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Scanning-tunneling-microscopy studies of the oxidation of Ge(111)-$c(2\times8)$

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Scanning tunneling microscopy was employed for an investigation of the oxidation process of the Ge(111)-$c(2\times8)$ surface at room temperature. Images of the same area of the surface were obtained for various exposures of oxygen. The results show that the oxidation proceeds by nucleation followed by expansion of the oxidized area.

Scanning tunneling microscopy (STM) has become a powerful tool for surface structural studies. An important application is the observation of dynamic surface processes during adsorption and reaction. Examples of previous such studies include the oxidation of Si(111)-(7×7),[1-3] the annealing of Au(111) at room temperature,[4] and the changes of surface structure of an electrode in an electrolytic cell.[5] The present work is a study of the oxidation of the Ge(111)-$c(2\times8)$ surface. Since Ge and Si belong to the same column in the Periodic Table, it is natural to expect that the surfaces of these two crystals will show similar oxidation behaviors. A comparison will be made between the results from the present work and the results of an earlier study of the oxidation of Si(111)-(7×7). This comparison is useful for developing an idea about the trend of the chemical behaviors of elemental-semiconductor surfaces.

The STM experiments were performed in a vacuum chamber with a base pressure in the 10^{-11}-torr range. The microscope used in this study has been described previously.[1] The Ge(111) sample used was cut from a single-crystal ingot, oriented by x-ray Laue diffraction, and mechanically polished on a water-lubricated pad loaded with alumina powder to a mirror finish. The sample was chemically etched in a CP-4 solution just prior to insertion into the vacuum chamber. Several cycles of sputtering with 1-keV Ar^+ ions at 900 °C followed by annealing at the same temperature for a few minutes resulted in a very sharp $c(2\times8)$ diffraction pattern. Sample heating was achieved through resistive heating by passing a current through the sample itself. After thermal annealing, the sample was allowed to cool down for at least six hours to near the room temperature before the oxidation experiment. During the STM measurement, a given region on the sample surface was repetitively scanned while oxygen was allowed to enter into the vacuum chamber via a precision leak valve. The oxygen pressure could be monitored by a nude ion gauge and by reading the ion current of the ion pump on the system. To avoid ionizing the oxygen the ion gauge remained off during the course of the STM measurement. The tips used in this experiment were made from tungsten wires with a diameter of 0.75 mm following the techniques employed for making field-emission tips. These tips were then cleaned and electroplated with a layer of gold to reduce their sensitivity to oxygen exposure during the experiment.

The clean Ge(111) surface has been examined by STM before.[6,7] Depending on the preparation conditions, $c(2\times8)$ and (2×2) domains with varying sizes can be seen. The $c(2\times8)$ reconstruction is usually the dominant one. The $c(2\times8)$ atomic structure can be described by the simple adatom model.[6] In this model, each $c(2\times8)$ unit cell of eight sites contains two adatoms and two rest atoms, and the adatoms and rest atoms each have a dangling bond. There is some electronic charge transfer from the adatoms to the rest atoms as a result of the reconstruction. Thus, STM pictures taken on this surface with a positive (negative) sample bias show predominantly the adatoms (rest atoms). Furthermore, the unit cell appears "buckled" such that the two adatoms (rest atoms) in the unit cell may show significantly different heights depending on the experimental conditions.[7]

Figure 1 shows a typical grey-scale image taken from our clean Ge(111)-$c(2\times8)$ over a large area. The picture is somewhat distorted by thermal drift. The sample bias used was $+2.0$ V, and each protrusion represents an adatom. The surface is seen to be mostly $c(2\times8)$ with occasional faults and some defects. The nature of the various kinds of defects is not known. Since the STM images reflect a complicated convolution of both the electronic and topographic effects on a surface, the images alone are not sufficient for an identification of the nature of the defects. The defects may also involve foreign atoms, but it is still impossible for STM to identify atomic species.

Figure 2 shows the results of a series of scans over a small area. Because of thermal drift, it is difficult to keep the scanning over exactly the same area. We simply took larger scans, and by comparing land marks on the pictures, such as features derived from defects, a frame corresponding to a given area is cut from each picture. The four pictures shown in Fig. 2 have been prepared in this manner and correspond to the same area. These pictures were taken with a sample bias of $+1.95$ V and each protrusion on the $c(2\times8)$ area corresponds to an adatom.

