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Influence of Arsenic on the Atomic Structure of the Si(112) Surface

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The surface science techniques of low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM) have been used to characterize the clean Si(112) surface and the influence of an As monolayer on the properties and structure of the surface. In agreement with previous studies, the clean surface is found by both LEED and atomically resolved STM images to be unstable with respect to faceting into other stable planes. Procedures for *in-situ* deposition of As onto clean Si surfaces were devised and XPS results show that approximately one monolayer of As can be deposited free of any contamination. The As/Si(112) surface is characterized by a sharper LEED pattern than for the clean surface and by STM images characterized by long rows along the $[\bar{1}10]$ direction with a regular width of 1.9 nm. This is consistent with a doubling of the periodicity in the $[11\bar{1}]$ direction of the bulk-terminated unit cell. This implies that As yields a stable but reconstructed Si(112) surface.

Key words: Si(112), Ag/Si, low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM)

INTRODUCTION

The As-passivated Si(112) surface is used as a substrate for the growth of CdTe and HgCdTe by molecular beam epitaxy (MBE) for the fabrication of focal-plane infrared detector arrays. As an alternative to growth on Si substrates, very-high-quality epitaxial films of HgCdTe can be grown on bulk single-crystal surfaces of CdZnTe, where there is almost perfect lattice matching between substrate and film, in contrast to the 19% lattice mismatch between HgCdTe and Si. However, for the large-scale production of HgCdTe focal-plane arrays, the practical advantages of Si over CdTe or CdZnTe substrates are overwhelming. These advantages have been described in detail by de Lyon et al.[1] The stringent demands of the vast microelectronics industry for large Si crystals of exceedingly high quality and purity have set standards that no other material comes even close to meeting. Thus, CdZnTe crystals are not only much more expensive than Si crystals, but have impurity levels that are higher and more variable, and have far more defects. From a manufacturing perspective, a Si substrate has the advantage that there is no problem with matching the thermal expansion of the Si-based readout devices. Furthermore, Si crystals have the size and strength needed to be safely handled with automatic wafer processing equipment. The practical imperatives for growing HgCdTe on Si substrates demand and justify expending considerable effort on solving the basic scientific and technical issues involved in the heteroepitaxy between these two materials. One such issue concerns the atomic structure of the Si(112) surface and how the structure is influenced by the deposition of an As layer prior to the growth of CdTe and HgCdTe.

The first report of epitaxial growth of CdTe on Si used Si(001) as substrate.[2] On the clean Si(001) surface, the CdTe(111)B orientation is obtained, where the (111)B notation indicates the $(\bar{1}\,\bar{1}\,\bar{1})$ Te polar surface, and the CdTe(111)A notation indicates

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the (111) Cd polar surface. A variety of strategies have been used to improve the quality of the CdTe layers.[3–5] These include use of a thin buffer layer of ZnTe since its lattice constant is intermediate between that of CdTe and Si and the use of vicinal (001) surfaces misoriented by as little as 1°. This latter approach minimizes defects associated with double-domain and twin formation. However, the Si(112) surface has been shown in many studies to yield high-quality epitaxial films of CdTe[6–11] and is now widely used. As de Lyon et al.,[1] note in their review: "The (112) orientation has come to be preferred for MBE growth because of its immunity to twin and hillock formation and its compatibility with p-type chemical doping by As." The advantages of the Si(112) surface as substrate were previously proposed in the general context of polar-on-nonpolar epitaxy by Wright et al.,[12] in a study of MBE growth of GaP on Si(112). Since GaP, ZnTe, and CdTe all have the zincblende structure, the same considerations apply in each case. In practice, the Si(112) surface is first covered with approximately one monolayer of As before CdTe growth is initiated. Although it is empirically found that the As layer promotes better growth,[13,14] the underlying reasons for this are not clear.

The atomic structure of various Si surfaces has been widely studied, with most of the attention directed at the Si(001) and Si(111) surfaces.[15] The structure of these two low-index surfaces are different from the ideal bulk-terminated planes, but the reconstructions are now well understood. The most important technique for establishing the actual structure of Si surfaces has been the scanning tunneling microscope (STM), which is capable of providing direct atomically resolved images. The principle underlying the reconstructions that form the equilibrium structures of Si(001) and Si(111) is that the lowest energy surface represents the best trade-off between minimizing the number of dangling bonds while also avoiding excessive stress. The same principle presumably applies to high index Si surfaces, only a few of which have been studied in any detail.

