

Ideal unreconstructed hydrogen termination of the Si(111) surface obtained by hydrogen exposure of the $\sqrt{3} \times \sqrt{3}$ -In surface

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Hydrogen exposure of the Si(111) $\sqrt{3} \times \sqrt{3}$ -In surface resulted in a replacement of the Si-In bonds by Si-H bonds as evidenced by core-level and angle-resolved photoelectron spectroscopy. Saturation of the Si dangling bonds by hydrogen atoms led to the formation of an unreconstructed Si(111)1 \times 1-H surface. Besides a peak due to Si-H bonds, a sharp peak, due to Si-Si backbonds, appeared in the valence-band spectra. The experimental dispersions of these states showed excellent agreement with calculated surface bands. The In atoms formed metallic islands on a small part of the surface ($\sim 5\%$).

Modification of semiconductor surfaces, in order to get new chemical, electrical, and structural properties, is an interesting topic from a technological as well as a fundamental point of view. Many semiconductor surfaces reconstruct in order to lower the high surface energy associated with the large number of dangling bonds on an ideal bulk-terminated surface. The Si(111)7 \times 7 surface, for example, exhibits several structural elements, such as adatoms, corner holes, and dimer rows which make the surface deviate substantially from an ideal truncation of the bulk. A simple way to obtain an unreconstructed Si(111) surface would be to saturate the dangling bonds by adsorbing hydrogen atoms. This would result in a significant lowering of the surface electronic energy and in addition lead to a chemical passivation of the surface. The structural simplicity and high symmetry would make the Si(111)1 \times 1-H surface very suitable for fundamental studies of adsorbate-substrate interactions. In technological applications the surface could be very useful, for instance, as a starting surface for molecular-beam epitaxial growth.

The effect of hydrogen exposure on the clean Si(111)7 \times 7 surface in ultrahigh vacuum (UHV) has been the subject of numerous studies as exemplified by Refs. 1-5. As evidenced by the "7 \times 1" low-energy electron-diffraction (LEED) pattern reported in these studies, the hydrogen atoms are not capable of removing the complex 7 \times 7 reconstruction of the surface. The hydrogen atoms can, however, remove the Si adatoms and form a 1 \times 1-H, monohydride phase, on the triangular terraces within the preserved 7 \times 7 unit cell, according to recent studies by photoelectron spectroscopy⁴ and scanning tunneling microscopy (STM).⁵

In this paper we present an *in situ* method to obtain a well-ordered Si(111)1 \times 1-H surface, which exploits the capability of In atoms to entirely remove the structural features of the 7 \times 7 reconstruction. It is well known that the Si(111) $\sqrt{3} \times \sqrt{3}$ -In surface consists of In adatoms in threefold sites on an unreconstructed Si toplayer.⁶⁻⁸ We show in this study that hydrogen exposure leads to a removal of the In adatoms and that a well-ordered hydrogen-terminated Si(111)1 \times 1 surface is formed. The high quality of the surface allowed us to identify a structure in the photoemission spectra which is due to Si-Si

backbond states. The importance of simple surfaces with a high degree of perfection for the observation of experimental features and phenomena has also been recently demonstrated in studies of a Si(111)1 \times 1-H surface prepared by wet-chemical methods.^{9,10} The high quality of this surface allowed the authors to measure the lifetime and to identify anharmonic effects for adsorbate-substrate vibrations.⁹

