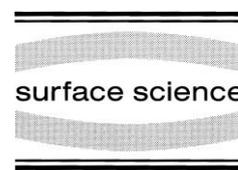




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Structure of a passivated Ge surface prepared from aqueous solution

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Abstract

The structure of a passivating sulfide layer on Ge(001) was studied using X-ray standing waves and X-ray fluorescence. The sulfide layer was formed by reacting clean Ge substrates in $(\text{NH}_4)_2\text{S}$ solutions of various concentrations at 80°C. For each treatment, a sulfide layer containing approximately two to three monolayers (ML) of S was formed on the surface, and an ordered structure was found at the interface that contained approximately 0.4 ML of S. Our results suggest the rapid formation of a glassy GeS_x layer containing 1.5–2.5 ML S residing atop a partially ordered interfacial layer of bridge-bonded S. The passivating reaction appears to be self-limited to 2–3 ML at this reaction temperature. © 2000 Elsevier Science B.V. All rights reserved.

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The chemical and electronic passivation of the surface of semiconductors is vital to their utility for device construction. Truncation of the surface of a crystal induces electronic defect states [1,2] that allow carriers to recombine, and ‘fixed’ charges residing at a semiconductor/insulator interface can hinder performance of a metal–insulator–semiconductor capacitor (and hence preclude construction of a working device) [3]. The predominance of Si for semiconductor devices can largely be attributed to the remarkable passivative

properties of SiO_2 , whereas the poor electrical properties [4] of III–V surfaces and their oxide interfaces have hampered widespread implementation of these semiconductors. An effective passivation treatment should be chemically stable, protect the substrate from oxidation, remove surface-induced [1,2] carrier recombination states, and exhibit a low density of fixed charges. For ease of processing, it is desirable that such a passivation reaction be carried out chemically at atmospheric pressure. Further, it would be convenient if the treatment relied upon a self-limiting reaction, i.e. a process whose kinetics slow down considerably after initial reaction. Of course, these

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criteria are all satisfied by the oxidation of silicon, but oxidation of Ge or III–V substrates does not fulfil these requirements.

Great improvements in the lifetimes of carriers for AlGaAs/GaAs transistors were realized with a passivation scheme in which the GaAs surfaces were sulfided using Na₂S solution [5]. This protocol allowed a 60-fold improvement in the current gain β of the transistor. Studies of the sulfidation of other III–V surfaces, notably InP(001) [6–8], followed, using Na₂S and (NH₄)₂S. Sulfiding was found to remove surface states from the band gap [6] and to slow down deleterious oxidation reactions [7,8]. Later, the sulfidation of a Ge(001) surface using (NH₄)₂S was studied by Anderson et al. [9] using low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). While also motivated by possible passivative applications, this work focused on the structure of the interface, and found that a (1×1) LEED pattern was observable upon insertion in a vacuum chamber.

Since the (001) face of a diamond-structure semiconductor has two dangling bonds per surface atom, a monolayer (ML) of a Group VI element, which will form two covalent bonds, may satisfy all the dangling bonds of the substrate by occupying a bridge site in a (1×1) geometry. Accordingly, it was demonstrated by LEED and XPS that 1 ML of elemental S deposited on Ge(001) in ultrahigh vacuum (UHV) leads to this predicted arrangement [10]. In addition, Te adsorbs on Si(001) [11,12] and Ge(001) [13] with the same local geometry, although stress-relieving defects are present to accommodate the size mismatch between this larger chalcogen and the substrate. For the aqueously sulfided Ge(001) surface [9], the appearance of a (1×1) LEED pattern and results from XPS suggested that these surfaces were similar to the surfaces prepared [10] in UHV. Accordingly, Anderson et al. concluded that the structure of the aqueously sulfided Ge(001) surface contained 1 ML of bridge-bonded S atoms. The sulfided surfaces were also stable in air [9], lending support to the idea that a S-terminated (1×1) surface would be (at least chemically) passivated.