From the first experimental studies of Si(112), it was clear that the structure is complex and often difficult to reproduce. Kaplan[16] used low-energy electron diffraction (LEED) to examine the structure of the clean and of the hydrogen and gallium covered Si(112) surface and found that the clean surface exhibited complex long-range reconstructions. Olshanetsky and Mashanov[17] used LEED to characterize several high Miller index Si surfaces and reported a 4 × 2 structure for Si(112), although they noted that they could not obtain good LEED patterns with bright and sharp reflections and low background from this surface. Wright, et al.,[18] observed a 2 × 2 pattern in a reflection electron diffraction study of Si(112). Yang and Williams[19] used LEED to explore the influence of carbon on the structure of Si(112) and concluded that the clean surface is stable with a 1 × 2 reconstruction corresponding to a doubling of the periodicity along the $[1\,1\,\bar{1}]$ direction. However, they also found that the stability of the surface was critically dependent on the degree of carbon contamination with faceting induced by carbon concentrations of just under 1%. In an early use of STM, Berghaus et al.[20] found that a large part of the surface consisted of narrow (111) terraces separated by double-layer steps. From some of the details in their images and the frequent observation of 7×7 reconstructed Si(111) facets, they concluded that the Si(112) surface is quite unstable. Wang and Weinberg[21] also investigated the Si(112) surface with LEED and STM and reported a 1×2 reconstruction, although no structural model was proposed. Various theoretical studies have been performed to understand the relative stability of the bulk-terminated and reconstructed surfaces.[22–25] A more recent STM study by Baski and Whitman[26] found that the Si(112) surface forms a novel sawtooth structure consisting of reconstructed (111)-7×7 and (337) nanofacets. In a later survey of the structures determined by STM of several Si surfaces with orientations between Si(001) and Si(111), Baski, et al.,[27] found that only a few orientations formed stable surfaces, which they defined as surfaces that consist of large flat terraces of the nominal orientation (although generally reconstructed) separated by steps consisting of one to three atomic layers. As shown below, our STM results for the clean Si(112) surface are generally in agreement with those of Baski and Whitman,[26] which supports their contention that the nanofaceted surface represents the equilibrium surface. In the Discussion section, we try to reconcile the results from LEED and STM reported in the literature as well as in our present study.

Although the structure of As on Si(112) has not been previously established, the structures formed by As on the Si(111) and Si(001) surfaces have been determined. The phases formed by various elements including As on Si surfaces have been reviewed by Lifshitz.[28] The procedure for preparing a well-ordered Si(111)-1×1-As surface with an As coverage of just under 1 ML is well known. It consists of exposing the surface to an As_4 flux, during which the sample is briefly flashed to a temperature of 850–1050°C, then cooled in the flux to 350°C. Numerous studies indicate a structure in which the topmost Si atoms of a bulk-terminated Si(111) surface are replaced by As atoms. The fact that the As atoms eliminate the Si dangling bonds is manifested by the extremely unreactive nature of the Si(111)-1×1-As surface. On the reconstructed Si(001)-(2×1) surface, a monolayer of As does not lift the reconstruction but does result in a sharpening of the LEED pattern. The structure involves As-As dimers with a separation of 0.255 nm with each As atom bonded to two Si atoms and to the other As atom of the dimer pair. Consequently, all As atoms are threefold coordinated with a doubly occupied lone pair. The As layer does not passivate Si(001) to the extent that it does Si(111) but it does reduce the saturation coverage of oxygen by 50% and the initial sticking coefficient of O_2 by a factor of 10 compared with the clean surface. These previous studies of As on Si(111) and Si(001) provide a useful starting point for interpreting the structures observed here with STM for As on Si(112).