The experiments were performed at the toroidal-grating monochromator beam line at the MAX synchrotron radiation facility in Lund, Sweden. An angle-resolving hemispherical analyzer was used for collecting and analyzing the photoelectrons. A highly *n*-type, As-doped ($\rho = 4-6$ m Ω cm), Si(111) crystal was preoxidized using an etching method¹¹ and cleaned *in situ* by resistive heating up to $\sim 950^\circ\text{C}$, which gave rise to a sharp 7 \times 7 LEED pattern. Approximately 0.45 monolayer of indium atoms was evaporated from a tungsten filament onto the sample held at room temperature. Subsequent heating up to $\sim 600^\circ\text{C}$ produced the following sequence of LEED patterns: three-domain 4 \times 1, $\sqrt{31} \times \sqrt{31}$, and $\sqrt{3} \times \sqrt{3}$. The hydrogen exposure of the $\sqrt{3} \times \sqrt{3}$ -In surface was made at a hydrogen pressure of 2×10^{-5} torr, with the sample facing a hot ($\sim 1700^\circ\text{C}$) tungsten filament at a distance of 7 cm. The sample was kept at a temperature of approximately 350°C during the 5000 L exposure to hydrogen. After this treatment, LEED showed a sharp 1 \times 1 pattern with low background indicative of a well-ordered, unreconstructed surface. There were no signs of other superstructure spots. The transformation from the $\sqrt{3} \times \sqrt{3}$ -In to the 1 \times 1-H(In) surface induced by hydrogen adsorption is reversible. A heating of the sample to $\sim 550^\circ\text{C}$ caused the hydrogen to desorb and the LEED pattern changed to $\sqrt{3} \times \sqrt{3}$. Photoemission spectra confirmed that the electronic structure of the $\sqrt{3} \times \sqrt{3}$ -In surface indeed was restored.

Spectra recorded from the $\sqrt{3} \times \sqrt{3}$ -In and the 1 \times 1-H(In) surfaces are shown in Figs. 1(a)-1(c) and 1(d)-1(f), respectively, together with the optimum fits for the core levels in (a), (b), (d), and (e). The values of the parameters for these fits¹² are given in Tables I and II. The valence-band spectrum from the $\sqrt{3} \times \sqrt{3}$ surface in Fig. 1(c) shows a pronounced peak A at 1.5 eV below E_F . It corresponds to emission from an In-induced surface

