Electronic structure of the 7×7 Si(111): Differences due to preparation

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The 7×7 Si(111) surface has been investigated with regard to the character of the surface-state band and the existence of a band gap. From the differences between energy-loss spectra taken at surfaces prepared by cleavage in ultrahigh vacuum and those prepared by polishing and heating, it has been proven experimentally that these differences are due to carbon contamination of the polished surfaces. There is strong evidence that this contamination is localized below the surface but within the space-charge region and cannot therefore be detected by Auger electron spectroscopy, resulting in the conclusion that the surface Fermi level of the intrinsic 7×7 Si(111) lies within a gap and is therefore not metallic. This conclusion has to be considered when the 7×7 Si(111) surface is described theoretically.

INTRODUCTION

Due mainly to photoemission data[1] and numerous theoretical studies, it is believed that the surface-state band of the 7×7 Si(111) surface is metallic. This would exclude structure models which are based on a surface band structure with the surface Fermi level within a gap or those where such an electronic structure follows from the underlying structure model.

It also has been more or less assumed that 7×7 Si(111) surfaces are identical, independent of their preparation and that there is no difference whether they are prepared by cleavage and annealing in ultrahigh vacuum (UHV) or by polishing followed by ion bombardment and heating in UHV. Discrepancies in our data with regard to these aspects may suggest the importance of systematically investigating this problem in more detail.

Assuming that the resolution of photoemission spectroscopy might not be sufficient to investigate the surface band structure in the vicinity of the Fermi level, one could favorably use high-resolution electron energy-loss spectroscopy (EELS), as has already been done very successfully on the 2×1 Si(111) surface.[2] Such a study on polished 7×7 Si(111) surfaces recently was carried out by Ibach *et al.*[3] The loss spectra they obtained showed a very broadened maximum in the intensity of elastically scattered electrons and a very high background intensity extending up to several hundreds of meV of electron-loss energy. This result was interpreted as being produced by transitions described by a Drude-type dielectric response of a metallic surface-state band. Later on, another explanation of the broadening of the elastic peak was proposed by Ibach and Mills.[4] Here, the observed broadening of the elastic peak is interpreted as a more general property of some semiconductors, namely, as being due to the excitation of a conduction-band plasmon of very small frequency.

Differing from the interpretation given in Ref. 3, the authors[4] distinguish between the broadening of the elastic peak and the increased background intensity and try to explain the background as due to interband transitions between the many subbands (possibly) existent on the 7×7 Si(111) surface. The fact that we could neither observe an unusual broadening nor an increased background intensity in our studies on 7×7 Si(111) surfaces prepared by cleavage and subsequent annealing was interesting enough to cause us to carry out a more detailed investigation on these surfaces, which will be reported in this paper.

EXPERIMENTAL

In order to have a direct control of the differences between surfaces prepared by polishing or cleavage, a sampleholder was constructed which allowed us to carry out *in situ* studies on two differently prepared faces on the same sample. One face of the sample was polished prior to mounting and the opposite face was prepared by cleavage in UHV. The sampleholder also allowed for direct resistive heating of the sample and for heating by electron bombardment as well as for cooling the sample to about 150 K. The temperature of the sample could be controlled by a W-W/Rh thermocouple placed in a hole of 0.8-mm diameter, drilled several mm deep directly into the sample.

As we assumed that the observed effect was caused either by contamination or by structural defects, much care was taken to clean up the polished surfaces. This could be done either by the conventional method of sputtering and annealing or by high-temperature heating only. Using low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), there was no difference observable between the two techniques. There was, however, a difference observable with EELS. Absolutely smooth and unstructured loss intensities in the loss range around 100 meV could be obtained much more easily by high-temperature heating only. A severe problem was caused by Ni contamination which we assume to occur by the "Mond" process[5] during the bakeout procedure of the UHV system via the production of nickelcarbonyl. It should also be mentioned that whenever we found Ni on

the polished surface before we cleaved the sample, we also reproducibly found Ni afterwards on the cleaved and heated face, indicating that Ni obviously migrates throughout the whole crystal.