EXPERIMENTAL

The experiments were conducted in an apparatus that consists of an ultrahigh vacuum surface analysis chamber coupled to a small As deposition chamber. The surface analysis chamber is equipped with LEED, x-ray photoelectron spectroscopy (XPS), and STM instruments and has a base pressure of 5×10^{-11} torr. The As source consists of a small resistively heated Ta crucible containing small chips of As. The As_4 effuses through a 1-mm-diameter hole in the crucible. The irregularly shaped P-doped (room-temperature (RT) resistivity of > 50 ohm-cm) Si(112) samples of approximately 1 cm^2 in area were cut from Si(112) wafers obtained from Umicore Electro-Optic Materials (Boston, MA). The Si samples were mounted on Mo STM holders and were indirectly heated by electron bombardment. The Si surface temperatures were monitored with an optical pyrometer above 600°C and for temperatures between 600°C and RT with an infrared pyrometer that was calibrated in separate experiments using a thermocouple directly attached to the Si surface. For As deposition, the Si samples were heated to 950°C, cooled to 900°C, exposed to the $As_4(g)$ as the sample was cooled to 360°C where the exposure was stopped, and then cooled to RT. A similar procedure is known to result in a self-limiting monolayer of As on Si(111)[29] and was also designed to mimic the procedures used for As deposition prior to MBE growth of CdTe. After deposition, the gate valve separating the deposition and analysis chambers was opened and the sample transferred into the main chamber for surface analysis.

RESULTS

Figure 1a shows a survey XPS spectrum of the Si(112) surface after As deposition. All peaks visible in the spectrum are due to either Si or to As, which demonstrates that our method is capable of depositing As onto the surface free of any significant contamination. Figure 1b shows spectra in the As 3d, Si 2p, O 1s, and C 1s regions. This shows that the surface is free of oxygen to within the noise level of the measurement and that the carbon is just barely detectable. Based on XPS sensitivity factors, this implies a carbon contamination level in the surface region of 4% and an oxygen level of less than 0.5%. The data can also be used to quantify the As coverage. In a separate XPS study of As on several different Si surfaces, Fulk et al.,[30] describe the assumptions involved in deriving a coverage from the XPS As 3d to Si 2p peak-area ratios. The key assumptions are that the As is present only at the surface and that the Si signal has contributions from many layers beneath the surface with each layer's contribution attenuated by the mean-free path of the photoelectrons. The coverages are given as the ratio of the number of As atoms to the number of Si atoms in the surface layer. In their study, they found that the As coverage on Si(111) is approximately one monolayer, as expected. Using the method of Fulk et al.,[30] we obtain an As surface coverage from the XPS data in Fig. 1 of 0.63 monolayer.

The LEED pattern shown in Fig. 2 for the clean Si(112) surface is quite similar to what was observed previously by Yang and Williams[19] and in particular by Wang and Weinberg[21] and our description follows that of the latter authors. The pattern consists of three bright rows with almost continuous streaking between the spots together with two faint rows between the bright rows. The spacing between the bright rows corresponds to the 0.384-nm surface lattice constant in the $[\bar{1}10]$ direction, and the faint rows indicate a periodicity twice that of the bulk structure and hence indicative of a 2× reconstruction in that direction. In the $[11\bar{1}]$ direction, the spacing of the spots is not uniform and there is almost continuous intensity between the spots. However, many of the spots have a separation corresponding to 1.92 nm, which is twice the surface lattice constant in the $[11\bar{1}]$ direction. Although this is the basis of the reported 1×2 reconstruction of this surface, there is clearly considerable disorder associated with this structure, particularly along $[11\bar{1}]$. A complete description of the surface needs to account for both this observation and for the structure directly observed with STM.

Figure 3 shows an STM image of the clean Si(112) surface that was acquired after annealing the sample to 1,150°C, a temperature typically used to obtain atomically resolved STM images of Si surfaces. The image is in excellent agreement with the images reported by Baski and Whitman,[26] although the image shown is for the empty states (positive bias of sample relative to the tip), whereas their images were of the filled states. Nevertheless, the same general features are observed and our interpretation follows theirs. Specifically, the surface consists of two types of nanofacets. The (111) nanofacets contain the well-known 7×7 reconstruction. As noted by Baski and Whitman,[26] the (111) nanofacets generally consist of one 7×7 unit cell. Since the size of this unit is known to be 7a, where $a = 0.314$ nm is the distance between pairs of Si atoms along the $[11\bar{1}]$ direction of the bulk-terminated Si(112) surface, the (111)-7×7 nanofacets would have an ideal width of 2.2 nm. Since the angle between the (111) and (112) planes is fixed by the crystal structure at 19.47°, the other nanofacet must be a (337) plane. The (337) plane is 4° from the (112) plane in the $[\bar{1}\bar{1}1]$ direction and has a unit cell that is 1.57-nm wide in the $[11\bar{1}]$ direction. This leads to a simple description of the ideal nanofaceted structure as consisting of seven units