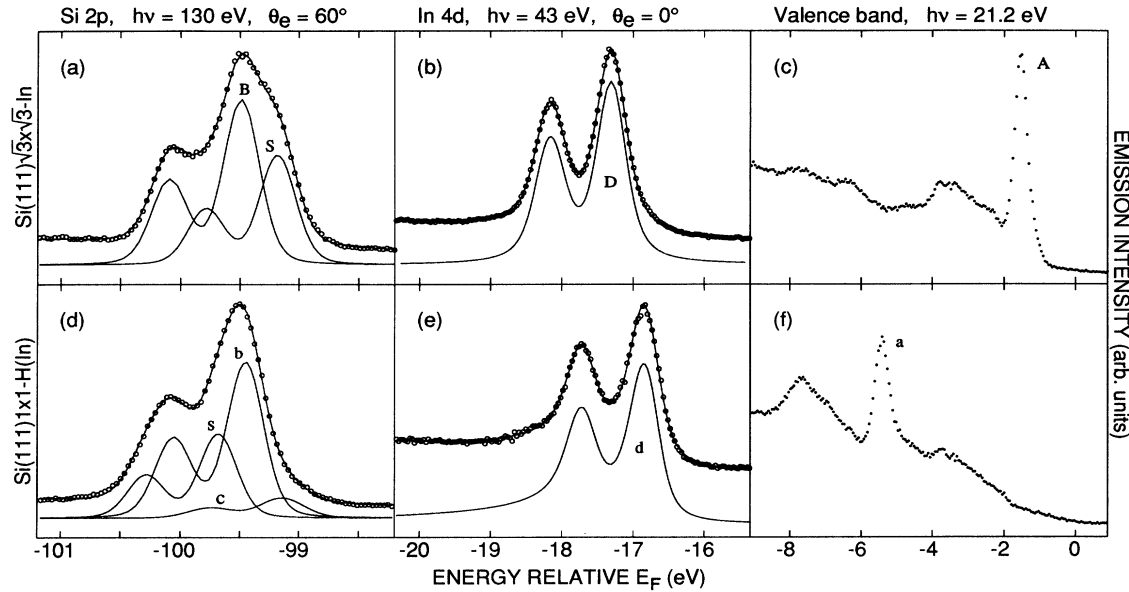


FIG. 1. Photoemission spectra (open and solid circles) for (a)–(c) the $\text{Si}(111)\sqrt{3}\times\sqrt{3}\text{-In}$ surface and (d)–(f) the $\text{Si}(111)1\times 1\text{-H(In)}$ surface, illustrating the electronic structure before and after the hydrogen exposure. The solid curves are the results of the fitting procedures. The valence-band spectra [(c) and (f)] were recorded at an emission angle $\theta_e = 27.5^\circ$ in the $[2\bar{1}1]$ azimuthal direction. For the surface state on the $\sqrt{3}\times\sqrt{3}\text{-In}$ surface (peak *A*) this corresponds to the \bar{M} point in the $\bar{\Gamma}\text{-}\bar{K}\text{-}\bar{M}$ direction of the $\sqrt{3}\times\sqrt{3}$ surface Brillouin zone.

state assigned to the bonds between the In adatoms and the Si substrate.⁶ The sharpness and the high intensity of peak *A* are indicative of a well-ordered surface. The Si 2*p* spectrum of the $\sqrt{3}\times\sqrt{3}\text{-In}$ surface in Fig. 1(a) is decomposed into a bulk component *B* and a surface component *S* with a core-level shift of -0.31 eV. The presence of a single shifted component *S* indicates that there is only one kind of Si atoms in an environment different from the bulk, in accordance with the models of In adatoms saturating the dangling bonds of the Si toplayer. The fit of the In 4*d* core level is shown in Fig. 1(b) and it consists of only one component *D* which is consistent with only one kind of site for the In atoms in the adatom model. No asymmetry could be observed in the In 4*d* spectrum.

The most spectacular effect of the hydrogen exposure is

TABLE I. Curve-fitting parameters for the components used to fit the Si 2*p* core-level spectra. The spin-orbit split, branching ratio, and Lorentzian width are 0.605 eV, 0.505, and 0.07 eV (FWHM), respectively. The binding energies of the bulk components (Si 2*p*_{3/2}) were measured in bulk-sensitive spectra ($h\nu = 108$ eV) relative to the Fermi level of a Ta foil. For the 7×7 surface, a binding energy of 99.39 eV was obtained.

Component		Binding energy (eV)	SCS (eV)	Gaussian width (eV)	Area
$\sqrt{3}\times\sqrt{3}\text{-In}$	<i>B</i>	99.49	...	0.32	0.60
	<i>S</i>		-0.31	0.32	0.40
$1\times 1\text{-H(In)}$	<i>b</i>	99.44	...	0.32	0.59
	<i>s</i>		0.23	0.32	0.32
	<i>c</i>		-0.31	0.40	0.09

revealed when comparing the valence-band spectrum of the $\sqrt{3}\times\sqrt{3}$ surface in Fig. 1(c) with the spectrum recorded from the hydrogen exposed surface in Fig. 1(f). Structure *A* is totally removed and a new sharp structure *a* at 5.45 eV below E_F appears in the spectrum. Or, in other words, the surface state originating from the Si-In bonds is replaced by a new one with a binding energy corresponding to Si-H bonds.^{3,4}

The Si 2*p* core-level spectrum from the $1\times 1\text{-H(In)}$ surface is shown in Fig. 1(d). The fit reveals one dominating surface component *s* shifted by 0.23 eV, which is in good agreement with the shift observed earlier for a Si surface atom with a bond to an adsorbed H atom.⁴ The spectrum has a tail on the high-energy side and a small contribution from a second shifted component *c*, with a larger Gaussian width, is needed in order to obtain a good fit.

