Self-Assembly of Alkyl Monolayers on Ge(111)[1a]

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There is growing interest in the assembly of covalently bonded organic monolayers on semiconductor surfaces. Such organic layers provide a means of surface passivation and, more significantly, offer a potentially important new methodology for the integration of chemical and biological functionalities into solid-state electronic devices.[2] Chidsey and co-workers[3] reported the assembly of robust, closely packed monolayers of long alkyl chains on Si surfaces from the free radical reaction of H-terminated Si with diacyl peroxides and/or alkenes which were shown to be effective for the immobilization of biomolecules.[4] Lewis and co-workers[5] prepared similar alkylated surfaces through the reaction of Cl-terminated Si surfaces with organolithium or Grignard reagents. The interfacial reactions leading to the formation of Si−C bonds in these studies resemble molecular organosilicon chemistry.[6] Other notable advances in the organic functionalization of semiconductor surfaces include the self-assembly of alkanethiols on GaAs[7] and covalent attachment of aryls[8] and thienyls[9] on Si(111), of carboxylic acids[10] and alcohols[11] on porous silicon, and of aromatic derivatives[12] and thiols[13] on InP.

Although the first transistors were made from Ge, it has received less technological interest relative to Si. Despite the fact that it has a higher carrier mobility than Si,[14] Ge does not form a robust passivation layer on its surfaces (unlike silicon oxide, germanium oxide is water soluble). Nonetheless, recent success in the fabrication of SiGe heterostructures for high-speed integrated electronics and optoelectronics has revived interest in Ge.[15] Considering the close parallel of organosilicon and organogermanium chemistry, it is likely that an analogous surface chemistry of germanium can be developed. To our knowledge, there is only one prior report of the ethylation of germanium surfaces some 35 years ago.[16] The resulting surface was characterized only by mass spectrometry and electrochemical measurements. Under the harsh conditions used, the etching produces an extremely rough surface with multichloride termination that is not practical for the processing of advanced materials (ca. 50 μm of material was removed from the surface).

Recently, one of us discovered that an ordered monochloride terminated (1×1) Ge(111) surface can be obtained by treatment with aqueous HCl.[17] This discovery opens the possibility of growing ordered organic films on the Ge(111) surface. In the present paper, we report the preparation and characterization of highly ordered organic monolayers on the Ge(111) surface by the reaction of Grignard reagents with Ge(111)−Cl. We have derivatized the surface with alkyl groups having different chain lengths and functional termini. Infrared absorption (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and ellipsometric measurements reveal that the $C_{18}H_{37}$ monolayer consists of stable, densely packed alkyl chains covalently bonded to the bare Ge(111) surface.

Single crystals of Ge(111)−Cl were prepared as described previously.[17] XPS[18] (Figure 1) confirmed the absence of Ge oxides (chemically shifted Ge (2p)) and the formation of covalent Ge−Cl bonds at the surface. The chloro-terminated Ge surface is air-stable and can be manipulated in ambient atmosphere for up to 2 h. Exposure of the chlorinated Ge surface to Grignard reagents including $CH_3(CH_2)_nMgX$ (n = 1, 2, 9, 13, 14, and 17; X = Cl, Br) and $R(CH_2)_2MgX$ (R = C_6H_5 and CH=CH_2) at 60−80 °C under a dry Ar atmosphere yielded alkyl monolayers covalently bonded to the Ge surface. The reaction time varied between 6 h (ethyl) and 7 days (octadecyl) depending on the chain length of the alkyl group (see Supporting Information). In a typical preparation for the decyl modified surface, a shard of freshly prepared Ge(111)−Cl was placed in an argon-filled quartz Schlenk tube. A solution of 1.0 M decylmagnesium chloride in THF was added to completely immerse the shard and heated at 80 °C for 48 h. The shard was thoroughly rinsed with dry THF and dry ethanol in an anaerobic environment and sonicated in ethanol and dichloromethane (5 min each). The wetting properties of the derivatized surfaces were consistent with high hydrophobicity.

The XPS survey spectra of these surfaces showed only Ge and C signals, with little or no detectable O, Mg, or halide peaks (Figure 1). The C(1s)/Ge(3d) ratio in the XPS scan increased monotonically with increasing chain length of the reagents from C_2 to C_{18} (inset in Figure 1), suggesting that alkyl monolayers are formed continuously and uniformly on the surface. The line through the points in the inset in Figure 1 provides a rough estimate of the film thickness and tilt angle of the alkyl chains. The length of the hydrocarbon chain, d, bonded to a Ge atom on the surface is defined by eq 1, where n is the number of carbons, θ is the tilt angle, and 1.96 is the length of the Ge−C bond.[3b]

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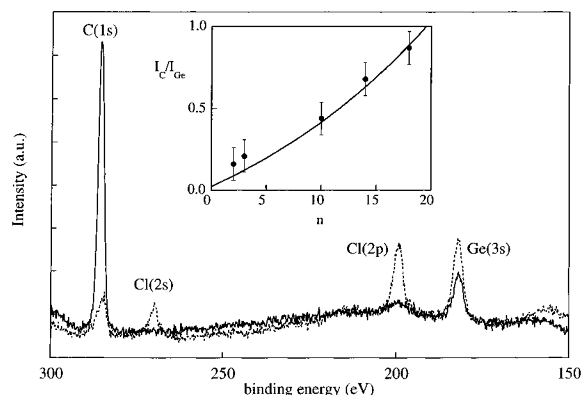

Figure 1. X-ray photoelectron survey spectra of Cl- (dotted line) and $C_{18}H_{37}$- (solid line) terminated Ge(111) surfaces. The inset is a plot of the intensity ratio, $I_{C(1s)}/I_{Ge(3d)}$, as a function of the alkyl chain length. The fit through the data is as described in the text (takeoff angle = 45°).