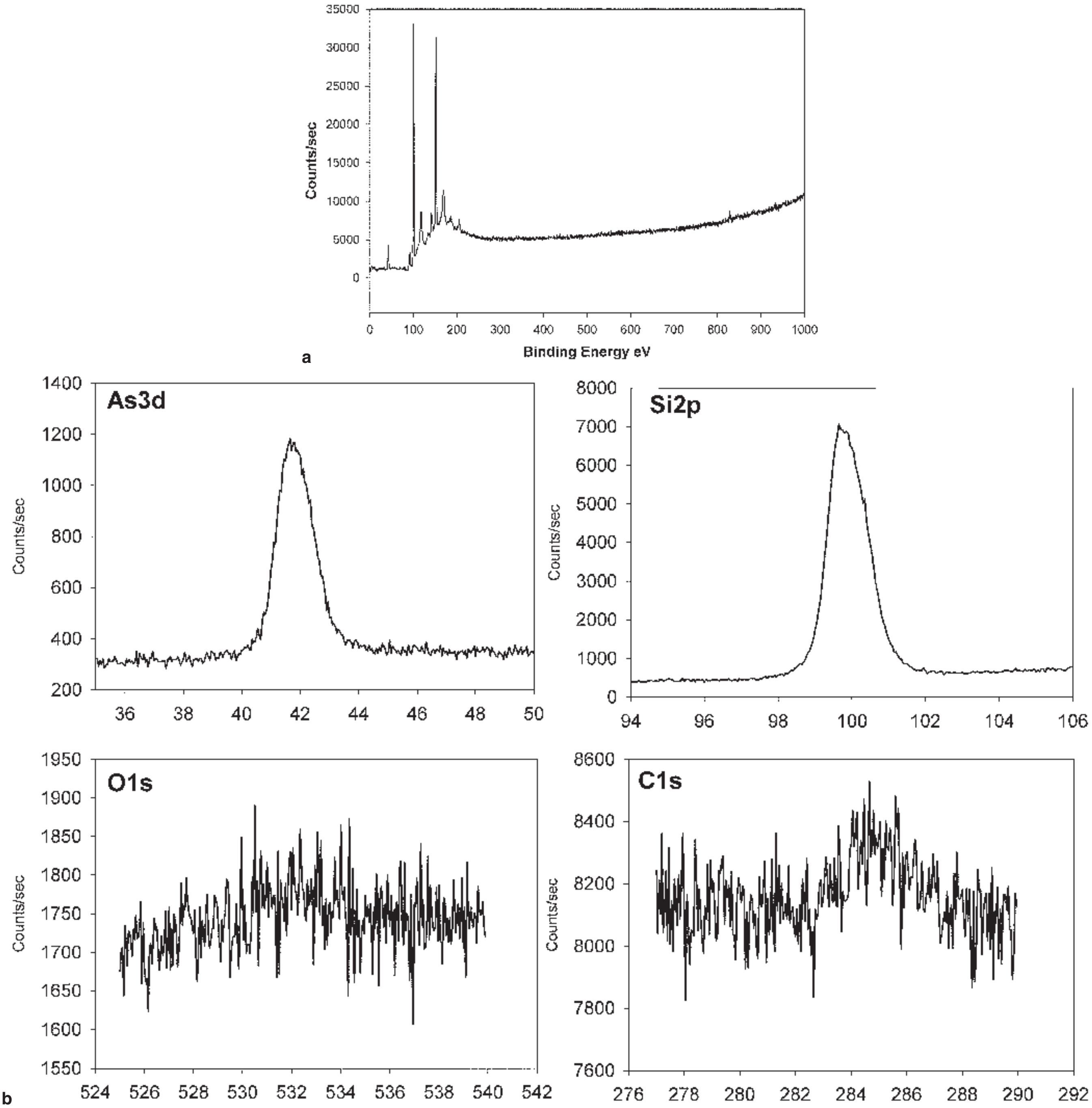

Fig. 1. XPS spectra of the As/Si(112) surface. (a) Survey spectrum. (b) Spectra of the As 3d, Si 2p, C 1s, and O 1s regions.

