X-Ray Scattering Study of Ag/Si(111) Buried Interface Structures

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Various interface structures formed between Si(111) and a *thick* Ag overlayer are investigated by grazing-incidence x-ray diffraction. The (7×7) reconstruction of Si(111) is preserved under a room-temperature deposited Ag film. Upon annealing to 250 °C the interface becomes (1×1). This is contrasted by the $(\sqrt{3}\times\sqrt{3})R30°$ structure formed by annealing a *thin* Ag film on Si(111). By depositing a thick Ag film on this $(\sqrt{3}\times\sqrt{3})R30°$ Ag/Si(111) surface at room temperature, the $(\sqrt{3}\times\sqrt{3})R30°$ reconstruction is suppressed.

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It is well known that a thin Ag film, on the order of 1–10 atomic layers thick, deposited on Si(111) will form a $(\sqrt{3}\times\sqrt{3})R30°$ structure (root-3 structure, for short) upon annealing to temperatures above about 200 °C [1–3]. This is considered a prototypical, nonreactive metal-semiconductor system, and its structure has been the focal point of a large number of studies employing a variety of surface-science techniques (readers are referred to Ref. [4] for an up-to-date discussion). A basic question concerning this system, which is the main topic of this study, is whether or not this root-3 reconstruction represents an interface structure between Si and Ag. This question relates to a larger issue concerning interface structures in general, that is, whether or not the structure observed at monolayer coverage ranges can be taken as an indication of the true interface structure.

Surface reconstructions can be observed quite easily with standard low-energy and medium-energy electron-diffraction techniques that are, however, totally inadequate for true interface structures involving a thick overlayer because of the very short penetration depth of the probing beam. Two techniques using high-energy, highly penetrating beams have been employed in recent years for interface studies: transmission electron microscopy (TEM) [5,6] and x-ray diffraction [7]. Both techniques involve substantial experimental difficulties. In the case of TEM, sample preparation is a significant problem. For x-ray diffraction, the interface signal is extremely weak because of the small scattering cross section of the interface. For these reasons, interface reconstructions for various material systems remain a relatively unexplored area.

The present study employs grazing-incidence x-ray diffraction to determine the Ag/Si(111) interface reconstruction. The diffraction experiment was carried out on beam line X-14 at the National Synchrotron Light Source, Brookhaven National Laboratory, and the samples were prepared by molecular-beam epitaxy at the University of Illinois. The Si(111) substrates were cut from commercial *n*-type wafers having a resistivity in the range of 1–10 Ω cm. Each substrate was outgassed overnight at about 600 °C in ultrahigh vacuum, and then resistively heated to about 1250 °C for 7 s. This procedure consistently produced clean, well-ordered (7×7) surfaces as determined by photoemission, Auger spectroscopy, and electron diffraction [8]. Ag was deposited by evaporation from an effusion cell. The deposition rate was monitored by a water-cooled thickness monitor, and was in the range of 3–6 Å/min. All of the samples used had a Ag thickness of 260 Å, and electron-diffraction patterns were recorded during the various phases of the preparation procedure. During x-ray-diffraction measurements, each sample was mounted on a feedback-controlled heater assembly within an evacuated, hemispherical Be dome. A thermocouple measured the sample temperature during the *in situ* annealing experiment. An x-ray wavelength of 1.592 Å was used.

Three kinds of samples were studied. The first kind was a Ag overlayer deposited on a room-temperature Si(111)-(7×7) surface. The electron-diffraction results are as follows. For increasing Ag coverages, the pattern changes from Si(111)-(7×7) into incommensurate Ag(111)-(1×1) in parallel epitaxy at a coverage of about 1 atomic layer. The Ag(111) pattern is initially fuzzy, but sharpens up considerably with the addition of just a few Ag atomic layers and remains sharp until the end of deposition [1–3,8]. The resulting film thickness is likely to be uniform to within a few atomic layers [9]. The second kind of sample was prepared from the first kind by postannealing to 430 °C for 60 s. The Ag(111)-(1×1) electron-diffraction pattern remains unchanged after the annealing. For comparison, if the annealing is done on a thin Ag film (~1–10 atomic layers), the resulting surface will be a root-3 reconstructed surface; the Ag in ex-

cess of that required for the root-3 reconstruction (~1 atomic layer) will form highly three-dimensional Ag beads. The third kind of sample was prepared by first depositing about 2 atomic layers of Ag, then annealing to 430°C to form the root-3 reconstruction, and then depositing 260 Å of Ag at room temperature. The resulting Ag film shows a fuzzy Ag(111)-(1×1) electron-diffraction pattern plus rings indicating some polycrystalline formation.