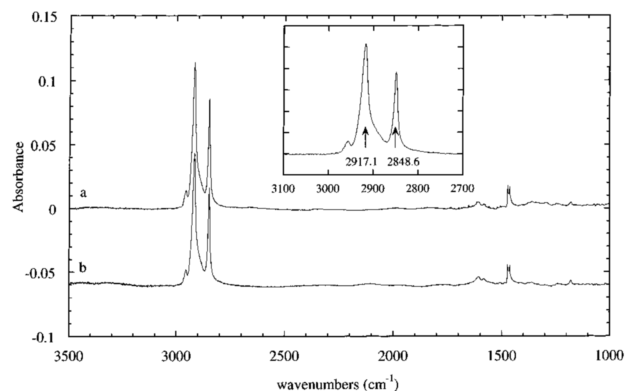

Figure 2. Infrared absorption spectra of the Ge(111)−$C_{18}H_{37}$ surface in (a) s- and (b) p-polarization referenced to the Ge(111)−Cl surface. The spectra have been offset for easy viewing. The inset shows the p-polarized spectrum of the C−H stretch region.

The C(1s)/Ge(3d) XP intensity ratio is related (eq 2) to the film

$$d = 1.96 + {}^{1}/_{2}(n - 1)2.52\cos(\theta) \qquad (1)$$

$$\frac{I_{C(1s)}}{I_{Ge(3d)}} = \beta\{\exp(d/\lambda \sin\alpha) - 1\} \qquad (2)$$

thickness, d, the photoelectron mean free path, $\lambda \approx 36$ Å,[19] the takeoff angle for the measurement, α, and the sensitivity coefficient, β. A value of $\beta \approx 0.68$ can be approximated as the relative photoelectron cross sections for C(1s) and Ge(3d).[20] The best fit to eqs 1 and 2 gives a value of $\theta \approx 25°$ leading to a film thickness of 21.4 Å for the Ge(111)−$C_{18}H_{37}$ surface (θ is assumed to be independent of chain length). Both n- and p-type Ge(111) substrates gave the same XPS results. The C(1s)/Ge(3d) intensity ratio from Ge(111)−$C_{18}H_{37}$ showed an exponential dependence on the photoelectron takeoff angle, α, as expected for an organic film of uniform thickness. Spectroscopic ellipsometry[21] provided an estimate of the film thickness of 24 Å for the Ge(111)−$C_{18}H_{37}$ surface, which agrees well with the estimate from XPS. This result is comparable to the reported data (21−25 Å) obtained from the solid-like octadecyl monolayers grafted on bare Si surfaces.[3b]

Contrary to the observation with the Si(111)−Cl,[5] the reaction of Ge(111)−Cl with alkyllithium reagents does not result in the formation of a satisfactory monolayer. This was evident by the presence of germanium oxide on the derivatized surfaces by XPS in samples prepared in this way. It is possible that cleavage of Ge−C or Ge−Ge bonds may occur by reaction with excess alklyllithium[22] or with hydroxide ion present in trace amounts in the reaction or formed when the reactions are quenched. Further work is underway to understand these differences.

Figure 2 shows IR spectra[23] of the $C_{18}H_{37}$-terminated Ge(111) surface. The symmetric and antisymmetric CH_2 stretching modes have absorption maxima at 2849 and 2917 cm^{-1}, respectively. These frequencies which are shifted 6−8 cm^{-1} from those in an isotropic liquid are generally considered to be diagnostic for the formation of a closely packed monolayer with a large proportion of alkyl chains assuming an essentially all-trans conformation.[3,7,24,25] The CH_2 twisting mode at 1178 cm^{-1} and the scissor mode at 1462 and 1472 cm^{-1} also are observed.[26] IR spectra of the Ge(111)CH_2CH_2R (R = C_6H_5 or CH=CH_2) clearly show C−H stretching in the alkenyl/aryl region above 3000 cm^{-1}. The lack of absorption above 3300 cm^{-1} is expected for a surface with little or no surface-bound water or hydroxyl groups.

The alkyl monolayers impart a significant stability toward oxidation of the Ge surface as evidenced by both IR and XPS measurements. The positions and intensities of absorptions due to the methylene stretch and the XPS C(1s)/Ge(3d) ratio of the Ge(111)−$C_{15}H_{31}$ surface did not change after 5 days of exposure to air or after immersing the surface in boiling water (30 min) or aqueous 20% HCl (10 min). Immersion into boiling chloroform followed by boiling water (1 h)[27] led to a 30% decrease of the IR intensity. These results are significant in terms of the passivation of Ge surfaces, since germanium oxide is susceptible to moisture corrosion which degrades the electronic properties of the surface (in sharp contrast to silicon oxide which provides ideal passivation of the Si surface).

In conclusion, the formation of densely packed long chain alkyl monolayers on the Ge(111) surface is a new addition to the family of monolayers on semiconductor surfaces. Close-packed films are only observed when the reactions are carried out with Grignard reagents. In contrast to reactions with Si(111)−Cl surfaces, organolithium reagents did not produce satisfactory monolayers. The facile integration of alkyl, aryl, and olefinic groups, together with the robustness of the films, opens new approaches to the passivation and functionalization of the Ge(111) surface. Further work on the structure and formation of the functionalized monolayers is underway.

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Supporting Information Available: Experimental details (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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