The In 4*d* spectrum of the $1\times 1\text{-H(In)}$ surface in Fig. 1(e) is best fitted with one single component *d*. This was also the case for the In 4*d* spectrum of the $\sqrt{3}\times\sqrt{3}$ surface, but now the core-level spectrum has got a highly asymmetric shape, indicative of a metallic character. Instead of the Lorentzian, a Doniach-Sunjić function with a

TABLE II. Curve-fitting parameters for the single components used to fit the In 4*d* core-level spectra. The Gaussian width (FWHM) is 0.32 eV for both spectra.

	Binding energy (eV)	Spin-orbit split (eV)	Lorentzian width (eV)	Singularity
$\sqrt{3}\times\sqrt{3}\text{-In}$	17.31	0.888	0.28	0.00
$1\times 1\text{-H(In)}$	16.82	0.850	0.22	0.14

singularity index α of 0.14 had to be used for the fit. There is also a shift in the binding energy of the In $4d$ level from 17.31 to 16.82 eV relative to the Fermi level which is closer to the value of 16.74 eV reported for pure metallic In.¹³ The intensity of the In $4d$ peak (relative to the fitted background) has decreased and is only $\sim 36\%$ of the intensity observed on the $\sqrt{3}\times\sqrt{3}$ surface. The changes of the In $4d$ spectrum strongly indicate that the In atoms form metallic islands on the surface after the hydrogen exposure.

Considering the convincing evidence of Si-H bonds from both valence-band and Si $2p$ spectra and the changes in the In $4d$ core-level spectra, the following picture of the 1×1 -H(In) surface can be assumed. The bonds between the Si top-layer atoms and the In adatoms are broken by the hydrogen atoms and the In atoms are moved into metallic islands. The hydrogen atoms saturate the dangling bonds of the unreconstructed Si substrate and an ideal Si(111) 1×1 -H, monohydride, surface is thus formed between In islands.

It is possible to estimate the surface area covered with the In islands from the observed decrease of the In $4d$ intensity. The observed intensity decrease to 36% is achieved when the In adatoms have formed islands that have a height of 8 layers, if one assumes hemispherical islands, as has been observed on the Si(100) surface,¹⁴ with fcc structure [$a=4.7$ Å and orientation In(111) \parallel Si(111)] and an escape depth of the photoelectrons of 4.5 Å.¹⁴ With islands of this height, less than 5% of the surface is covered with In.

Concerning the interpretation of the Si $2p$ spectrum from the 1×1 -H(In) surface, the c component is far too large to be explained by emission from Si atoms underneath the In islands. In addition, the absence of an In $4d$ component with the same binding energy as for the $\sqrt{3}\times\sqrt{3}$ -In surface and the total removal of the surface-state peak A , which corresponds to Si-In bonds, rule out an interpretation of the c component as due to remaining In adatoms.

From bulk-sensitive Si $2p$ core-level spectra ($h\nu=108$ eV) a value of 0.68 eV was obtained for $E_F - E_V$ on the 1×1 -H(In) surface [based on a value of 0.63 eV for Si(111) 7×7],¹⁵ which is surprising since on the hydrogen-terminated surface no band bending is expected⁴ (due to the lack of intrinsic surface states in the band gap)¹⁰ and E_F would thus be close to the conduction-band edge, for this highly n -doped sample. The Fermi level at the Si-In interface has, on the other hand, been determined to be close to the valence-band edge ($E_F - E_V \approx 0.2$ eV).¹⁶ With In islands present, a rather large lateral variation of the Fermi-level position can thus be expected. An asymmetric broadening, indicative of such a variation, was also observed on the high-energy side of the bulk-sensitive spectrum ($h\nu=108$ eV) for the 1×1 -H(In) surface. Since no compensation was made for the asymmetric broadening, in the fit of the surface-sensitive 1×1 -H(In) spectrum [Fig. 1(d)], the appearance of the c component may therefore mainly be an effect of the lateral variation of the Fermi-level position.