Figure 1 shows omega scans (rocking curves) for the room-temperature prepared Ag/Si(111) through a set of selected rods as indicated in the figure. The incoming and outgoing x-ray beams make an angle of 2.4° relative to the sample surface for all scans. This is larger than the critical angle of about 0.5° for Ag, and more than one-half of the incident x-ray intensity reaches the interface. The (h,k) labels used in the figure refer to a hexagonal coordinate system for the Si(111) surface, and $l=0.5$ for all of the scans [7]. The results show an intense (1,0) peak of Si(111) and many $\frac{1}{7}$-order peaks. No peaks are found for scans through rods corresponding to the root-3 reconstruction; two of the scans through $(\frac{2}{3},\frac{2}{3})$ and $(\frac{4}{3},\frac{1}{3})$ are included in Fig. 1. Furthermore, continuous linear scans (data not shown) along the high-symmetry axes (1,0), (−1,1), and (1,1) within the region included in Fig. 1 reveal no additional diffraction peaks except a sharp, intense peak located at (1.32,0) derived from a rod of the Ag film. This rod position, as well as others outside the range of Fig. 1, indicates that the Ag film has a lattice constant equal to the bulk value and is in parallel epitaxy with respect to the substrate, in agreement with our electron-diffraction measurements. We conclude from these observations that the interface reconstruction remains (7×7) without any trace of the root-3 reconstruction. The intensity distribution for the $\frac{1}{7}$-order peaks is, however, different from that for the clean Si(111)-(7×7) surface [10]. The most noticeable difference is the absence of the $(\frac{3}{7},0)$ peak for the Ag-covered surface, which is one of the strongest for clean Si(111)-(7×7). On the other hand, the $(\frac{6}{7},0)$ and its symmetry-equivalent peaks remain intense after Ag coverage. This difference in intensity distribution may be attributed to a Ag-induced partial modification to the Si(111)-(7×7) reconstruction which is known to consist of "adatoms" on a partially faulted surface layer [10,11]. It is likely that the deposition of Ag disrupts the adatom reconstruction because the adatoms are only loosely bonded to the surface [12], but the stacking fault remains because of geometrical constraints and a correspondingly large energy required for atomic rearrangement. The line shapes of the peaks in Fig. 1 can be well fitted by Lorentzians. The half width at half maximum, after resolution correction, is less than 0.1°, indicating a correlation length for the (7×7) reconstruction greater than 340 Å.

Similar scans were carried out for the sample prepared at room temperature and annealed to 430°C. None of the $\frac{1}{7}$-order peaks seen in Fig. 1 was observed. Furthermore, careful scans through a number of root-3 rods as

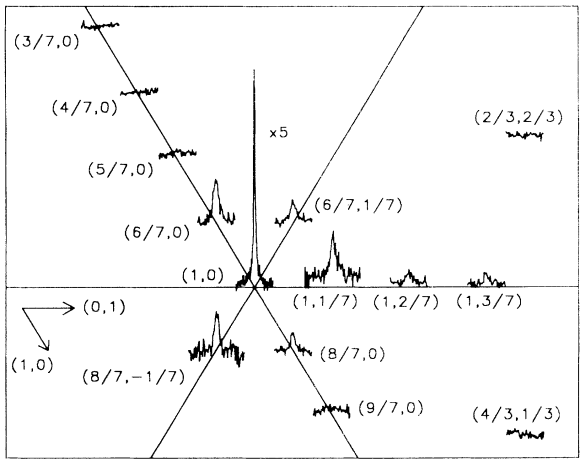

FIG. 1. Rocking curves for in-plane scattering from the interface of a thick Ag film prepared on Si(111)-(7×7) at room temperature. The Si(1,0) peak has been reduced by a factor of 5. Omega is the rotational angle of the sample.

