Preparation of Atomically Smooth Germanium Substrates for Infrared Spectroscopic and Scanning Probe Microscopic Characterization of Organic Monolayers

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The suitability of antimony-doped germanium crystals for use as infrared attenuated total reflection wave guides and conducting substrates for scanning tunneling microscopic imaging of absorbed organic monolayers has been evaluated. We have used repetitive ion bombardment followed by resistive heating of a germanium crystal under ultrahigh vacuum conditions to produce large, atomically flat regions on a Ge(111) crystal face. Through the combined use of STM, Auger spectroscopy and low-energy electron diffraction, we have demonstrated that monolayer quantities of tellurium electrochemically deposited onto the Ge surface dramatically reduce the rate of surface oxidation and permit the use of germanium crystals as STM substrates in air. The first STM images acquired in air with Ge as the conductive substrate are reported. No degradation of IR spectral quality occurs when using the Te-covered, Sb-doped Ge crystals as ATR elements. These findings suggest that Te-coated, atomically flat, low-resistivity Ge substrates are suitable for both IR spectroscopic and STM imaging of organic monomolecular films.

Introduction

Crystalline germanium is a semiconductor material with the crystal structure of diamond and a lower melting point and smaller bandgap (by 0.47 eV) than silicon. The structural and electronic properties of germanium and silicon surfaces are of interest due to the importance of these materials in the semiconductor and optoelectronics industries.[1] The surface structures for the low-index planes of Ge single crystals have been thoroughly investigated.[2,3] The three-fold symmetric Ge(111) surface undergoes reconstruction to the (2×1) surface structure upon cleavage at room temperature and to the $c(2 \times 8)$ surface structure upon annealing at 100 °C. Surface reconstructions result in decreased surface free energy and reactivity.

In addition to its optoelectronics applications, germanium is widely used in spectroscopic applications. High-purity, optical quality germanium is readily available and has enabled Ge to be widely used as an attenuated total reflectance (ATR) crystal material in infrared (IR) spectroscopy. In particular, Ge has been extensively used as a substrate for IR studies of monomolecular films.[4−8]

The focus of our current research is the characterization of organized, two-dimensional monomolecular structures at interfaces in their native aqueous environment.[4−13] Our immediate aim is the development of an integrated approach permitting infrared spectroscopic measurements

and scanned probe imaging to be performed on the same monomolecular film bound to a single substrate. Vibrational spectroscopy is a powerful tool for the study of ultrathin organic structures at interfaces; however, the information obtained is of a macroscopic, surface-averaged nature. Scanning probe microscopies (*i.e.*, STM and AFM) are powerful methods for imaging the morphology and topology of surfaces at atomic resolution and provide information on the real space, two-dimensional structure of monolayer surfaces. Thus, the potential advantage in combining these two powerful methods for studying ultrathin films provides a strong incentive to find a common substrate.

A necessary requirement for combining the IR/STM techniques is the selection of a substrate that is both IR transparent and electrically conductive. We propose using germanium for this purpose. The problems associated with using normal, optical quality, ATR-type germanium crystals for combined IR/ATR applications are 3-fold: (1) high purity, optical quality germanium crystals are typically highly resistive (~50 Ω cm), rendering them unsuitable as a conducting substrate for many STM applications. Doping germanium with extra (extrinsic) charge carriers is a common method of enhancing its conductivity. (2) Germanium used for infrared spectro-

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scopic purposes is polished to an average surface roughness of ~0.20 μm, acceptable for spectroscopic applications but unacceptable for tunneling microscopy. (3) Under ambient conditions, germanium forms a thin, disordered, nonconducting oxide layer on the surface that increases surface roughness and resistivity. Indeed, STM measurements taken on a clean Ge(111) surface during exposure to oxygen at ambient temperature indicate that oxidation proceeds by random nucleation at grain boundaries rather than at defect sites.[14,15] Continued exposure results in rapid expansion of the oxidized regions and the formation of a disordered structure.