The problem with Ni was solved after we oxidized the sample in nitric acid prior to mounting it to the sample-holder. It is therefore assumed that the Ni produced during the bakeout process cannot penetrate the SiO_2 layer and can be removed together with the oxide during the first heat treatment. A sample prepared this way could easily be cleaned by quickly heating it to 1550 K and keeping it at that temperature for about 2 min. The fast increase in the temperature seems to be important as it obviously avoids the development of the so-called "milky" phase.

In addition to LEED, AES, and EELS data, surface photovoltage (SPV) measurements were also carried out with the EELS spectrometer. This can easily be done by using the effect that changing the contact potential of the reflecting surface causes the electron beam to be deflected from its original trajectory, so that it no longer hits the entrance slit of the analyzer. Readjusting the beam by changing the sample bias therefore yields a direct measurement of the change of the surface voltage. It is obvious that the accuracy of the method strongly depends on the angle of incidence and the beam energy, and it is easy to achieve a resolution of a few mV.

RESULTS

Figure 1 shows a comparison of electron energy-loss (EEL) spectra taken from a cleaved surface and a polished surface of the same sample. The corresponding spectrometer function has a full width at half maximum (FWHM) of 5 meV. As can be easily seen, there is a difference in
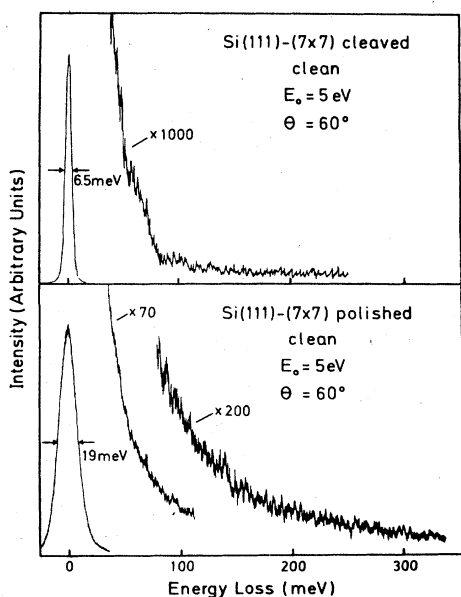
the two FWHM of a factor of about 3, and the background intensities differ by a factor of 25 at 100 meV.

Figure 2(a) shows the response of the angular half width and the energetic half width of the elastically reflected electrons, and the background intensity (measured
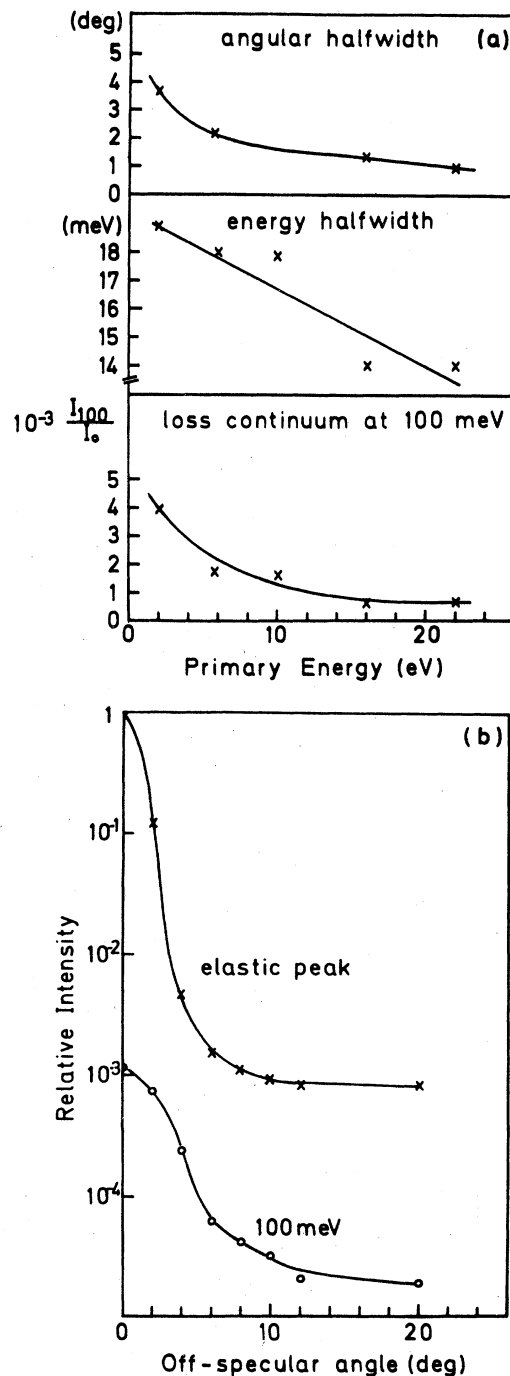

