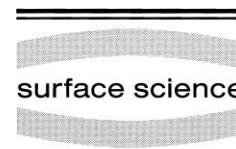




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## Preparation of clean and atomically flat germanium(001) surfaces

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### Abstract

A two-part procedure for preparing clean and atomically flat Ge(001)-(2 × 1) surfaces is presented and characterized. The ex situ part of the procedure consists of a wet chemical treatment followed by exposure to ultraviolet-generated ozone. The in situ part of the procedure consists of outgassing for several hours in ultrahigh vacuum followed by flash annealing. Scanning tunneling microscopy shows that the surfaces are flat on the > 50 nm length scale and that atomic resolution can be achieved. X-ray photoelectron spectroscopy shows the formation and removal of an oxide layer. It is estimated that approximately 0.02–0.03 monolayers of carbon are present at the annealed surface. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Germanium; Low index single crystal surfaces; Scanning tunneling microscopy; X-ray photoelectron spectroscopy

The preparation of clean and smooth Ge(001)-(2 × 1) surfaces has been hampered by the fact that there is a poor lattice match between GeO<sub>2</sub> and germanium. This mismatch leads to an inhomogeneous oxide layer. The oxide layer is also thin and water soluble, which permits contamination to reach the Ge/GeO<sub>2</sub> interface. Once at the Ge/GeO<sub>2</sub> interface, the contamination is difficult to remove. To prepare clean surfaces, the most commonly used method has been ion sputtering. While producing very clean surfaces, ion sputtering has a number of possible disadvantages as com-

pared with resistive heating. For example, it is difficult to clean large areas, is much more time-consuming, and can result in degradation of the smoothness of the surface. This last point is particularly important when preparing surfaces for surface-sensitive measurements, such as scanning tunneling microscopy (STM), X-ray scattering and high-resolution electron diffraction, which rely on an atomically smooth vacuum/solid interface.

There are literature reports of preparation methods using resistive heating [1–5]. In these methods a passivation layer is formed on the surface by an ex situ treatment, followed by removal of the passivating layer in situ. Two different passivation layers have been reported in the literature. These methods leave the Ge(001) surface terminated with sulfur by (NH<sub>4</sub>)<sub>2</sub>S treatment [5] or with

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oxygen by the growth of  $\text{GeO}_2$  layers [1–4]. Growth of  $\text{GeO}_2$  is the preferred method because growth of  $\text{GeO}_2$  is better understood. Preparation of  $\text{GeO}_2$  layers falls under two categories: oxide formation by exposure to ultraviolet (UV)-generated ozone [3,4] or oxide formation by wet processing [1,2,4]. We have prepared samples using a procedure that combines both types of oxide formation. The results of this combined methodology are presented in this letter.

The samples used in all of our experiments were cut from Ge(001) wafers purchased from Eagle Picher and were *p*-doped with a resistivity of 0.10–0.39  $\Omega$  cm. The wet chemical treatment portion of our preparation method follows the recipe originally proposed by Okumura et al. [1]. This wet chemical treatment was chosen in part because it works well in the normal air environment of a laboratory. The sample was initially degreased by soaking in electronic grade methanol. It was then stripped of its oxide layer by dipping in HCl (36%)/ $\text{H}_2\text{O}$  1:4 for 30 s and re-oxidized by dipping in  $\text{H}_2\text{O}_2$  (30%)/ $\text{H}_2\text{O}$  1:10 for 60 s. The process of stripping the oxide layer and reforming the oxide layer was repeated three times. To prepare the final oxide layer, the surface was dipped in HCl/ $\text{H}_2\text{O}$  1:4 for 30 s to remove the oxide one last time, and then dipped in  $\text{NH}_4\text{OH}$  (28%)/ $\text{H}_2\text{O}_2$  (30%)/ $\text{H}_2\text{O}$  1:2:20 for 60 s. The procedure up to this point is the same as proposed by Okumura et al. [1]. The samples were then transferred directly into a small beaker of electronic grade methanol. We found that if we allowed the sample to dry in the laboratory atmosphere spots of contamination were clearly visible. Any methanol left on the surface was removed by lightly pulling lens paper across the surface, using capillary action to remove the residual fluid.

The samples were mounted in a sample holder and exposed to the UV/ozone treatment as quickly as possible after completion of the wet chemical treatment. A low-pressure mercury arc lamp was used to generate the ozone. Typical exposure times were 15 min. Immediately after exposure to ozone the mounted samples were transferred to an ultra-high vacuum (UHV) chamber via a turbo-pumped load-lock system.