Therefore, for germanium ATR crystals to be suitable as substrates for the STM imaging of adsorbed films, methods must be found to (a) remove its native oxide layer, (b) produce large, atomically flat faces, and (c) prevent subsequent air re-oxidation of the clean and ordered surface. In this report, we describe a protocol for preparing germanium ATR crystals with atomically flat regions resistant to air oxidation, thus enabling them to be used as both an attenuated total reflectance wave guide and a scanning probe microscopy substrate. This method produces well-ordered germanium surfaces via cycles of ion bombardment and annealing of single-crystal Ge ATR elements in an ultrahigh vacuum (UHV) environment, followed by electrochemical deposition of monolayer quantities of tellurium (in an antechamber at ambient pressure). The tellurium monolayer acts to impede reoxidation of the surface upon removal of the crystal from the UHV environment. Scanning tunneling microscopic (STM) images of large, well-ordered, atomically flat regions at atomic resolution have been obtained from these substrates for time periods as long as 6 h outside the UHV environment. Such images should provide a basis for comparison with those acquired from Langmuir–Blodgett (L–B) monolayer films subsequently deposited on the Te-coated germanium substrate; therefore images from the monomolecular organic film may be easily differentiated from those of the substrate itself. In addition, the leveling of surface roughness accomplished by the ion bombardment/annealing steps should yield high quality L–B film deposits.

Materials and Methods

Materials. Tellurium dioxide (Puratronic, 99.9995%) was obtained from AESAR/Johnson Matthey (Ward Hill, MA) and was used as received. Sulfuric acid blank solutions were prepared with ultrapure water obtained from a Barnstead Nanopure deionization system (Dubuque, IA) and had a nominal resistivity of 18 MΩ cm. Glassware was cleaned in a $K_2Cr_2O_7/H_2SO_4$ solution and copiously rinsed with ultrapure water. Tellurium deposition was performed from solutions containing 0.25 mM TeO_2 in 20 mM H_2SO_4. The phospholipid 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) was used as received from Avanti Polar Lipids (Alabaster, AL).

The n-type, antimony-doped Ge(111) substrates used in these studies were obtained from Eagle-Picher (Quapaw, OK) with a specified resistivity of 0.14 to 0.18 Ω cm. The crystals were cut into parallelograms of dimensions 50 × 10 × 2 mm with the ends cut diagonally at a 45° angle. The crystals were polished by Semiconductor Processing Co. (Boston, MA) to 5 Å average smoothness and a 5 μm flatness. A tungsten wire was spot welded to a notch on the end of the crystal and provided electrical contact for both the electrochemical and thermal annealing experiments.

Methods and Instrumentation. The germanium sample surface was reproducibly cleaned and ordered in a UHV surface analysis instrument through repetitive cycles of Ar^+ ion bombardment and resistive heating. This procedure typically

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involved a 0.5–1.0 h ion bombardment step (3–8 μA crystal current) followed by a 10–20 min annealing (5 V, 13 A). Surface cleanliness and order were subsequently verified by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), respectively. Electrochemistry was carried out in an antechamber coupled directly to the UHV surface analysis instrument in order to avoid any exposure to air. Potentials were measured *vs* Ag/AgCl (1 mM KCl).

The UHV surface analysis instrument incorporated optics for AES, LEED, and thermal desorption spectroscopy and has been previously described in detail.[16] LEED experiments were performed using a set of four grid optics (Perkin-Elmer). AES was performed using a cylindrical mirror electron energy analyzer (CMA, Perkin-Elmer). AES experiments used a 1 mm² beam size with a 2.5 μA beam current at 3 kV.

Infrared spectra of monolayer films were acquired using a Digilab FTS-40 Fourier transform infrared spectrometer (Bio-Rad, Digilab Division, Cambridge, MA) equipped with a narrow band, liquid-N_2-cooled HgCdTe detector (Infrared Associates, Orlando, FL) at 4 cm^{-1} resolution with triangular apodization and one level of zero filling. The Ge crystals were mounted in a 4X ATR beam condenser (Spectra-Tech, Inc., Stamford, CT) placed within the IR sample compartment. The incoming IR radiation was polarized using an Al wire-grid polarizer on KRS-5 (Model IGP225, Molectron Detector, Inc., Portland, OR). ATR absorbance spectra were obtained by ratioing in absorbance mode the single beam IR spectrum of a monolayer-covered substrate to that of the blank substrate. Typically, 1024 scans were co-added to improve the signal-to-noise ratio. The IR spectra presented herein have not been smoothed.

