short-term stable resistance to oxidation in atmosphere. This observation led us to suspect that alkanethiols ($CH_3(CH_2)_{n-1}SH$) may react with Ge surface, producing an alkyl monolayer. Compared to the laborious pathways described for alkyl monolayers on Ge, we will demonstrate here that alkanethiols readily react with HF-treated Ge surface at room temperature to form a high-quality monolayer.

Materials and Methods

Sample Preparation and Monolayer Formation. The resistivity of Ga-doped Ge(111) wafers used in this study ranges from 1.0 to 3.0 Ω·cm. This range of resistivity allows high-resolution electron energy loss spectroscopy without sample charging. The as-received samples (Eagle-Pitcher) are first sonicated in acetone for 5 min to dissolve

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organic contaminants and blow-dried with N_2. The samples are then rinsed in deionized water to dissolve GeO_2.[20] After water rinse, the Ge samples are blow-dried with N_2 and immersed in a concentrated HF solution (49 wt % in H_2O) for 10 min to remove residual oxide.[21,22] X-ray photoelectron spectroscopy shows the absence of any chemically shifted GeO_x at this stage, consistent with the surfaces being hydrogen-terminated, as proposed earlier.[21,23] The germanium samples are subsequently blow-dried with N_2 and immediately immersed in alkanethiol solution (10^{-3} M in 2-propanol). We have examined alkanethiols with two different chain lengths: $n = 8$, octanethiol (Aldrich, 98%), and $n = 18$, octadecanethiol (Aldrich, 98%). The samples are left in the solution for various durations. We have determined that 1 day exposure is adequate for obtaining high-quality films. To prevent substantial evaporation of 2-propanol during exposure, the container holding Ge samples is sealed with Parafilm. After the monolayer formation, the Ge samples are sonicated in neat 2-propanol for 1 min, and blow-dried again with N_2. These steps are all carried out in ambient air (20 °C and 50% relative humidity).

For comparison, octadecanethiol-coated Au(111) samples are also prepared by the procedure we have reported previously.[24] The samples prior to the alkanethiol application consist of a sacrificial SiO_2 overlayer with approximately 1.5 μm thick Au film deposited on GaAs. The sacrificial layer protects the Au surface against contamination until the time of use. The oxide layer is removed by etching in the concentrated HF solution (49 wt % in H_2O) for 5 min. At this stage, no silicon oxide is observed based on HREELS.[24] The images taken by atomic force microscopy after the HF etch show that the Au films comprise large (approximately 1000 Å wide) crystalline (111)-terminated grains. Immediately after removing the sacrificial oxide layer, the samples are placed in a 1 mmol solution of octadecanethiol (Aldrich, 98%) in ethanol for 24 h. Upon removal from the solution, the samples are rinsed in ethanol and dried with N_2.

Contact Angle Analysis. A Ramé-Hart Model 100 contact angle goniometer is used to measure static contact angles on sessile drops.[25] The volume of the drops is about 5 μL; the contact angle is found to be independent of the droplet volume in the 1 to 20 μL range.

Atomic Force Microscopy. A Digital Instruments Nanoscope III is used to image the sample surfaces before and after monolayer formation. The samples are scanned in the ambient air at room temperature, using the tapping mode to minimize possible damage to the sample surfaces.

X-ray Photoelectron Spectroscopy. A PHI 5400 small spot system is used for these studies with an Al K_α source. The base pressure in the XPS system is in the 10^{-9} Torr range. A survey spectrum and high-resolution spectra of C(1s), O(1s), S(2p), and Ge(3d) regions are taken for each sample. The method used to estimate the film thickness is described in the Results and Discussion section.

Spectroscopic Ellipsometry. A Wollam M-44 spectroscopic ellipsometer is used to estimate independently the monolayer film thickness. A broad band of light (300 to 600 nm) from a Xe-arc lamp is linearly polarized and directed onto the film surface at an angle of 75° to the surface normal.[26] The polarization change of the reflected beam is measured through a rotating analyzer while the amplitude change is detected on a diode array detector. The diode array eliminates the use of monochromator and allows simultaneous detection of amplitude changes at 44 wavelengths. By introducing the ellipsometric angles Ψ and Δ, one can express these changes in terms of complex reflection coefficient (ρ) defined as

$$\rho = \frac{R_p}{R_s} = \tan(\Psi)\ e^{i\Delta} \tag{1}$$

where R_p and R_s are Fresnel reflection coefficients for p and s polarized light, respectively. Provided that the optical properties of the subject films are known, the film thickness can be calculated from the measured ρ. The specific procedure used to estimate the monolayer film thickness is described in the Results and Discussion section.