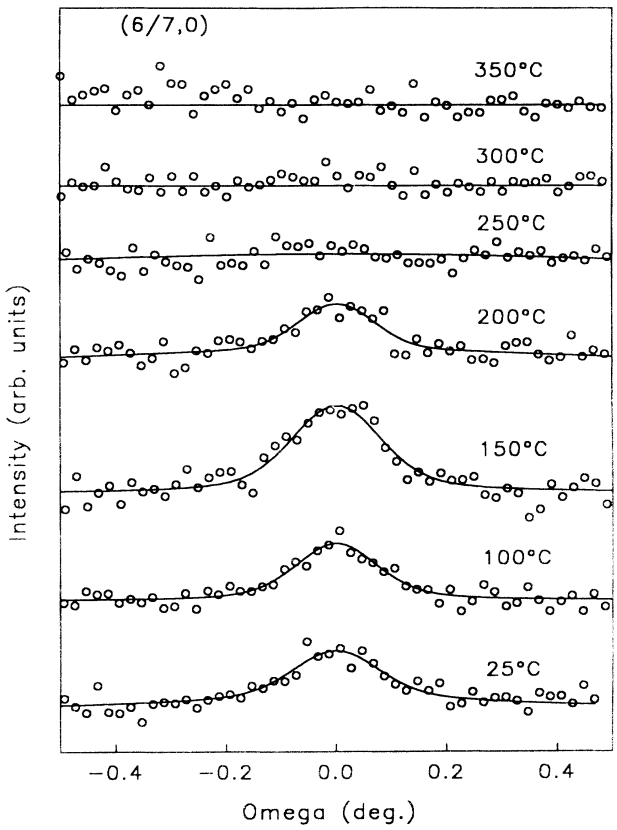

FIG. 2. Evolution of the $(\frac{6}{7},0)$ peak after progressive annealing to the indicated temperatures. Omega is the rotational angle of the sample.

well as along several high-symmetry line segments in the reciprocal net showed no signs of any reconstruction peak. Thus, the interface structure after annealing is (1×1), not root-3. The root-3 reconstruction is a surface phenomenon, having nothing to do with the interface.

Figure 2 shows the annealing behavior of the $(\frac{6}{7},0)$ peak of the (7×7) reconstruction. A room-temperature prepared sample was progressively annealed at each of the indicated temperatures for 5 min. After each annealing step, the sample was allowed to cool down to near room temperature and a scan was taken. The results show that the peak intensity increases somewhat after annealing to 150°C, and then decreases to zero after a 250°C anneal. The initial increase is likely due to a partial reordering of the interface. It is conceivable that the initial interface is partially disordered due to a random displacement of the Si adatoms, and part of this disorder can be annealed away. The final decrease of the peak intensity at 200–250°C represents the removal of stacking faults and any remnants of the (7×7) reconstruction.

Figure 3 shows three scans over one of the root-3 rods, $(\frac{5}{3},\frac{2}{3})$. This rod gives rise to an intense peak in the root-3 reconstructed surface [13,14]. The bottom curve in Fig. 3 is for the sample before the annealing (25°C), and the other two curves are for the sample after annealing to 250 and 300°C. No diffraction peaks are found. We have also taken scans over other root-3 rods, including $(\frac{2}{3},\frac{2}{3})$ and $(\frac{4}{3},\frac{1}{3})$ which give rise to comparably intense peaks in the root-3 reconstructed surface. In all of these scans, and for annealing temperatures up to 430°C, we have found no evidence of the root-3 reconstruction.

Considering the fact that the (7×7) reconstruction can be preserved as a metastable structure under a Ag film deposited at room temperature, one might suspect that the root-3 reconstruction could also be preserved. To investigate this possibility, we took scans over various root-3 rods for the third kind of sample mentioned earlier. No root-3 peaks were found in these scans. Thus, the root-3 structure is destroyed by Ag deposition at room temperature. We believe that the preservation of the (7×7) reconstruction is related to the surface stacking fault; to remove the stacking fault a large number of Si atoms will have to be moved and many bonds will have to be severed [10,11]. This gives rise to a kinetic barrier which is not overcome until annealing to 200–250°C. Although the detailed structure of the root-3 reconstruction is still a hot subject of debate [4], it is generally agreed that this reconstruction involves no stacking fault, and this may be the reason for the lower kinetic barrier for converting the initially root-3 surface to the stable (1×1) interface.

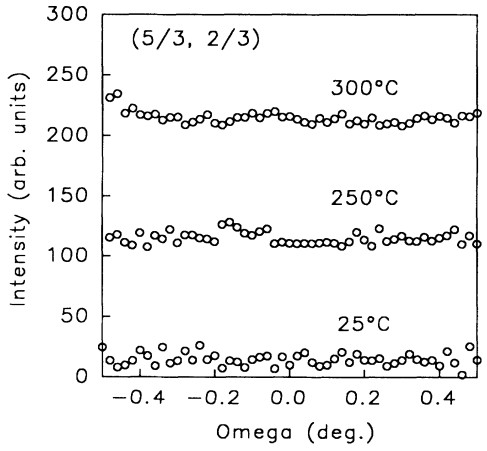

FIG. 3. Rocking curves (omega scans) through the $(\frac{5}{3},\frac{2}{3})$ rod after annealing to the indicated temperatures. Omega is the rotational angle of the sample.