STM images were obtained with a NanoScope III scanning probe microscope (Digital Instruments, Santa Barbara, CA) operating in height mode and using a Pt/Ir tip. Most images were obtained at a tunneling current of 500 pA, at a bias of −1000 mV, and at a scan rate of 61 Hz. The image presented here has not been flattened or digitally processed in any way.

Preparation of Monomolecular Films. Monomolecular films of the phospholipid DPPC were prepared by standard Langmuir–Blodgett (L–B) methods, as described in detail elsewhere.[6,7] Prior to L–B transfer of the phospholipid monolayers, the Sb-doped Ge substrate was prepared by immersing the atomically flat Ge substrate in 20 mM H_2SO_4 for 30 min. In the case of Sb-doped Ge substrates treated with Te, these crystals were prepared by immersing the atomically flat Ge substrate in a 0.25 mM TeO_2/20 mM H_2SO_4 solution at open circuit for 1 min prior to L–B transfer of the phospholipid monolayer.

Results and Discussion

Cleaning and Ordering of the Germanium Crystal. Polished Ge crystals possess a high degree of roughness on the atomic scale. Attempts to obtain STM images of Ge surfaces in air never achieved atomic resolution under a wide range of scanning conditions, presumably due to the presence of the amorphous, insulating GeO_2 surface layer. Since GeO_2 is known to be soluble in acidic solutions,[23] attempts were made to reduce the amount of surface oxide and degree of surface roughness. However, immersion in a 10 mM H_2SO_4 cleaning solution did not produce a leveling of surface disorder or the ability to obtain atomic scale images.

The surface oxide layer of Ge can be removed electrochemically thereby exposing a clean germanium surface. A typical voltammogram of oxide formation and removal is shown in Figure 1A. Potential cycling negative of the rest potential ($E_{rest} = -0.37$ V) results in reduction of the surface oxide which occurs at a peak potential of −0.68 V; hydrogen evolution occurs at potentials negative of −0.88 V *vs* Ag/AgCl. Scanning the potential positively from hydrogen evolution gave voltammetric features consistent first with the formation of a monolayer of GeO_2 (based on quantitation of charge passed) followed by bulk germanium oxidation (Figure 1A). Oxidation of the

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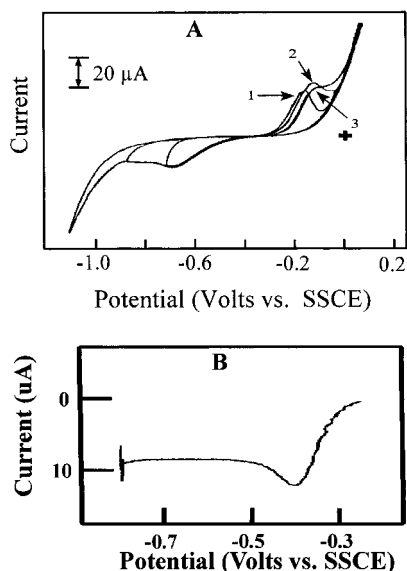
Figure 1. Cyclic voltammograms of a Ge(111) crystal: (A) in 20 mM H_2SO_4 electrolyte solution where the electrode potential was initially scanned negatively from the rest potential (-0.37 V) and three consecutive cycles to increasingly negative potentials are shown; (B) in 0.25 mM TeO_2 + 20 mM H_2SO_4 solution, taken in UHV antechamber at ambient pressure (filled with ultrapure argon) after cleaning and ordering by ion bombardment and annealing. Both voltammograms were obtained using a sweep rate of 5 mV/s, a Ag/AgCl(1 M KCl) reference electrode, and a Au counter electrode.

surface monolayer was observed at a peak potential of -0.15 V (at potential sweep rates less than 5 mV s^{-1}).[17,18] Potential cycling positive of -0.08 V resulted in the oxidation of bulk Ge, whereupon the bulk GeO_2 dissolved into solution due to its increased solubility under these acidic conditions. Long polarization times at potentials positive of -0.08 V did not result in the appearance of a peak (on the subsequent negative potential sweep) associated with reduction of bulk GeO_2; only reduction of a monolayer of GeO_2 was observed.