High-Resolution Electron Energy Loss Spectroscopy. A LK-3000 HREEL spectrometer is used to obtain the vibrational spectra of the monolayer sample surface. The spectrometer is placed in a UHV chamber with the base pressure of 10^{-10} Torr. The HREEL spectra are obtained in the specular mode with an incident electron energy of 6 eV. To improve the resolution, the spectra are taken with the substrate held at liquid N_2 temperature (120 K). The resolution of the elastic peak typically ranges from 40 to 50 cm^{-1}. The signal intensity of the elastic peak is approximately 10^4 cps. The spectra are unchanged even after several hours of exposure to the incident electron beam. To study the thermal stability of the monolayers, the substrate temperature is ramped at 2 K/s to a specified annealing temperature, held at the level for 5 min, and then cooled to 120 K for the HREELS measurements. The steps are successively repeated for increasing annealing temperatures to probe the thermal stability of the monolayer.

The same UHV system contains an Auger electron spectroscopy (AES) system (Physical Electronics 10-155A). Because the high electron beam energies used in AES (3 keV in the present study) damage the monolayers,[27] this technique is only used to determine the state of the surface following the monolayer desorption.

Results and Discussion

Contact angle measurements using sessile drop method are performed on the thiol-coated Ge(111) and, for comparison, on the much-studied thiol-coated Au(111). For both octanethiol and octadecanethiol-coated Ge, the water contact angle ($\theta^{Ge}_{H_2O}$) is 101° while the hexadecane contact angle (θ^{Ge}_{HD}) is 40°. No contact angle data are reported in ref 17 for alkyl monolayers on Ge. However, our values compare well to the angles we obtained on octadecanethiol-coated Au(111): $\theta^{Au}_{H_2O} = 110°$ and $\theta^{Au}_{HD} = 49°$. Given that the water and hexadecane contact angles are similar and relatively high for both octanethiol and octadecanethiol-coated Ge, the monolayer coverage should be relatively high, and the films possess a high degree of orientational ordering.[28]

Atomic force microscopy is used to image the surfaces before and after the monolayer formation. The surface topography is essentially unchanged following the coating process, resulting in a root-mean-square roughness of approximately 1 Å. To further characterize the alkanethiols on Ge(111), the monolayer-coated samples are analyzed by X-ray photoelectron spectroscopy. Figure 1 shows representative survey spectra taken at the takeoff angle of 42°, with 1 eV resolution and averaged over 8 scans. Signature peaks for C and Ge are clearly visible. The C(1s)/Ge(3d) intensity ratio is greater for octadecanethiol (~1.2) than for octanethiol (~0.54) consistent with their chain length ratios. Furthermore, the intensity ratio increases with increasing takeoff angle, defined as the angle between the surface normal and the detector orientation. The takeoff angle dependence indicates that the film thickness is uniform. The insets of Figure 1 show close-up spectra of S(2p) and Ge(3d) regions for the octadecanethiol sample. With increasing takeoff angle, the S(2p)/C(1s) intensity ratio drops. This behavior is consistent with the S atoms being at the monolayer/Ge interface. Very little oxygen is observed with XPS. By varying the takeoff angle, we have identified that oxygen is present mostly on the surface possibly

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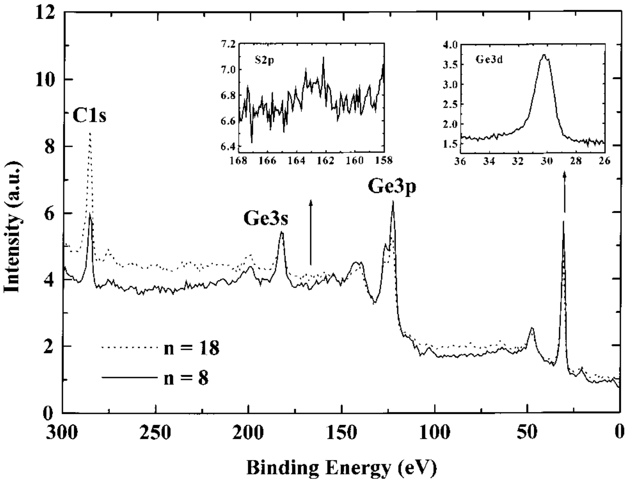

Figure 1. X-ray photoelectron spectra of octane- and octadecanethiol on Ge(111) surface. The insets show the S(2p) and Ge(3d) close-ups for octadecanethiol.

due to contamination. Furthermore, the close-up of the Ge(3d) peak shows the absence of any GeO_x species (Figure 1 inset).