The present paper describes a series of measurements that probe the structure of a Ge(001) sur-

face sulfided in (NH₄)₂S solution. Although our high-resolution X-ray standing wave data support occupation of a bridge site for some of the reacted S, we found that 2.4 to 3 ML of S reacted with the Ge(001) substrate under a wide range of reaction conditions (1 ML = 6.25×10^{14} cm⁻²). We explain our findings with a model of the surface where several layers of amorphous GeS_x are formed by the reaction, and a submonolayer of S occupies ordered bridge sites at the GeS_x/Ge(001) interface. The results are reminiscent of the native oxidation of Si(001).

Experiments were carried out on polished Ge(001) single crystal substrates. As discussed in more detail below, a variety of passivation protocols were used, but generally involved successive degreasing, rinsing in deionized water, HF etching, sulfidation in hot (80°C) ammonium sulfide [(NH₄)₂S] solution, rinsing in either water or methanol, and blow drying.

Coverage calibrations were made by comparison of the X-ray fluorescence from the samples to a S coverage standard. The coverage standard was constructed by evaporating ~ 10 Å of Sb₂S₃ onto a Si substrate, and then capping this layer with ~ 200 Å of Al. This composition was chosen for several reasons. The use of Si and Al as substrate and cap should allow the S content to be measured directly with Rutherford scattering spectrometry (RBS). Moreover, Sb₂S₃ evaporates as a molecule [14], ensuring a stoichiometric film. Since the Rutherford cross-section for Sb is much greater than for S, the use of Sb₂S₃ allowed a more sensitive (if indirect) measurement of the S content. RBS spectra were analyzed by RUMP [15], which found a Sb coverage of $2.1 \pm 0.2 \times 10^{15}$ cm⁻², implying a S coverage of $3.2 \pm 0.3 \times 10^{15}$ cm⁻² (the dominant source of the coverage uncertainty is the uncertainty in the ion stopping power tables used to analyze the RBS spectra [16]). Due to the low atomic number of S, the direct measurement by RBS of the S coverage had large error bars, but the resultant value and uncertainty encompassed the indirect coverage value derived from the Sb measurement.

Both the X-ray fluorescence (XRF) measurements and structural measurements by X-ray standing waves (XSW) were conducted at the

DuPont–Northwestern–Dow consortium's undulator beamline 5ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory. A high-heat-load Si(111) monochromator was used to select a 7 keV beam from the undulator output, and then the beam was further monochromated and dispersion-matched to the Ge(001) substrate using a Si(004) two-bounce channel-cut crystal. The X-ray flux through a 3 mm wide by 1 mm high slit placed just upstream of the sample was approximately 10^{12} photons/s. Using a vacuum chuck, the samples were gently held on a four-circle diffractometer inside a thin polyethylene bag flushed with He (to eliminate Ar fluorescence and reduce absorption of the 2.3 keV S fluorescent K X-rays). An energy-dispersive Ge detector optimized for soft X-rays was used to detect the S XRF.

Coverage measurements were conducted by comparing the S fluorescence from the Al/Sb₂S₃/Si standard with that from the S/Ge samples under identical conditions. (The absorption length of the S X-rays in Al is 2.4 μm , so that absorption in the 200 \AA Al capping layer of the standard was negligible.) The XSW measurements were made by scanning the sample through the ~ 50 μrad wide Ge(004) Bragg reflection with a microstepping motor driving the ω rotational stage of a Huber 422 two-circle goniometer. At each angular step in the scan, an X-ray fluorescence spectrum was collected using the Ge detector described above and the diffracted X-ray intensity was measured simultaneously using an ion chamber. The XSW technique as applied to surface structural determinations has been reviewed by Zegenhagen [17].

A typical XSW scan from a (NH₄)₂S-reacted Ge(001) sample is shown in Fig. 1. The S fluorescent yield (normalized to unity for off-Bragg angles) is represented by the open circles, while the incident X-ray reflectivity is represented by the closed circles. Best fits to the reflectivity (using dynamical diffraction theory) and the S fluorescence yield are shown by the smooth lines. For this sample, we found values of $P_{004} = 0.90 \pm 0.01$ and $F_{004} = 0.15 \pm 0.02$.