FIG. 2. (a) Dependence of the angular and the energetic FWHM of the elastically reflected electrons and the relative background intensity measured at 100-meV loss energy of a polished surface on the primary energy. (b) Relative intensities with respect of the off-specular angle of the elastic peak and the background intensity at $\hbar\omega = 100$ meV. The intensities are related to the specular intensity of the elastically reflected electrons.

FIG. 1. Comparison of ELS spectra of clean 7×7 Si(111) surfaces. The upper spectrum is taken from a surface prepared by cleavage in UHV and the lower spectrum represents the spectral behavior of a polished surface. Both spectra were taken from the same sample with the same spectrometer resolution.

at $\hbar\omega = 100$ meV), to variation of the primary energy. The observed dependence strongly indicates[6] that both the broadening of the elastic peak as well as the increased background intensity are due to transitions excited via dipole scattering.[4] This is strongly supported by the experimental data shown in Fig. 2(b) representing the behavior of the background intensity and elastic intensity in off-specular scattering.

Interesting information can be obtained from the decrease of the angular half width with increasing primary energy. Using simple kinematic diffraction arguments,[7] a mean distance between structural defects on the order of 500 Å fits the experimental data exactly. It should be mentioned that with a primary energy of 5 eV the coherence of our spectrometer is about ten times higher than that of a conventional LEED system.

Figure 3(a) shows a loss spectrum of a polished surface saturated with atomic hydrogen. As can be seen, the FWHM and the background intensity are now drastically reduced. This effect has been observed already[3] and has been explained by the saturation of the dangling bonds. Without going into detail, it should be mentioned that, based upon infrared data and theoretical considerations, the losses in Fig. 3(a) are related[8-10] to the stretching vibration of a hydrogen atom on top of a Si atom (257 meV), to its bending mode (77 meV), and to the scissor mode of a SiH$_2$ configuration (110 meV). A more detailed discussion will be published in another paper.[11] The SiH$_2$ configuration can be completely desorbed at 530 K. A spectrum of a surface where this configuration has been desorbed is shown in Fig. 3(b). Obviously, the FWHM has already broadened, while the background intensity is still small.

It should be emphasized that no broadening or increased background is observed on a 7×7 surface produced by cleavage and annealing during any stage of hydrogen adsorption or desorption. A further indication that the reduction of the FWHM and the background upon hydrogen adsorption is not simply due to the saturation of the dangling bonds is found from ELS spectra of 7×7 Si(111) surfaces covered with oxygen. Such spectra are shown in Fig. 4 (for a detailed discussion see Ref. 12).

Inspection of these spectra shows clearly that there is absolutely no change of the FWHM or the background. As it is known that oxygen also saturates the dangling bonds it is obvious that hydrogen must play a different role with regard to the effects described before.

Simply the fact that cleaved surfaces have no broadening or increased background suggests that polished surfaces may be affected extrinsically. Thus, in order to exclude the polishing process itself or any polishing material, spectra were taken from surfaces prepared by cleavage outside the system in air and then cleaned by heat treatment in UHV. These surfaces behaved identically to the polished surfaces. This excludes any special effect due to polishing. Additionally a surface was prepared by cleavage in UHV and then sputtered. The resulting EEL spectrum showed the characteristic features of an unstructured surface (small elastic intensity, no increase in the FWHM, slightly increased background intensity). Annealing such a surface to 900 °C for several minutes results in an EEL spectrum identical to that of a surface only cleaved and annealed.