The tilt angle of long alkyl monolayers is estimated from the ratio of C(1s) photoelectron peak intensity (I_{C1s}) to Ge3d peak intensity (I_{Ge3d}), following the analysis done in ref 17. The intensity ratio is expressed as

$$\frac{I_{C1s}}{I_{Ge3d}} = \beta\left\{\exp\left(\frac{d}{\lambda \sin \alpha}\right) - 1\right\} \tag{2}$$

The sensitivity factor ratio (β) is approximated as the relative photoelectron cross sections for C(1s) and Ge(3d), yielding $\beta = 0.68$. The film thickness (d) is expressed as a function of Ge−S interlayer distance (d_{Ge-S}), S−C bond length (l_{S-C}), incremental distance per CH_2 group (l_{C-C}), number of carbon atoms in the alkyl chain (n), and tilt angle (θ) by

$$d = d_{Ge-S} + \{l_{S-C} + (n-1)l_{C-C}\}\cos\theta \tag{3}$$

where d_{Ge-S}, l_{S-C}, and l_{C-C} used in this study are 2.36,[29] 1.83,[30] and 1.27 Å,[4,31] respectively. The photoelectron mean free path (λ) is approximately 36 Å (refs 13 and 17), and the takeoff angle for the measurement (α) is 42°. Solving Equations 2 and 3 simultaneously yield a film thickness of 24 Å and a tilt angle of 20° for the octadecanethiol monolayer on Ge. These values compare well to the earlier reported values on alkyl monolayers on Ge(111) prepared by Grignard reaction.[17,18]

Spectroscopic ellipsometry is used to determine the film thickness independently from the XPS analysis. The optical properties of self-assembled monolayers are approximated in this study by those of polyethylene films.[17,32] Assuming a two-layer model where a polyethylene film is placed on top of a Ge substrate, the estimated film thickness is 25 Å, in good agreement with the XPS result. Figure 2 demonstrates the goodness of the model; the model-generated Ψ and Δ virtually overlap the experimentally measured values.

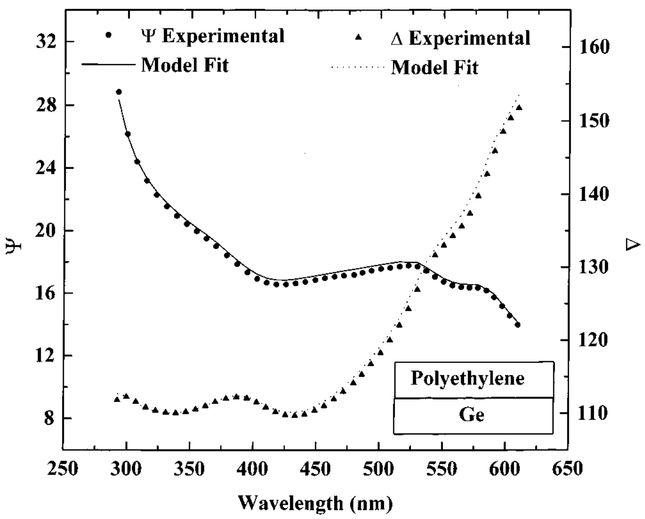

Figure 2. Ellipsometric angles Ψ and Δ of octadecanethiol film on Ge(111).

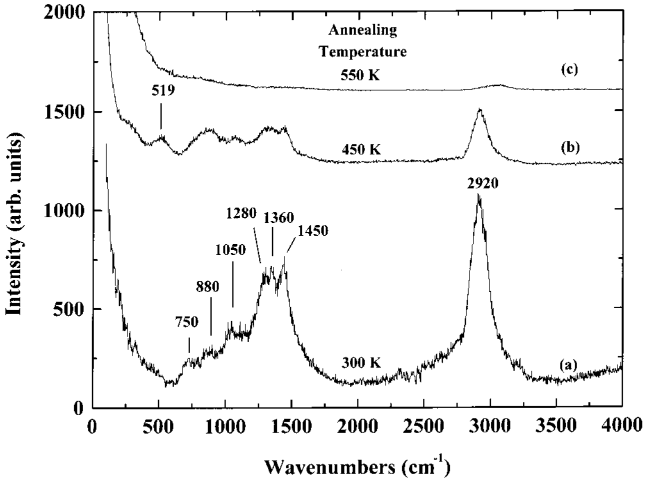

Figure 3. Electron energy loss spectra of octadecanethiol on Ge(111) as a function of annealing temperature.