of the (337) nanofacet for every one unit of the (111)-7×7 nanofacets. Although Baski and Whitman[26] report that the (111)-7×7 nanofacets are invariably one unit cell in width, they list various ways that the (337) nanofacets can differ from their ideal widths of 5 × 7 × a = 11.0 nm. For this reason, although they describe the surface as only quasi-periodic in the $[1\,1\,\bar{1}]$ direction, the nanofacets have a fairly narrow width distribution. The actual atomic structure within the (337) nanofacets is not discussed by Baski and Whitman[26] nor does it appear to have been addressed in the literature.

The LEED patterns of the As-covered Si(112) surface that we have obtained are similar in overall appearance to those of the clean surface, although with As/Si(112), the spots are perhaps slightly sharper with fewer distinct spots within the bright rows compared with the clean surface. There is also evidence for large facets in that changes in the pattern with beam energy indicate that the observed pattern represents a superposition of diffraction spots from planes with different orientations with respect to the incident electron beam. This makes it difficult to provide a simple description of the LEED

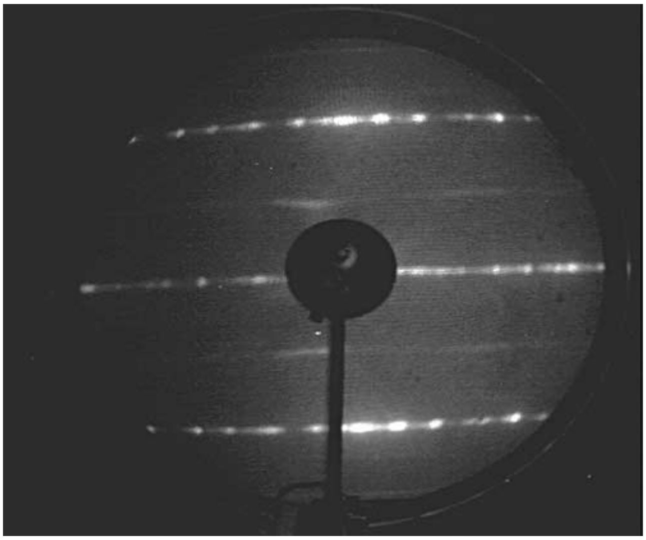

Fig. 2. LEED pattern from the clean Si(112) surface at a beam energy of 57.8 eV.

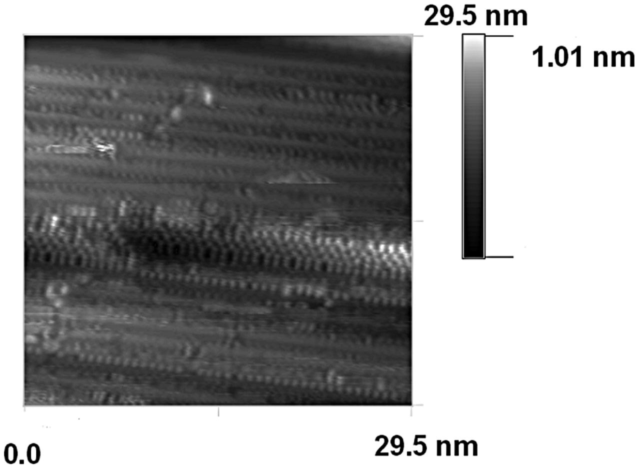

Fig. 3. STM of clean Si(112). After RCA treatment, the surface was heated slowly to 600°C, flashed to 950°C, then cooled from 950°C to RT at 2°C/sec.