This result suggests that carbon deposited onto the surface during the bakeout process may induce the observed
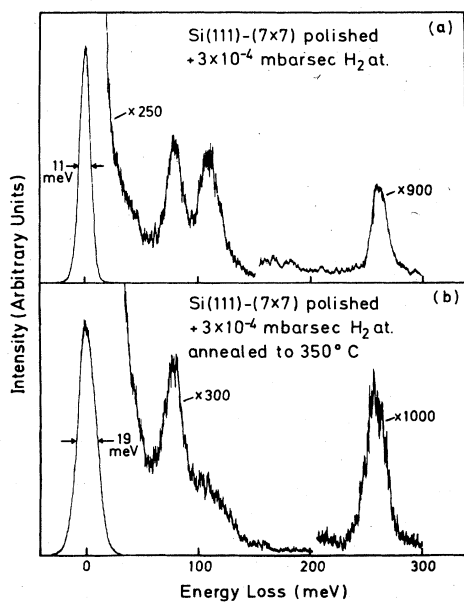

FIG. 3. (a) Vibrational spectrum of hydrogen adsorbed on a polished 7×7 Si(111) surface. (b) Vibrational spectrum of hydrogen after desorption of the SiH$_2$ configuration.
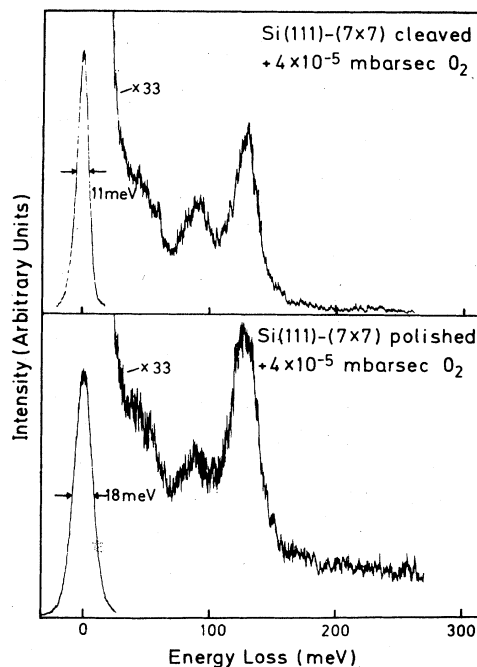
FIG. 4. Vibrational loss spectra of oxygen adsorbed on a cleaved surface (upper spectrum) and on a polished surface (lower spectrum).

effect and in order to demonstrate this, the following procedure was carried out with a cleaved/annealed sample: The sample was exposed to 5×10^4 L (1 L = 10^{-6} Torr sec) CO at a surface temperature of 1050 K. After this exposure the sample was heated to 1250 K in order to desorb oxygen. Auger and ELS spectra taken from such a surface are shown in Fig. 5. The EEL spectrum exhibits, besides a loss of carbon vibrational intensity at about 112 meV, a slightly increased background intensity. Heating the sample to 1550 K revealed an EEL spectrum without any loss peak but with a strongly increased background intensity. The corresponding Auger spectrum did not show any contaminants (sensitivity: $\frac{1}{1000}$ of the Si signal). Repeating the whole cycle several times finally revealed an ELS spectrum identical to that of a clean, polished surface with respect to both the FWHM and background (see lower part of Fig. 1).

From this result, it is believed that carbon is not completely removed from the sample either by high-temperature heating or by sputtering, but instead may penetrate into the sample deeply enough so that it cannot be detected by Auger spectroscopy where it forms very stable silicon carbide. We also believe that the so-called milky phase may occur via a three-dimensional silicon-carbide clustering on the surface at temperatures between 1200 and 1500 K. This is supported by our observation that this phase does not occur when the increase in temperature up to 1550 K is very fast. This three-dimensional clustering may also explain why no carbon can be detected with AES for reasons of sensitivity.

In order to see whether there is a difference in the electronic structure, EEL spectra were taken up to a loss energy of 2.5 eV. No qualitative difference between the two different surfaces could be observed and the spectra measured in previous experiments[2] with less resolution and sensitivity were completely reproduced. Further information was obtained by photovoltage measurements using laser light of 633 nm. While the contact potential of the cleaved surface decreased by about 200 meV when illuminated at room temperature, there was no measurable change observed on the polished surface. The FWHM, as well as the background intensity, was not at all affected by illumination. It is also important that the adsorption of hydrogen or oxygen did not change the photovoltage

effect at all. Each carbon treatment of a cleaved surface as described above, however, decreased the photovoltage by about 40 meV.