The surface electronic structure of the 1×1 monohydride surface was studied in detail. Besides a strong struc-

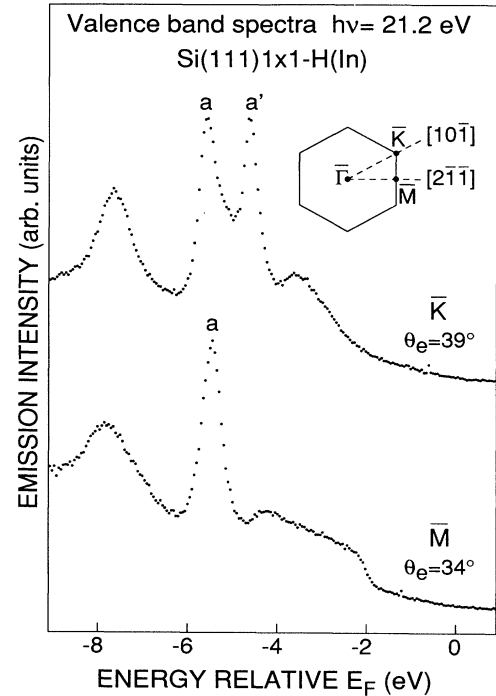


FIG. 2. Angle-resolved photoemission spectra, obtained from the Si(111) 1×1 -H(In) surface, probing \mathbf{k}_{\parallel} points near $\bar{\mathbf{K}}$ and $\bar{\mathbf{M}}$ of the 1×1 SBZ (see inset) for the hydrogen-induced states a and a' .

ture a in the valence-band spectra due to the Si-H bonds, a new sharp feature a' appeared at an energy of ~ -4.6 eV around the $\bar{\mathbf{K}}$ point of the 1×1 surface Brillouin zone (SBZ). Photoemission spectra corresponding to the $\bar{\mathbf{K}}$ and $\bar{\mathbf{M}}$ points of the 1×1 SBZ for structures a and a' are shown in Fig. 2. The experimental dispersions for the hydrogen-induced structures are in Fig. 3 compared with surface-state bands from a tight-binding calculation for the ideal Si(111) 1×1 -H, monohydride, surface by Pandey.² The calculation yielded two hydrogen-induced surface-state bands located in band-gap pockets of the projected valence bands. The lower band corresponds to

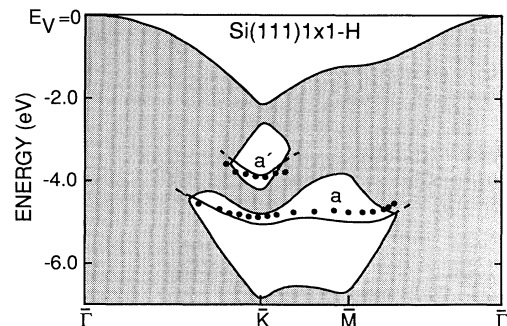


FIG. 3. Calculated surface band structure for the Si(111) 1×1 -H surface (lines) and projected bulk bands (shaded area) from Pandey (Ref. 2). The experimental data of the Si(111) 1×1 -H(In) surface are shown by solid circles.

the Si-H bond and is observed also on the “ 7×1 ”-H surface.²⁻⁴ The upper band, corresponding to a' , has not been experimentally observed before and was identified in the calculation as due to Si-Si backbonds. As can be seen, the agreement between theory and experiment is excellent. The photoemission studies of the “ 7×1 ”-H surface²⁻⁴ were not able to reveal the existence of the backbond state. This is probably explained with a lesser degree of order on that surface. In fact, even a well-ordered “ 7×1 ”-H surface has a rest atom layer that is not perfect due to the remaining corner holes and dimer rows from the 7×7 reconstruction.