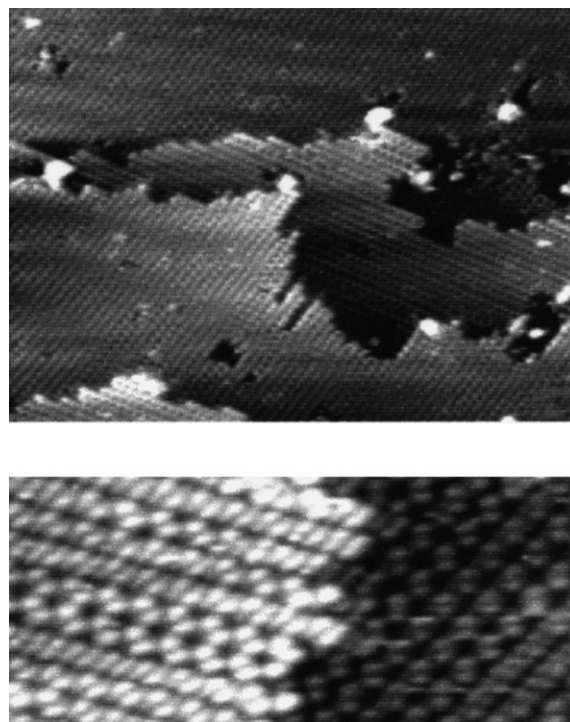


Fig. 1. Scanning tunneling microscopy images of the Ge(001)-(2  $\times$  1) surface. The top image is 520  $\text{\AA}$   $\times$  380  $\text{\AA}$  and the bottom is 140  $\text{\AA}$   $\times$  60  $\text{\AA}$ . The images were acquired with a sample bias of  $-2.2$  V and a tunneling current of 150 pA.

The in situ preparation consisted of outgassing the samples at 573 K for at least 5 h followed by flash annealing to 1000 K while maintaining a chamber pressure of  $< 5 \times 10^{-10}$  Torr. Shorter time periods for outgassing were not investigated but might well be effective. The outgassing is used to remove high-molecular-weight carbon species that deposit on the sample during the time in atmosphere. Indeed, X-ray photoelectron spectroscopy (XPS) studies showed a large decrease in the carbon signal after outgassing.

Fig. 1 shows two representative STM images of the annealed Ge(001)-(2  $\times$  1) surface. The top image shows an area 520  $\text{\AA}$   $\times$  380  $\text{\AA}$ ; dimer rows are clearly visible as are three step edges running horizontally across the surface. Well-ordered, flat terraces are easily observed over the length scale of the image. The lower image shows an area 140  $\text{\AA}$   $\times$  60  $\text{\AA}$ ; the individual dimers on the surface are clearly resolved and a step edge can be seen

running vertically through the image. There are several protrusions visible in the top image. The chemical nature of these protrusions is not known. Carbon contamination on silicon results in the formation of silicon carbide protrusions on the surface [6]. Carbon does not, however, form a carbide with germanium [7]. Since STM gives only limited chemical information, we turned to XPS to better determine the cleanliness of the surface.

The XPS Ge(3d) and C(1s) spectra before and after removal of the protective oxide layer are shown in Fig. 2. The spectrum before annealing (dashed line) was taken after outgassing at 573 K for 5 h. The Ge(3d) XPS spectrum of the oxidized surface (dashed line) shows two peaks at 29.5 and 32.6 eV. The peak at 32.6 eV arises from the GeO<sub>2</sub> layer. This peak is removed by annealing to 1000 K, as evidenced by the disappearance of the peak in the spectrum containing the solid line. The small shift of 0.5 eV in the bulk germanium signal is attributed to a 0.5 eV change in band bending. One can clearly see from the Ge(3d) spectra that we have created protective GeO<sub>2</sub> layers and, in turn, have completely removed them. Additionally the O(1s) spectra, not shown, show complete removal of the oxide layer after annealing. The C(1s) spectra both before and after annealing show the presence of some carbon. To help quantify the amount carbon on the surface, we exposed the nominally clean surface to 300 L of cyclopentene at room temperature. In other experiments [8], to be published elsewhere, we found that cyclopentene adsorbs to the surface through a [2+2] cycloaddition reaction with a packing density of two cyclopentene molecules for every three germanium dimers, resulting in 10 carbon atoms for every six germanium atoms. The integrated area of the carbon signal on the nominally clean surface referenced to the Ge(3d) signal is 591, and the integrated area of the carbon signal on the cyclopentene-saturated surface referenced to the Ge(3d) signal is  $11.0 \times 10^3$ . The carbon surface coverage for the 'clean' surface, within the probe depth of XPS, is 0.09 monolayers (ML). This result is most likely an overestimation of the amount of carbon at the surface because the escape depth of electrons from C(1s) orbitals is between 10 and 20 Å [9]. We estimate, based on photo-