DISCUSSION

As indicated by the experimental findings described above, it is obvious that there is little point in interpreting the observed spectral broadening and the enhancement of the background seen in the ELS spectra of 7×7 Si(111) polished surfaces as due to intrinsic surface-electronic-structure effects. It has been shown by the differences seen between cleaved and polished surfaces that these effects by no means prove the existence of a metallic surface-state band. This raises the question as to whether the structure seen in ultraviolet photoelectron spectra (UPS) near the Fermi level would also be observed under the same experimental conditions, i.e., with the same resolution and surface preparation. The very sharp spectral features of the clean cleaved surface (Fig. 1) also clearly indicate that there is no excitation of a conduction-band plasmon. This mechanism, if visible, could probably be enhanced by increasing the charge density in the conduction band during illumination; but as already mentioned, illumination had no effect at all on the FWHM. The fact that carbon contamination and annealing causes the cleaved surface to behave like a polished one supports our previous statement that the initial carbon, which can be observed prior to cleaning the sample, is not completely removed but instead migrates into the material deep enough to become undetectable for AES. There it forms very stable siliconcarbides.

Because it was very difficult in our experiment to determine quantitatively the amount of carbon necessary to broaden the FWHM of the elastic peak, only a rough estimation can be given at the moment. After several cycles of exposing the sample to CO at 1050 K, it became obvious that the loss intensity of the carbon-induced peak at 112 meV always saturated at about the same level. Thus, assuming that this intensity is produced by about one monolayer and that only a neglectable amount has migrated below the surface, the total amount of carbon can be estimated to be roughly about four to five monolayers, because four to five cycles were necessary to arrive at a complete agreement between a polished and a cleaved surface. Unfortunately, due to the nature of the scattering process, no unambiguous determination is possible as to whether the observed additional intensity on the polished surfaces appears from electronic transitions or from vibrational excitations in the loss range under discussion.

Both possibilities should be considered here. However, models based on vibrational excitations would require such strong assumptions that the resulting models would not be very convincing. Thus, we prefer to suggest a model which can explain the observed effects by electronic transitions only.

From previous ELS measurements[2] it is known that the cleaved and the polished 7×7 Si(111) surfaces both exhibit a surface-state transition maximum at around 1.75 eV which is known as the $S1$ loss. The existence of this maximum clearly demonstrates that the critical points of
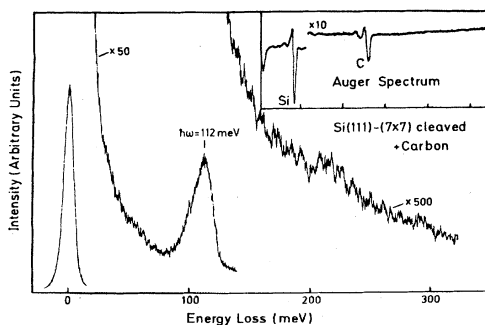

FIG. 5. Auger spectrum of a carbonized 7×7 Si(111) surface (inset) and corresponding vibrational loss spectrum. The surface was prepared by cleavage in UHV.

the combined density of states are separated by about that energy. Whether or not there is a real gap in the surface band structure cannot be decided exactly from ELS measurements; however, the observed loss intensity below the $S1$ loss demonstrates that there has to be a range where the density of states is vanishingly small.

From conductivity, SPV, and field-effect measurements[13,14] it is known furthermore that in the case of P-type materials the band-bending causes depletion as is schematically shown in Fig. 6(a). This is in contrast to polished/annealed surfaces[15,16] which reveal a band-bending pattern shown in Fig. 6(b). The differences between these two band-bending structures demand a fairly high density of states located below the Fermi level within the space-charge region. It is therefore assumed that these extra states may be induced by silicon-carbide localized in the surface region as indicated in Fig. 6(b) by the dashed line.