In summary, we have used the Si(111)- $\sqrt{3}\times\sqrt{3}$ -In surface to prepare an unreconstructed hydrogen-terminated

Si(111) surface by hydrogen exposure in UHV. It is shown that hydrogen can break Si-atom bonds, which leads to transport of adatoms on the Si(111) surface. Two surface-state bands were identified on the Si(111)- 1×1 -H surface and they showed very good agreement with the Si-H state and a Si-Si backbond state obtained in a surface band-structure calculation.²

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¹T. Sakurai and H. D. Hagstrum, *Phys. Rev. B* **12**, 5349 (1975); H. Froitzheim, U. Köhler, and H. Lammering, *Surf. Sci.* **149**, 537 (1985); Y. J. Chabal, *Phys. Rev. Lett.* **50**, 1850 (1983); E. G. McRae and C. W. Caldwell, *ibid.* **46**, 1632 (1981).

²K. C. Pandey, *Phys. Rev. B* **14**, 1557 (1976); K. C. Pandey, *IBM J. Res. Dev.* **22**, 250 (1978).

³D. E. Eastman, F. J. Himpsel, J. A. Knapp, and K. C. Pandey, in *Physics of Semiconductors*, Proceedings of the Fourteenth International Conference, edited by B. H. Wilson, IOP Conf. Proc. No. 43 (Institute of Physics and Physical Society, London, 1979), p. 1059.

⁴C. J. Karlsson, E. Landemark, L. S. O. Johansson, U. O. Karlsson, and R. I. G. Uhrberg, *Phys. Rev. B* **41**, 1521 (1990).

⁵K. Mortensen, D. M. Chen, P. J. Bedrossian, J. A. Golovchenko, and F. Besenbacher, *Phys. Rev. B* **43**, 1816 (1991).

⁶J. M. Nicholls, P. Mårtensson, G. V. Hansson, and J. E. Northrup, *Phys. Rev. B* **32**, 1333 (1985).

⁷J. E. Northrup, *Phys. Rev. Lett.* **53**, 683 (1984).

⁸J. Nogami, Sang-il Park, and C. F. Quate, *J. Vac. Sci. Technol. B* **6**, 1479 (1988).

⁹P. Guyot-Sionnest, P. Dumas, Y. J. Chabal, and G. S. Higashi, *Phys. Rev. Lett.* **64**, 2156 (1990); P. Dumas, Y. J. Chabal, and G. S. Higashi, *Phys. Rev. Lett.* **65**, 1124 (1990).

¹⁰R. S. Becker, G. S. Higashi, Y. J. Chabal, and A. J. Becker, *Phys. Rev. Lett.* **65**, 1917 (1990).

¹¹A. Ishizaka and Y. Shiraki, *J. Electrochem. Soc.* **133**, 666 (1986).

¹²The experimental data was fitted with theoretical line shapes, each consisting of a Gaussian convoluted with a Lorentzian [for a Doniach-Šunjić function in the case of Fig. 1(e)]. The background contribution in the spectra was represented by a straight line.

¹³R. A. Pollak, S. Kowalczyk, L. Ley, and D. A. Shirley, *Phys. Rev. Lett.* **29**, 274 (1972).

¹⁴J. Knall, J.-E. Sundgren, G. V. Hansson, and J. E. Greene, *Surf. Sci.* **166**, 512 (1986).

¹⁵F. J. Himpsel, G. Hollinger, and R. A. Pollak, *Phys. Rev. B* **28**, 7014 (1983).

¹⁶G. Margaritondo, J. E. Rowe, and S. B. Christman, *Phys. Rev. B* **14**, 5396 (1976).

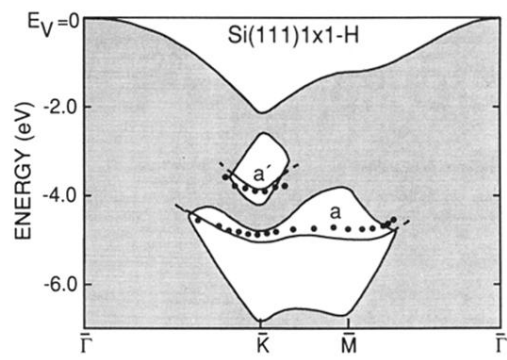


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