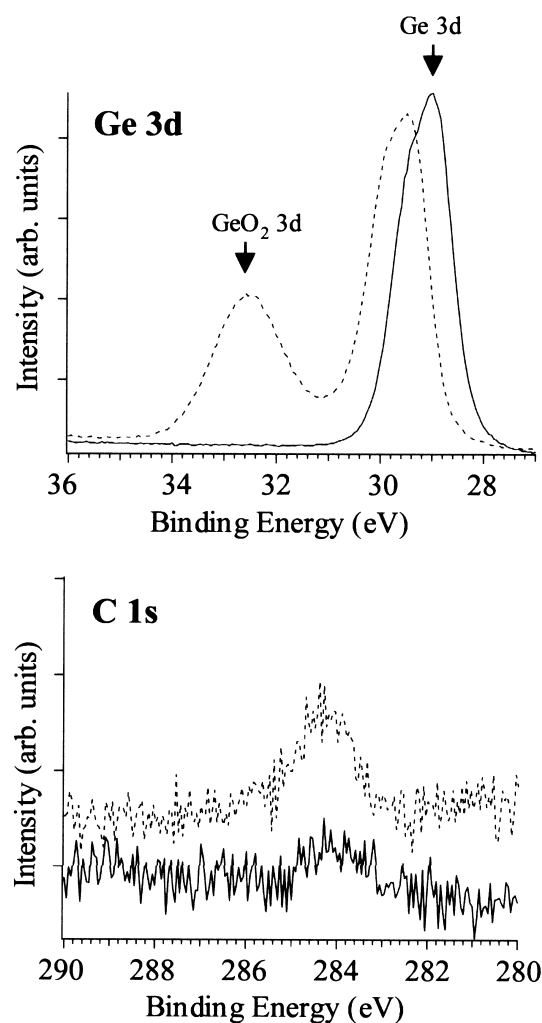


Fig. 2. Ge(3d) and C(1s) X-ray photoelectron spectra of the surface before and after removal of the oxide layer. The dashed line indicates the spectrum acquired before annealing while the solid line indicates the spectrum acquired after annealing.

electron escape depths and the number of bright protrusions observed by STM, the coverage of carbon at the outermost surface layer to be approximately 0.02–0.03 ML.

We made numerous efforts to remove the residual carbon, but to no avail. Several variations of the method were tried. These included: increasing the number of etch cycles from three to four, dipping in the HCl/H<sub>2</sub>O 1:4 mixture for 60 s instead of 30 s, and exposure to ozone for up to

30 min. None of these variations had any significant effect. Annealing temperatures from 900 K to 1000 K were also investigated. It was possible to resolve atoms on all the surfaces prepared over this temperature range. It should be noted that the upper end of this temperature range produced somewhat smoother surfaces as measured by STM. There are several possibilities for the source of residual contamination. The germanium wafer could contain trace impurities of carbon. The acids used to clean the wafer may have contained some contamination resulting in some residual carbon being left at the Ge/GeO<sub>2</sub> interface. While not perfectly clean, the samples were clean enough to easily resolve atoms with STM. They were also clean enough to enable experiments looking at the adsorption of cyclic unsaturated alkenes on the surface with STM [8].

Our results can be compared with the previous work of Zhang et al. [3]. Their sample preparation involved a degreasing procedure, followed by a deionized water rinse and UV/ozone oxidation. Our efforts at reproducing this procedure always left carbon at the germanium surface after oxide removal in ultrahigh vacuum. The carbon concentration was consistently 5 to 10% of a monolayer [10]. The carbon can be removed by argon-ion sputtering, but then the sputtering damage needs to be removed by annealing and germanium deposition, by digermene for example [10]. It is believed that the carbon contamination is a result of the final water rinse, since the water will dissolve the protective GeO<sub>2</sub> layer, which is subsequently regrown in the laboratory environment where hydrocarbons can also react at the germanium surface. The UV/ozone exposure at this point would leave the carbon at the germanium interface with an oxide layer on top of it. Similar observations have been made by several investigators [3,4,11].

Gan et al. [4] also examined the effectiveness of germanium surface preparations. The best results were obtained with an HF etch followed by oxidation with an H<sub>2</sub>O<sub>2</sub> dip, provided the treatment was carried out in a cleanroom.

We believe that the effectiveness of our procedure lies with the fact that a new Ge/GeO<sub>2</sub> interface is created and does not require the use

of a cleanroom. The formation of a new interface is necessary because GeO<sub>2</sub> is water soluble. The consequence of this water solubility is that by the time the commercially bought wafers are used for experiments they are contaminated, not only on top of whatever oxide might remain but also on the bare surface. As mentioned earlier in this letter there have been two methods reported in the literature for growing GeO<sub>2</sub> layers. We found that neither of these methods prepared surfaces that could easily be imaged using STM. Ultimately we found that the surfaces that looked smoothest in scanning tunneling microscopy images were those which were prepared using a combination of both methods. The motivation for starting with the wet process is that it results in the surface being etched and probably does a better job of removing surface contamination than ozone does. While the wet treatment does create an oxide layer it is probably not completely impermeable, due to the fact that the wet process involves water. Thus we then subjected the samples to ozone, which not only helps to fill in any holes in the oxide, but also has the additional effect of volatilizing any low-molecular-weight carbon species that are still left at the surface.

In conclusion, we have presented a relatively quick and easy method for preparing Ge(001)-(2 × 1) surfaces. The process sequence is:

1. repetition of chemical oxide formation by H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O 1:10 treatment and oxide etching by HCl/H<sub>2</sub>O 1:4 solution;
2. protective oxide formation by NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O 1:2:20 treatment and UV/ozone treatment; and
3. outgassing of the wafer at 573 K and flash annealing at 1000 K in UHV.

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