High-resolution electron energy loss spectroscopy is used to probe characteristic vibrational modes of octadecanethiol-coated Ge(111). The spectrum in Figure 3a shows signature peaks for the C−H stretching mode at 2920 cm^{-1}, the CH_3 symmetric deformation at 1360 cm^{-1}, and the CH_3 rocking mode at 880 cm^{-1}.[33−38] The peaks near 1450 and 1280 cm^{-1} are associated with CH_2 scissors deformation and CH_2 twist-rock modes, respectively. The rock-twist mode of CH_2 at 750 cm^{-1} stems from long chains of methylene units that contain more than four carbon atoms[24,33] and constitutes a unique feature of long alkyl chains. Another carbon skeletal mode appears near 1050 cm^{-1}, which corresponds to C−C stretching. The Ge−S stretching mode expected near 540 cm^{-1} is not observed.[39] This could be due to the broad elastic peak or to the presence of the monolayer attenuating the associated signal. The broad HREEL spectral

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resolution (70 cm^{-1}) in comparison to FTIR spectral resolution ($<$16 cm^{-1}) precludes resolving the peaks in the C–H stretching region.[17,18] However, Figure 3a compares well to the HREEL spectra reported on other monolayer systems, including alkanethiols on Au[24] and alkyl monolayers on Si.[12] The described signature peaks of long alkyl chains collectively evidence the presence of octadecanethiol monolayer on Ge(111) surface.

Thermal behavior of the monolayers is monitored with HREELS. The vibrational peaks remain unchanged upon annealing the sample to 350 K. Upon annealing to 450 K, the peak intensities are significantly reduced, signaling partial desorption of the monolayer film (Figure 3b). With the partial desorption, the Ge substrate should be more accessible to the incident electrons. Accordingly, a peak at 519 cm^{-1} appears that may be attributed to the Ge–S stretch. The monolayer desorbs completely at 550 K (Figure 3c) in comparison to 450 K observed on octadecanethiol-coated Au(111) obtained under the same temperature ramp rates.[24,40] These results additionally support that the monolayer is covalently bonded to the Ge(111) surface. An Auger electron spectrum taken after annealing the sample to 550 K shows no S remaining on the surface, suggesting that the entire molecule desorbs primarily by the Ge–S bond cleavage.

The monolayer chemical stability is also investigated in ambient air and various solutions. A 12 h exposure to laboratory air at 30–35% relative humidity results in no changes in the contact angles. This stability is adequate to allow the monolayer system to be used in releasing MEMS structures.[2] After 1 day, $\theta^{Ge}_{H_2O}$ decreases to 90° whereas $\theta^{Au}_{H_2O}$ remains unchanged. This result, consistent with their lower initial contact angles, indicates that the films on Ge are not as well packed as they are on Au. On both octadecanethiol-coated Ge and Au samples, the water contact angle decreases to about 90° after 30 min in boiling chloroform. After 30 min of immersion in boiling water, however, the water contact angle on Ge(111) drops to about 80° whereas it remains unchanged on Au(111). This behavior may be attributed to water attacking Ge at the monolayer/Ge interface, leading to oxidation. The subsequent dissolution of germanium oxide in water may lead to the monolayer loss by a lift-off process. In contrast to alkanethiol monolayers on Ge, the alkyl monolayers formed on the Ge(111) surface via Grignard reagent are chemically more robust[17,18] due to their strong Ge–C bonds.

Conclusions

In summary, we have demonstrated that alkanethiol monolayers readily form on HF-treated Ge(111) surface. The resulting surfaces are hydrophobic. The presence of C1s, S2p, and Ge3d X-ray photoelectron peaks along with their observed dependence on takeoff angle supports that thiols are bound to the Ge surface with S being at the monolayer/Ge interface. The film thickness values obtained by XPS and spectroscopic ellipsometry agree with the values reported for alkyl monolayer on Ge. The signature vibrational peaks of long alkyl chains shown by HREELS are consistent with earlier HREEL spectra on similar monolayer systems. The monolayer is found to be thermally stable up to 450 K. The thermal stability supports that thiols are covalently bonded to Ge(111). The primary desorption channel appears to be the breakage of the Ge–S bond.

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