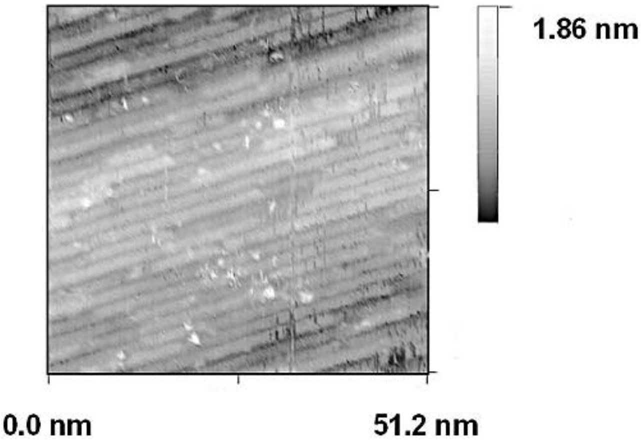

Fig. 4. STM image of As/Si(112) obtained by cooling from 900°C to 360°C in an As_4 flux, stopping the flux at 360°C, then cooling to RT.

pattern that reconciles its appearance with the STM results for this surface. Figure 4 shows an STM image of a qualitatively different structure for As/Si112) compared to the clean surface. The As-covered surface reveals long rows oriented along the $[\bar{1}10]$ direction, but with a much more regular spacing between the rows of 1.9 ± 0.1 nm in the $[11\bar{1}]$ direction. For As/Si(112), there is no evidence of two distinct facets and each row appears to have the same structure.

DISCUSSION

A successful structural model of the clean Si(112) surface should account for the observations made with both LEED and STM, which provide complementary information. Whereas only periodic surface structures give rise to spots in LEED, periodicities in STM images are often less apparent. It is interesting to consider what sort of LEED pattern would be expected for the quasi-periodic nanofaceted structure proposed by Baski and Whitman[26] for the ideal Si(112) surface. Along the $[\bar{1}10]$ direction, the periodicity corresponding to the separation between the bright rows in the LEED pattern is evidently of the order of a Si-Si bond length and its observation with STM would require resolving individual Si atoms, something that is not seen in our images or in those of others. Since the (111)-7×7 nanofacets are only one unit cell in width, they should not contribute to any periodicity in the $[11\bar{1}]$ direction. The combination of seven units of (337) and one unit of (111)-7×7 gives a repeat unit of 13.19 nm in the $[11\bar{1}]$ direction, which would give spots in the LEED pattern spaced seven times more closely than the spots within the bright rows in the LEED pattern in Fig. 2. Since this is on the order of the size of the spots themselves, it should not be possible to detect this periodicity with LEED, even though it is one of the most characteristic features of the STM images. A faceted surface is generally manifested in LEED by superimposed patterns from the individual facets, provided the facets are large enough. However, periodicity within the (111)-7×7 nanofacets is present only in the $[\bar{1}10]$ direction so that at most such nanofacets would contribute to streaking in the $[11\bar{1}]$ direction at positions between the bright rows of spots in Fig. 2. Most likely, these nanofacets just contribute to the high background in the LEED pattern. Thus, the periodicities that contribute to the LEED pattern would originate entirely from the (337) facets. The (337) lattice constant in the $[11\bar{1}]$ direction is 1.57 nm and the seven units in each nanofacet should be in phase with the units in the other nanofacets. Therefore, we would expect rows of closely spaced spots along the $[11\bar{1}]$ direction in the LEED pattern, as is observed.

The characteristic feature of the As/Si(112) surface is the regular 1.9-nm rows seen in the STM image. Since the lattice constant of the bulk-terminated Si(112) unit cell in the $[11\bar{1}]$ direction is 0.941 nm, the LEED and STM images imply that the As removes the nanofaceting characteristic of the clean surface and produces a stable Si(112) surface with