Figure 2(a) shows the beginning surface. The alternating rows of the adatoms have a somewhat different appearance. This is due to the "buckling" as noted above. This apparent buckling does depend on the tip and

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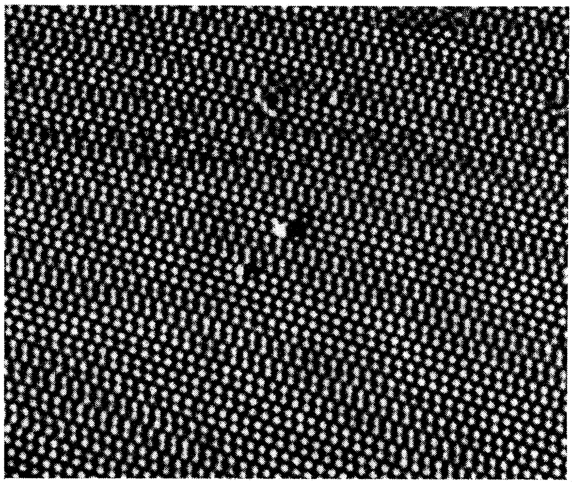

FIG. 1. A STM image of Ge(111)-$c(2\times 8)$. This is a raw image that has not been corrected for distortion caused by thermal drift. The width of the image is about 370 Å. The sample bias voltage and current are +2.0 V and 0.2 nA, respectively. Each protrusion (white area) represents an adatom.

changes from time to time during the oxygen exposure, due to a change in the electronic properties of the tip. An examination of Fig. 2(a) reveals that two adatoms appear missing or repressed on the surface. Again, the nature of these defects is not known. Figure 2(b) shows the same area after 76 langmuirs (L) of oxygen exposure. Because of a change in the tip, the buckling is not apparent anymore. The two missing adatoms can still be recognized easily, however. A small region, consisting of three neighboring adatoms, within the lower left quadrant exhibits a change in appearance due to oxidation. Figure 2(c) shows the result of a higher oxygen exposure of 85 L. Clearly, the oxidized region seen in Fig. 2(b) has significantly expanded, while simultaneously another region of oxidation appears within the upper right quadrant. Both of these two oxidized regions are seen to expand further and join into one contiguous region in Fig. 2(d) for a total oxygen exposure of 98 L. In this figure, yet another region of oxidation shows up near the left border as a result of the expansion from an oxidized part initiated at a point outside the picture frame. The oxidized areas are disordered, and we do not know the oxygen coverage within these areas.

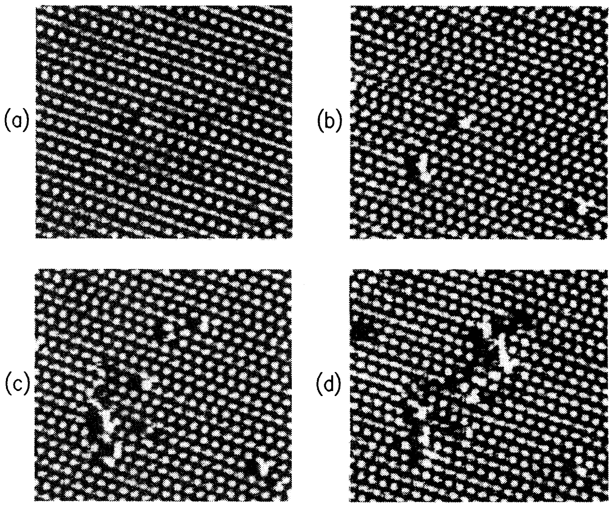

FIG. 2. STM images of Ge(111)-$c(2\times 8)$ over a given area under various oxygen exposures. The sample bias voltage and current are +1.95 V and 0.08 nA, respectively. (a) is a picture of the starting surface, and each protrusion (white area) represents an adatom. The oxygen exposures for (b)–(d) are 76, 85, and 98 L, respectively.

By raster scanning over the same area during the oxygen exposure, we were able to follow the oxidation process in real time, although we show only a few representative images in the present case. A possible problem of this approach, however, is the partial blockage of oxygen by the tip. Thus, the exposure values may have to be corrected. The blockage effect is clearly dependent on the shape (sharpness) of the tip, which is unknown. Another uncertainty may arise due to the high electric field present within the tunneling gap, which might assist or modify the oxidation process. In our experiment the scanned area is $(250\ \text{Å})^2$ or $(600\ \text{Å})^2$, and the actual probed area during the sequence is larger due to thermal drift. We did not observe any significant difference between the central part and the peripheral part of the image. Also, different sample bias voltages for both polarities were tried in the experiment and did not seem to cause any difference, suggesting that the electric-field effect is unimportant.