Germanium crystals were subsequently cleaned and ordered in the ultrahigh vacuum instrument by cycles of argon ion bombardment followed by resistive heating of the Ge(111) crystal. Surface cleanliness and order were subsequently verified using AES and LEED. Figure 2 shows the AES spectrum of the germanium crystal after the annealing step. All transitions observed belong to germanium and provide clear evidence that the surface is free of oxygen and carbonaceous contaminants. A LEED pattern acquired following thermal annealing of the Ge-(111) crystal displayed a sharp (1 × 1) pattern confirming the presence of a well-ordered surface. The annealing temperatures used in these experiments were apparently not high enough to promote the reconstruction of the Ge-(111) to form the $c(2 × 8)$ surface unit cell observed by others.[3] In other experiments with Ge(111), using higher annealing temperatures, we did observe some fractional LEED intensity corresponding to a $c(2 × 8)$ structure.

Deposition of Tellurium on the Ge(111) Crystal Face. Cleaned and ordered crystals were immersed in a 0.25 mM TeO_2/20 mM H_2SO_4 solution at open circuit. The rest potential, initially -0.30 V, shifted to -0.24 V over a 1 min period. When the potential was scanned negatively, the diffusion-limited, bulk deposition of tellurium was observed with a peak occurring at -0.40 V (Figure 1B). Figure 3A depicts the Auger spectrum taken after

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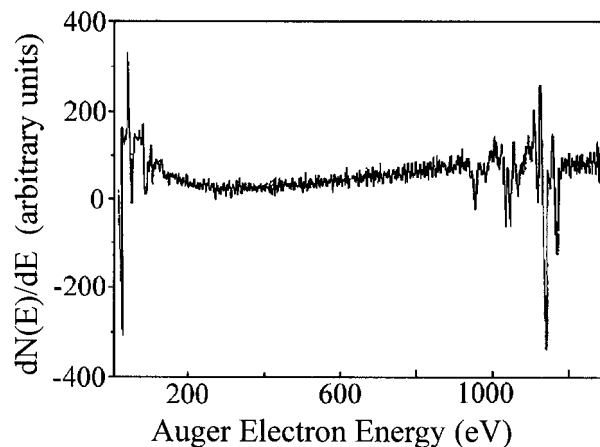

Figure 2. Auger spectrum of a clean Ge(111) crystal face. The signals at ~1200 eV correspond to the LMM transition for germanium.

open-circuit immersion of the Ge(111) crystal in TeO_2 solution. The primary spectral transitions are those of tellurium (~500 eV) and germanium (~1200 eV). Auger spectra were also acquired following more extensive bulk deposition of tellurium at potentials negative of -0.40 V. A comparison of the relative peak intensities obtained for the extensive bulk tellurium deposition on germanium to those for the open circuit deposition reveals that the relative peak intensities in Figure 3A are indicative of Te deposits in the range of one to two monolayers.

Ordered (1 × 1) LEED patterns showing significant diffuse intensity were observed following the open circuit deposition of tellurium on the clean Ge(111) surface. Following thermal annealing, a well-ordered, (2 × 2) LEED pattern was observed. The change in the LEED pattern from a 1 × 1 to a 2 × 2 Te overlayer upon annealing suggests a decrease in the Te coverage. We postulate that Te atoms have been desorbed during the annealing step. The Auger spectrum obtained after open circuit Te deposition on Ge(111) and thermal annealing indicates a Te coverage corresponding to $^1/_4$–$^1/_2$ monolayers (Figure 3B). This is in agreement with previous LEED studies involving exposure of Ge(111) surfaces to tellurium vapor.[19]

Auger spectra of the Te:Ge(111) surface were also acquired as a function of time of O_2 exposure from the ambient laboratory environment. For a Ge(111) (2 × 2): Te surface, a 3 min exposure to ambient O_2 resulted in the appearance of an oxygen signal at ~500 eV. The O:Te peak height ratio of 0.91 (at 3 min exposure) increased approximately 30% upon an additional 12 min of exposure. In contrast, the Ge(111) (1 × 1):Te surface exhibited an O:Te ratio of 0.34 (after 3 min exposure) and increased by only 13% upon an additional 12 min exposure. Thus, it appears that although the Ge(111) (1 × 1):Te surface may not be completely passivated, it is more so that the (2 × 2):Te surface.