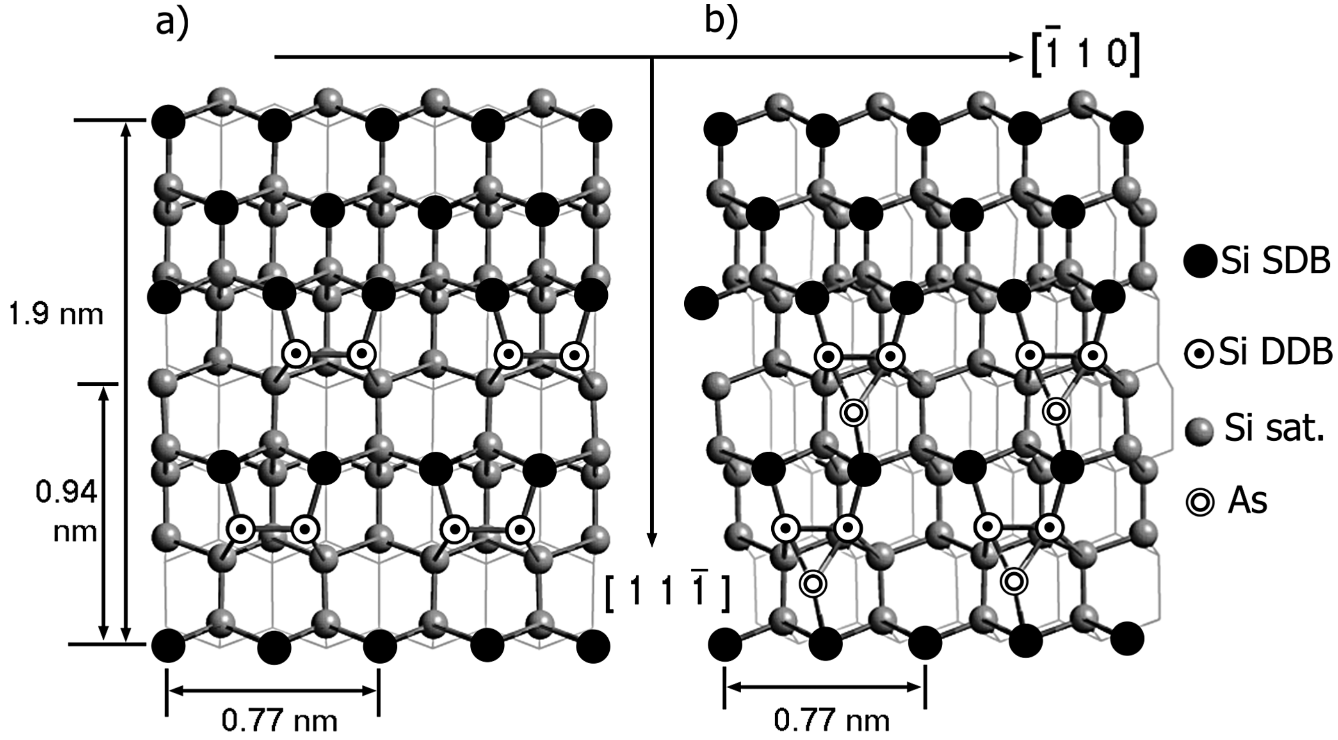

Fig. 5. A structural model of the As/Si(112) surface showing a 1×2 reconstruction corresponding to STM images that show 1.9-nm-wide rows indicating a doubling of the periodicity in the $[1\ 1\ \bar{1}]$ direction relative to the bulk-terminated Si(112) surface. (a) View of the underlying 2×2 reconstructed Si(112) surface. (b) Placement of As atoms on the 2×2 reconstructed surface shown in (a). The Si atoms have either a single dangling bond (SDB), a double dangling bond (DDB), or no dangling bonds (sat.).

a 2× reconstruction in the $[11\bar{1}]$ direction. This simplifies developing a structural model of the As-covered surface. One possible model is shown in Fig. 5. This is based not only on the observed periodicities but also on analysis of additional details within the images. A full description of this model will be presented elsewhere.

CONCLUSIONS

We have reproduced the LEED patterns and STM images observed in previous studies of the clean Si(112) surface and we argue that the sawtooth nanofaceted structure proposed by Baski and Whitman[26] is consistent with the observed LEED patterns. The nanofaceted structure is absent for the As-covered Si(112) surface. Instead, the As/Si(112) surface yields STM images indicating a 1×2 reconstruction with a period of 1.9 nm in the $[11\bar{1}]$ direction, a value that is twice the bulk-terminated surface lattice constant in this direction. This suggests that As stabilizes the Si(112) against nanofaceting. However, larger scale faceting was observed with LEED for the As-covered surface. The LEED patterns also show evidence for a doubling of the periodicity in the $[\bar{1}10]$ direction, but observation of this reconstruction would require higher resolution than is generally achievable with STM. A structural mode of the As/Si(112) surface that incorporates our current understanding of the LEED and STM data is proposed.