The results from a series of XRF and XSW measurements are summarized in Table 1. These

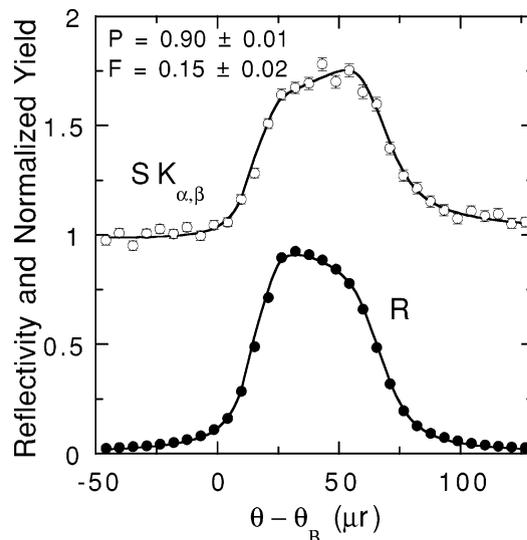


Fig. 1. XSW scan for the (004) diffraction planes for sulfided Ge(001) (sample A). The S coverage is 2.4 ML. The solid lines are best fits to the reflectivity R and S fluorescence yield using dynamical diffraction theory.

samples were all prepared by the following procedure. Syton polishing was followed by rinsing in water, degreasing in trichloroethane and acetone with ultrasonic agitation, and rinsing in deionized water. The samples were etched in 29% HF solution (3:2::HF:H₂O, using 48% HF solution), and became hydrophobic. Next, they were directly transferred to a beaker of (NH₄)₂S solution held at 80°C. As indicated in Table 1, sample A was immersed in undiluted, 24 vol% (NH₄)₂S aqueous solution, sample B was immersed in (NH₄)₂S solution diluted to 4 vol% with water, sample C was immersed in (NH₄)₂S solution diluted to 0.4 vol% with water, and sample D was immersed in (NH₄)₂S solution diluted to 0.1 vol% with methanol. The samples were allowed to react in solution for 20 min, then rinsed several times in methanol with ultrasonic agitation, and finally blown dry with difluoroethane. In addition to those reported in Table 1, the values of P_{004} and F_{004} reported for sample A were closely reproduced in several other preparation trials using undiluted (NH₄)₂S solution (24 vol%) followed by rinsing in water. (Coverage measurements were not conducted for these samples.)

Table 1
Representative S coverages and XSW results for indicated surface preparations of S/Ge(001)

| Sample | (NH ₄) ₂ S solution | θ (ML) | P_{004} | F_{004} | θ_c (ML) |
|--------|--|---------------|-------------|-------------|-----------------|
| A | 24% in H ₂ O | 2.4 ± 0.3 | 0.90 ± 0.01 | 0.16 ± 0.01 | 0.39 ± 0.05 |
| B | 4% in H ₂ O | 2.3 ± 0.3 | 0.90 ± 0.01 | 0.15 ± 0.01 | 0.35 ± 0.05 |
| C | 0.4% in H ₂ O | 1.9 ± 0.3 | 0.90 ± 0.01 | 0.18 ± 0.01 | 0.35 ± 0.06 |
| D | 0.1% in methanol | 2.9 ± 0.3 | 0.88 ± 0.01 | 0.13 ± 0.01 | 0.38 ± 0.05 |

The last column in Table 1 reports the coherent coverage θ_c for each sample. The coherent coverage, which is defined as the product of the coherent fraction and the total coverage, $\theta_c = F_{004}\theta$, is a measure of the total number of S atoms (in ML) that are located at a position in registry with the Ge substrate.