The topology of the tellurium-coated Ge(111) crystal was determined in air by STM. Large numbers of ordered regions were observed. Figure 4 is a STM image typical of those obtained. The well-ordered nature of the tellurium monolayers formed using the surface cleaning and ordering procedure described above is apparent in this image. High-quality images were obtained for up to 6 h after removal of the crystal from the UHV environment. STM imaging eventually became more difficult, due to a decrease in stability in maintaining either the tunneling

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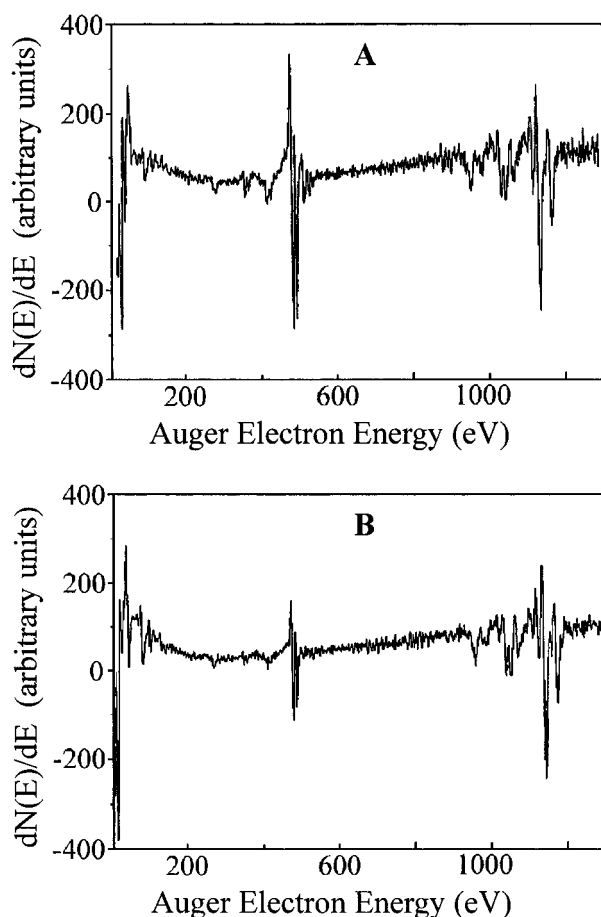
Figure 3. (A) Auger spectrum of a clean Ge(111) crystal face following the electrochemical deposition of Te monolayers. The signals at ~1200 eV correspond to the LMM transition of germanium while the doublet at ~500 eV corresponds to the MNN transition of tellurium. (B) Auger spectrum of a clean Ge(111) crystal face following the electrochemical deposition of Te monolayers and thermal annealing.
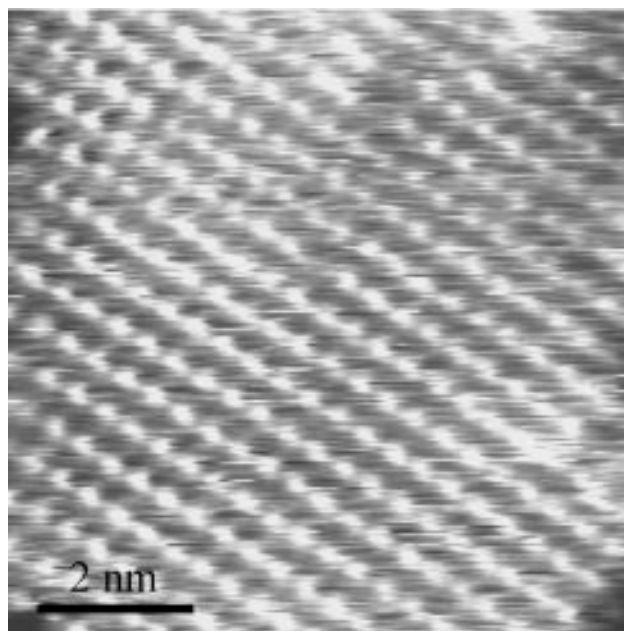

Figure 4. STM image obtained in air of the surface of the Ge(111) crystal face following the electrochemical deposition of Te monolayers. This image was acquired in height mode at a bias of −1.0 V, a setpoint current of 500 pA, and a scan rate of 61 Hz.

current or voltage. It is interesting to note that stable imaging could be reacquired after simple reimmersion of the crystal into the TeO₂ solution for a few minutes.