As in most surface-science experiments involving gas adsorption, there is always a question about the starting surface cleanliness and dosing-gas purity. Based on our many experiments on clean Ge(111)-$c(2\times 8)$ involving STM, electron diffraction, and photoemission, we conclude that the procedure followed in this experiment should provide a good starting surface without any significant residual-gas contamination.[7,8] This is based on comparisons between images and spectra taken at widely separated times after sample preparation (the Ge surface could be imaged just a short time after the anneal despite a large thermal drift). The dominant residual gas in any ultrahigh-vacuum chamber is hydrogen. We have performed a set of experiments on the hydrogenation of the related Si(111)-(7×7) surface at room temperature (results unpublished). The effects of hydrogenation were easily detected in the image under various bias conditions, and the resulting surface showed considerable disorder. We did not observe any such effects in the present experiment. Based on these considerations, the possibility of significant hydrogen contamination of our starting surface can be ruled out. During the oxidation measurements, the oxygen partial pressure of about 2×10^{-8} torr in the chamber was maintained by a continuous flow of fresh oxygen, which was pumped away continuously by the system ion pump. By keeping the ion pump on, the impurity partial pressures were kept low. Even with the precautions, there is a slight chance that the oxidation observed here is initiated by adsorption of minority gas species. Unfortunately, this point cannot be settled as no technique exists at present for positive species identification on an atom-by-atom basis.

The oxidation of Ge(111) has been investigated before by Auger spectroscopy, work-function measurements, and thermal desorption.[9] It was reported that the initial sticking coefficient was about 0.01 and showed a sharp drop as the coverage increased. Defects on the starting surface were thought to be a possible cause for the initial high sticking coefficient. This result is not necessarily at variance with the present result. The techniques of Auger spectroscopy, work-function determination, and thermal desorption measure the average behavior over a large area on the surface. Most samples do have macroscopic scratches or pits that may contain a high density of defects of various kinds. The oxidation behavior of these "bad" spots may be quite different. With a large-area probe, both the "bad" spots and "good" areas contribute to the signal. In contrast, a much smaller, nearly atomically perfect area containing just two simple defects is examined in the present STM study. Therefore, it is difficult or impossible to make quantitative connections between the results of these two experiments.

The present work can be summarized as follows. The oxidation appears to proceed by nucleation at random spots followed by an expansion around these spots. It took considerable oxygen exposure for the nucleation centers to form. The nucleation did not occur at the initial defect sites. This is contrasted by the case of Si(111)-(7×7) in which defects play a dominant role in such processes, namely, they act as nucleation centers. Once the oxidation has been initiated, further oxygen exposure of Ge(111)-$c(2\times8)$ results in a rapid expansion of the oxidized regions. A similar expansion behavior has also been observed for Si(111)-(7×7). On both the Ge and Si surfaces, the oxidation results in a disordered structure. In these experiments, the absolute exposure values may be uncertain by a scaling factor due to the possibility of partial blockage of the dosing gas by the scanning tip.

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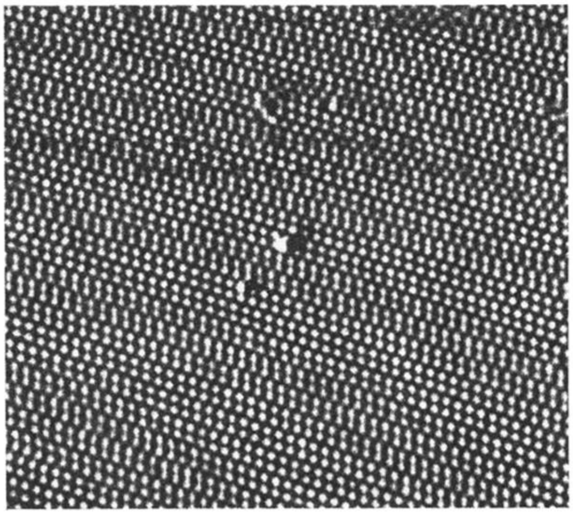

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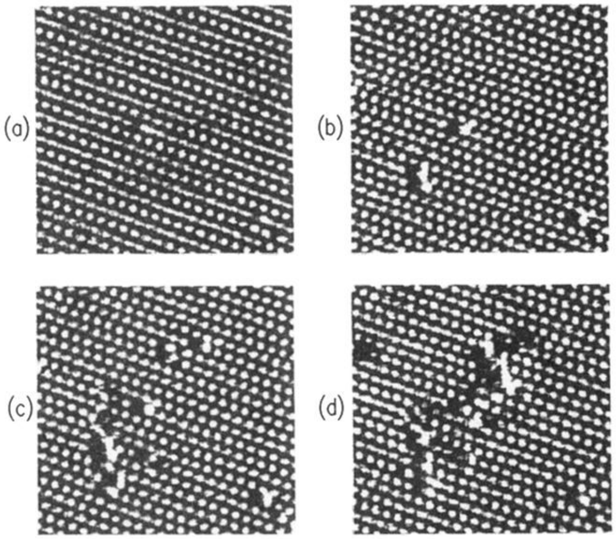

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