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REFERENCES

1. T.J. de Lyon, J.E. Jensen, M.D. Gorwitz, C.A. Cockrum, S.M. Johnson, and G.M. Venzor, *J. Electron. Mater.* 28, 705 (1999).
2. R. Sporken, S. Sivananthan, K.K. Mahavadi, G. Monfroy, and M. Bourerche, *Appl. Phys. Lett.* 55, 1879 (1989).
3. Y. Xin, N.D. Browning, S. Rujirawat, S. Sivananthan, Y.P. Chen, P.D. Nellist, and S.J. Pennycook, *J. Appl. Phys.* 84, 4292 (1998).
4. Y.P. Chen, J.P. Faurie, S. Sivananthan, G.C. Hua, and N. Otsuka, *J. Electron. Mater.* 24, 475 (1995).
5. Y.P. Chen, J.P. Faurie, and S. Sivananthan, *J. Electron. Mater.* 22, 951 (1993).
6. T.J. de Lyon, S.M. Johnson, C.A. Cockrum, O.K. Wu, W.J. Hamilton, and G.S. Kamath, *J. Electrochem. Soc.* 141, 2888 (1994).
7. M. Kawano, A. Ajisawa, N. Oda, M. Nagashima, and H. Wada, *Appl. Phys. Lett.* 69, 2876 (1996).
8. A. Million, N.K. Dhar, and J.H. Dinan, *J. Cryst. Growth* 159, 76 (1996).
9. S. Rujirawat, D.J. Smith, J.P. Faurie, G. Neu, V. Nathan, and S. Sivananthan, *J. Electron. Mater.* 27, 1047 (1998).
10. B. Yang, Y. Xin, S. Rujirawat, N.D. Browning, and S. Sivananthan, *J. Appl. Phys.* 88, 115 (2000).

11. T.J. de Lyon, D. Rajavel, S.M. Johnson, and C.A. Cockrum, *Appl. Phys. Lett.* 66, 2119 (1995).
12. S.L. Wright, M. Inada, and H. Kroemer, *J. Vac. Sci. Technol*. 21, 534 (1982).
13. N.K. Dhar, P.R. Boyd, M. Martinka, J.H. Dinan, L.A. Almeida, and N. Goldsman, *J. Electron. Mater.* 29, 748 (2000).
14. N.K. Dhar, C.E.C. Wood, A. Gray, H.Y. Wei, L. Salamanca-Riba, and J.H. Dinan, *J. Vac. Sci. Technol. B* 14, 2366 (1996).
15. J.D. Browski and H.-J. Müssig, *Silicon Surfaces and Formation of Interfaces—Basic Science in the Industrial World* (Hackensack, NJ: World Scientific, 2000).
16. R. Kaplan, *Surf. Sci.* 116, 104 (1982).
17. B.Z. Olshanetsky and V.I. Mashanov, *Surf. Sci.* 111, 414 (1981).
18. S.L. Wright, H. Kroemer, and M. Inada, *J. Appl. Phys.* 55, 2916 (1984).
19. Y. Yang and E.D. Williams, *Surf. Sci.* 215, 102 (1989).
20. Th. Berghaus, A. Brodde, H. Neddermeyer, and St. Tosch, *Surf. Sci.* 184, 273 (1987).
21. X.-S. Wang and W.H. Weinberg, *Surf. Sci.* 314, 71 (1994).
22. D.J. Chadi and J.R. Chelikowsky, *Phys. Rev. B* 24, 4892 (1981).
23. D.J Chadi, *Phys. Rev. B*. 29, 785–792 (1984).
24. C. H. Grein, *J. Cryst. Growth*, 180, 54 (1997).
25. S. Makefors, *Surf. Sci.* 443, 99 (1999).
26. A.A. Baski and L.J. Whitman, *Phys. Rev. Lett*. 74, 956 (1995)
27. A.A. Baski, S.C. Erwin, and L.J. Whitman, *Surf. Sci.* 393, 69 (1997).
28. V.G. Lifshits, A.A. Saranin, and A.V. Zotov, *Surface Phases on Silicon* (New York: Wiley, 1994), pp. 85–90.
29. M. Copel, R.M. Tromp, and U.K. Kohler, *Phys. Rev. B* 37, 10756 (1988).
30. C. Fulk, R. Sporken, B. Gupta, I. Batra, D. Zavitz, J. Dumont, M. Trenary, N. Dhar, J. Dinan, and S. Sivananthan, *J. Electron. Mater.* 34, 846 (2005).