Sectional and Fourier analysis of STM images gave unit cell dimensions of $a = 4.2 \pm 0.1$ Å, $b = 5.0 \pm 0.2$ Å. The interatomic spacing on a clean Ge(111) surface is 2.45 Å. Thus, the Te unit cell corresponds to a Ge(111)−p(2 × √3):Te lattice structure (also known as $c(4 \times 2)$:Te). Since this structure differs from the 2 × 2 lattice determined from our LEED data, we speculate that further adlayer rearrangement occurred upon removal of the crystal from the UHV environment. The gradual oxidation of the surface by prolonged exposure to O₂ provides support for this hypothesis. Tests of this hypothesis are planned.

Our ability to obtain high quality STM images of the tellurium adlayer in air indicates that the tellurium-coated Ge(111) surface is resistant to adventitious oxidation. The small increase in intensity of the Auger lines for oxygen with time are consistent either with oxygen adding to defect sites or step edges in the tellurium monolayer. Therefore, full coordination of all substrate and overlayer atoms probably does not occur in this system. Atomic layers of group V and VI elements on various semiconductor surfaces have been shown to lead to a (1 × 1) structure and complete surface passivation only if all dangling bonds on the substrate surface *and* overlayer atoms are eliminated, resulting in a fully coordinated layer of surface atoms and overlayer atoms.[20] Full coordination *is* predicted to occur for group VI elements on Ge(100)

surfaces.[20] Further studies are planned to investigate the deposition of Te on the other two low-index planes of Ge, *i.e.*, Ge(110) and Ge(100). We anticipate that the protocol described above will also produce atomically flat surfaces resistant to oxidation for both ordered Ge(100) and Ge(110) crystal faces as well.

Infrared Spectra of Organic Films on Tellurium-Coated Ge(111) ATR Crystal. While doping of germanium succeeds in making the Ge crystal more conductive, the optical transmission characteristics of a doped Ge crystal are somewhat reduced relative to the normal, undoped Ge used as ATR elements. To evaluate the impact of the dopant, we have compared the IR spectrum of a DPPC monolayer deposited by the Langmuir−Blodgett technique on a conventional germanium ATR wave guide to the IR spectrum of the monolayer on an Sb-doped Ge-(111) ATR wave guide. Figure 5A depicts the IR spectrum of a DPPC monolayer on a Sb-doped Ge ATR crystal. The major spectral features are the C−H stretching vibrations between 3000−2800 cm⁻¹, the C=O stretching vibration at ~1740 cm⁻¹, the CH₂ scissoring vibration at ~1467 cm⁻¹, and the phosphate headgroup vibrations between 1200−1000 cm⁻¹. The quality of this spectrum is comparable to those obtained on normal, optical-quality Ge ATR crystals.[4−8] Thus, this level of Sb-doping appears to have little effect on the quality of the resulting ATR-IR monolayer spectrum.

Spectral comparisons were made to assess the impact of a tellurium overlayer as well. Figure 5B presents the spectrum obtained for a DPPC monolayer on a Sb-doped, Te-covered Ge substrate. Comparison of the two spectra in Figure 5 reveals that the presence of atomic layers of Te on the Ge crystal has no impact on the quality of the resulting IR monolayer spectrum. The one difference between the two spectra lies in the low frequency portion of the spectrum (between ~1300 and 1000 cm⁻¹). This difference is in the PO₂⁻ region and indicates changes when the phospholipid monolayer film is transferred onto the Te-covered Ge ATR crystal (Figure 5B). These