It is known that carbon can act as a donor in the bulk of Si (Ref. 17) but it may act differently in the present situation. Furthermore it is also possible that silicon-carbide may cause structural defects which can induce acceptor states.

The spectral differences between the two surfaces can now be easily understood. The smallest intense transition possible on the cleaved surface is the S_1 transition, while on the polished surface intraband transitions across the Fermi level with transition energies starting at $\hbar\omega \to 0$ meV become possible. This causes the broadening of the elastic peak and the increase of the background intensity. As the momentum transfer is roughly proportional to the loss energy, the decrease of the background intensity with increasing loss energy is easy to understand, as the dipole scattering probability decreases with increasing momentum transfer.

Within this model it is also easy to explain the effect of hydrogen and oxygen adsorption: It was shown[16] that the adsorption of hydrogen lifts the surface Fermi level on both surfaces by about 200 meV. From Figs. 6(a) and 6(b) it can be seen that this has no effect on the cleaved surface, but on the polished surface this shift causes the unoccupied part of the lower surface-state band to become
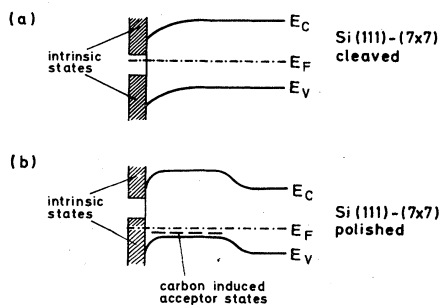

FIG. 6. (a) Schematic diagram of the electronic structure of the intrinsic (cleaved) 7×7 Si(111) surface. (b) Schematic diagram of the electronic structure of the polished surface. The dashed line indicates schematically the position of the carbon-induced extrinsic acceptor states.

smaller and smaller until its upper edge crosses the Fermilevel and no intraband transition is possible. In contrast to hydrogen, the adsorption of oxygen has only a small effect on the position of the Fermi level[16] and this explains why no reduction can be observed. The fact that the background in the oxygen spectra (Fig. 4) appears quite large has to be explained in a different way. A more detailed analysis shows that the background intensity is in fact unchanged but that the elastic peak intensity is extremely reduced because the surface becomes disordered. This causes a broadening of the angular distribution of the elastic peak and only part of its intensity is collected by the constant aperture of the spectrometer. As the undisturbed angular divergence of the elastic beam is smaller than that of the inelastic intensity, the reduction of the elastically scattered electrons is stronger than that of the inelastically scattered electrons.

It should be pointed out that the background reduction upon hydrogen adsorption can be partially accounted for by a similar effect and in this case the elastic intensity increases considerably.[11] The assumption that the carbon impurities induce localized states within the space-charge region rather than at the surface itself is strongly supported by our observation that the photovoltage effect occurs only at cleaved surfaces and is independent of the coverage of hydrogen or oxygen. This can easily be explained if one assumes that at cleaved surfaces without extrinsic bulk states the recombination has to occur only via the surface states. In contrast to polished surfaces the recombination can take place much faster via the extrinsic carbon-induced states, so that no photovoltage is seen at room temperature.

SUMMARY

With respect to our EELS data on the clean cleaved 7×7 Si(111) surface, it can be stated that there is no hint of an intrinsic metalliclike surface-state band. On the polished surface, however, the observed effects can consistently be explained by a change in the position of the surface Fermi level, giving rise to considerable extra loss intensity which is possibly in concordance with the observed intensity enhancement of the UPS signal around the Fermi energy. We showed that this change can be produced by carbon contamination. It should be pointed out, however, that the intrinsic electronic band structure of the surface is identical on both faces independent of the surface preparation, and that the observed differences can only be accounted for by band-bending effects. As a consequence, this has to be considered in the interpretation of experimental results concerning or involving the surface-state band structure and above all the development of 7×7 Si(111) structure models and their theoretical description. Whether or not carbon is the only contaminant which can induce this effect cannot be decided at the moment. One could, for instance, carry out an experiment with a boron-doped crystal. It is, however, not clear whether boron acts in the same way as carbon does, especially after heating. It would be worthwhile, however, to measure the bulk states of carbon in silicon after the same heat treatments to investigate the effect of carbon directly in all details.

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