It is interesting to note that the metastable (7×7) interface structure is converted into (1×1) at 200–250°C (Fig. 2), the same temperature range in which a *thin* Ag film on Si(111) is converted into the root-3 structure. It is quite possible that this is the characteristic annealing temperature for removing stacking faults, and therefore both systems undergo changes at similar temperatures. The atomic structure for the (1×1) system is likely to be considerably simpler than the root-3 structure, which is believed to consist of both Ag and Si adatoms decorating a bulk-truncated Si, and the Si(111)-(7×7) structure. The driving force for these complicated (7×7) and root-3 reconstructions is a balance between the reduction in electronic energy from the saturation of the dangling bonds and the increase in strain energy due to the structural deformation. When a thick metallic Ag overlayer is laid on Si(111), it has a high density of delocalized, easily deformable [15] valence electron cloud available for saturating the charge deficiency in all of the dangling bonds. To first order, there is no electronic energy to be gained by rearranging the substrate atoms and the dangling bonds; any such rearrangement of the Si atoms from the bulk-truncated structure will simply cause an increase in strain energy. In view of this, it is perhpas not surprising that the stable interface structure between Ag and Si, which are mutually insoluble and form no stable compounds, is (1×1).

In summary, the stable interface structure between Si(111) and a thick Ag overlayer has a (1×1) symmetry. A metastable (7×7) structure is formed by depositing Ag on Si(111)-(7×7) at room temperature. Upon annealing to 200–250°C, this metastable structure is converted to (1×1). The root-3 reconstruction obtained by annealing a thin Ag film on Si(111) is a surface structure, having nothing to do with the interface. The root-3 reconstruction cannot be preserved as a metastable structure under a Ag film deposited at room temperature. This work illustrates interesting phenomena related to the structure and phase transitions of buried interfaces. An important conclusion is that the reconstruction observed at monolayer coverage ranges during overlayer buildup does not necessarily represent the true interface structure.

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[1] K. Spiegel, Surf. Sci. **7**, 125 (1967).

[2] J. A. Venables, J. Derrien, and A. P. Janssen, Surf. Sci. **95**, 441 (1980).

[3] G. Le Lay, Surf. Sci. **132**, 189 (1983).

[4] M. Katayama, R. S. Williams, M. Kato, E. Nomura, and M. Aono, Phys. Rev. Lett. **66**, 2762 (1991).

[5] J. M. Gibson, in *Surface and Interface Characterization by Electron Optical Methods*, edited by A. Howie and U. Valdre (Plenum, New York, 1986), p. 55.

[6] J. M. Gibson, H.-J. Gossmann, J. C. Bean, R. T. Tung, and L. C. Feldman, Phys. Rev. Lett. **56**, 355 (1986).

[7] I. K. Robinson, W. K. Waskiewicz, R. T. Tung, and J. Bohr, Phys. Rev. Lett. **57**, 2741 (1986).

[8] A. L. Wachs, T. Miller, A. P. Shapiro, and T.-C. Chiang, Phys. Rev. B **35**, 5514 (1987).

[9] A. L. Wachs, A. P. Shapiro, T. C. Hsieh, and T.-C. Chiang, Phys. Rev. B **33**, 1460 (1986); T.-C. Chiang, in *Metallic Multilayers and Superlattices*, edited by M. Hong, S. Wolf, and D. C. Gubser (The Metallurgical Society, Warrendale, PA, 1988), p. 167.

[10] I. K. Robinson, W. K. Waskiewicz, P. H. Fuoss, and L. J. Norton, Phys. Rev. B **37**, 4325 (1988).

[11] K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, Surf. Sci. **164**, 367 (1985).

[12] For Ge(111)-$c(2\times8)$ which also has adatoms on the surface, it has been shown that Ag deposition at room temperature (partially) removes the Ge adatoms [A. L. Wachs, T. Miller, and T.-C. Chiang, Phys. Rev. B **33**, 8870 (1986)].

[13] T. Takahashi, S. Nakatani, N. Okamoto, T. Ishikawa, and S. Kikuta, Jpn. J. Appl. Phys. **27**, L753 (1988).

[14] E. Vileg, A. W. Denier, van der Gon, J. F. van der Veen, J. E. MacDonald, and C. Norris, Surf. Sci. **209**, 100 (1989).

[15] It takes very little energy to transfer electrons from within the Fermi surface to unoccupied states with very different k values.