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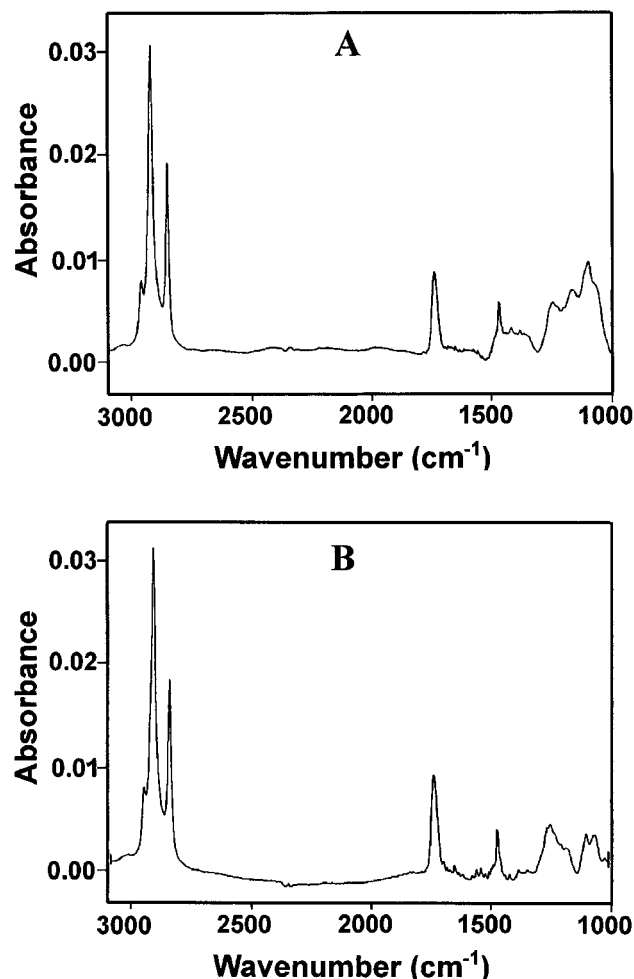
Figure 5. Attenuated total reflectance infrared spectrum obtained on a monolayer of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine deposited on an Sb-doped Ge(111) ATR crystal using Langmuir–Blodgett methods (A) before and (B) after electrochemical deposition of Te monolayers.

differences suggest interaction of Te with the phosphate-containing headgroup of the DPPC monolayer. Such ionic interactions have been shown to lead to changes in the IR phosphate vibrations of phospholipid headgroups.[21,22]

Summary

A method for the preparation of atomically flat, low resistivity germanium surfaces resistant to oxidation is reported. Cyclical UHV ion bombardment/resistive heating produces large, atomically flat areas on the Sb-doped Ge(111) substrate. Deposition of monolayer quantities of Te on the flat Ge substrate retards the subsequent reoxidation of the Ge upon removal from the UHV chamber. We have been able, for the first time, to image the surface of the modified Ge substrate in air using STM. This method enables the use of germanium as a substrate for the scanning probe microscopic characterization of organic thin films.

We have prepared organized monomolecular films on this modified germanium substrate using Langmuir–Blodgett surface chemistry techniques. ATR-IR spectra show little difference in the quality of the monolayer spectrum obtained with this modified Ge substrate compared to normal, optical quality Ge ATR elements. These results illustrate the possibility of using these modified Ge crystals as ATR wave guides in ATR-IR spectroscopic applications.

With this modified Ge substrate, simultaneous IR spectroscopic measurements and STM imaging on the same monomolecular film may be possible. The advantage of this combined approach is that it can unite two very powerful methods for studying ultrathin films. Vibrational spectroscopy has shown itself to be a powerful tool in the study of ultrathin organic structures at interfaces; however, the information obtained is of a macroscopic, surface-averaged nature. Scanning probe microscopies (*i.e.,* STM and AFM), on the other hand, are new and powerful methods for imaging the morphology and topology of surfaces at near-atomic resolution, and have the advantage of providing information on the real-space, two-dimensional structure of monolayer surfaces. Using the modified Ge substrates described in this report, the orientation and molecular conformation of the thin film can be determined by infrared spectroscopy with simultaneous determination of the microdomain structure, spatial distribution, and intrinsic structural morphology using STM/AFM methods. The combination of the two techniques has the potential to significantly improve our understanding of the formation, structure, and reactivity of organized monomolecular films.

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