The LEED and XPS results of Anderson et al. [9] suggested that only a single monolayer of S exists at the chemically reacted surface, and that this monolayer passivates the Ge(001) surface from further chemical activity. The S monolayer was thought [9] to be similar in structure to one prepared by deposition of elemental S on clean Ge(001) in UHV. In that structure, the S atoms occupy bridge positions in a (1 × 1) arrangement, leading to only one surface-related Ge oxidation state [10]. Our data are not consistent with this model for the (NH₄)₂S-passivated surface. Instead, we propose that a disordered (glass-like) GeS_x layer resides atop a partially ordered interfacial layer.

Our XRF results indicate that, under a wide range of concentrations of (NH₄)₂S solution, 2–3 ML of S are reacted with the Ge substrate. Thus, there does appear to be a self-limiting reaction of Ge sulfidation in (NH₄)₂S solution, but the reacted layer is more extensive than the 1 ML suggested by the results of Anderson et al. [9]. The sulfidation of Ge(001) is instead reminiscent of the oxidation of Si(001), which forms a thin native oxide limited to ~15 Å under a wide range of oxidation conditions at room temperature.

Perhaps the most striking result reported in Table 1 is the consistency of the coherent coverage θ_c under a wide variety of preparation conditions. Even though the concentration of the (NH₄)₂S solution was varied by a factor of 240, the resultant θ_c varied by only 10%. Thus, the structure of

the reacted layer that is correlated to the Ge substrate is highly regular and repeatable. The consistency of this result, despite the variation in the total S coverage, suggests that the ordered S population is located at the Ge interface.

The XSW results reported in Table 1 are consistent with a S submonolayer located at a bridge-like position. The sum of covalent radii [18] for S and Ge would place a bridge-site S atom at an adsorption height of 1.25 Å above the last Ge layer. That position is consistent with our XSW results, which show that a S population of approximately 0.4 ML is located at an adsorption height of 1.27 ± 0.02 Å. In this model, the remaining 1.5 to 2.5 ML of S occupy positions uncorrelated with the Ge lattice, consistent with bonding in a glassy network of GeS_x.

Our data are also consistent with a closely related model of the surface layer. The ordered S component could represent the transition from a locally ordered, crystalline phase of GeS_x residing at the interface and an amorphous GeS₂ layer (that would be expected for thick layers). An appealing picture is that this transition results from the creation of a partially ordered (perhaps epitaxial) GeS_x compound layer whose registry with the substrate is lost within a few angstroms, presumably due to different lattice constants and the proclivity [19] of Ge and S to form glassy structures. This model would be reminiscent of an often-proposed picture of the intensely studied oxidation of Si: there have been recurring reports (see e.g. Ref. [20]) of a partially ordered interfacial SiO_x compound whose order completely breaks down for SiO₂ layers more than several angstroms thick.

While we have found significant differences between the structure of a (NH₄)₂S-passivated Ge(001) surface and that reported by Anderson et al., several of our findings are consistent with

their results. In both studies, a self-limiting, passivating reaction was found, rendering the surface stable in air. Both studies lend support for at least a partial layer of bridge-bonded S at the Ge surface. However, we find that 2 to 3 ML of S reacts with the Ge substrate over a wide range of $(\text{NH}_4)_2\text{S}$ concentrations and two different solvents. Our results suggest that the sulfidation of Ge more closely resembles the oxidation of Si than the adsorption of S on Ge in UHV.

We cannot, however, specify with the present data the origin of the differences between this study and that of Anderson et al. [9]. Although every effort was made to replicate the experimental conditions of that study, we found significant differences in the results. The total S coverage in our samples exceeded that suggested by LEED and XPS for the specimens of Anderson et al. Thus, it seems likely that Anderson's samples were characterized by a fairly ordered S interface of approximately monolayer thickness, while our samples exhibited a similar interface but covered by a thin, glassy GeS_x layer. Possible explanations for these differences include: the density of surface Ge steps, the miscut of the substrate, or different impurities present during the sulfidation processes.

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