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High-temperature annealing and surface photovoltage shifts on Si(111)7×7

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The relation between annealing temperature and surface photovoltage (SPV) shifts on the Si(111)7×7 surface of lightly *n*-doped substrates has been studied by core-level and valence-band photoelectron spectroscopies at 100 K. The SPV shift was found to depend strongly on the annealing temperature and the photon flux. Between 900 and 1150 °C the magnitude of the SPV shift shows a general decrease with annealing temperature. After a narrow plateau, the SPV shift becomes positive for annealings at 1250 and 1270 °C. As a consequence, the adatom surface state of the 7×7 surface appears above the Fermi level. The unexpected SPV shift can be explained by the formation of a *p*-type layer during high-temperature annealing of the Si sample. The role of boron and carbon contaminations has been discussed in this context in the literature. By correlating the SPV shifts with the C 1*s* and B 1*s* core-level signals, we conclude that carbon, but not boron, is involved in the formation of the *p*-type layer. Further, our results show that the annealing temperature plays a crucial role when binding energies are determined from photoemission spectra at low temperature. The effect is of particular importance in the study of surface band-gap openings related to phase transitions at low temperature.

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I. INTRODUCTION

Si surfaces have been widely used as prototypical templates for various low-dimensional atomic and electronic structures. A common problem during the cleaning process of the Si substrates is carbon contamination and the formation of silicon carbide on the surface. Two alternative methods are commonly used to overcome these problems. The first method relies on removal of C from the surface by flashing the sample in ultrahigh vacuum (UHV) at temperatures above ~1150 °C.[1,2] The second alternative involves chemical etching. One example of the latter is the Shiraki method,[3] where the native oxide is removed and a thin high-quality oxide that protects the surface is formed as the final step. The silicon-carbide formation is thereby reduced, and a fairly clean surface can be produced at low temperature (700–850 °C).[3] Nowadays, high-temperature annealing (1150–1250 °C) is widely used in surface studies as it is considered to give high-quality surfaces with large terraces and few impurities. However, besides a reproducibly well-ordered surface, one consequence of the high-temperature annealing (1150–1250 °C) is, as we will show in this paper, a modification of the doping concentration and a formation of a *p*-type layer near the surface region.

As a result of extensive studies, the atomic and electronic structures of the 7×7 surface are well established.[4–9] In previous photoemission studies, the Fermi-level pinning position was found at 0.65 eV above the valence-band maximum (VBM) on an HF-etched Si(111) sample annealed at 900–1000 °C, while a value of 0.58 eV was reported on the 1100–1200 °C annealed sample.[10,11] The Fermi-level position of the 7×7 surface is believed to be stable since it is determined by the high density of adatom surface states. In the case of an *n*-type sample with a bulk Fermi level close to the edge of the conduction band, this will result in an upward band bending, i.e., electrons will move from the bulk to the unoccupied adatom states resulting in a net negative charge on the surface. When the sample temperature is reduced, the recombination rate of photon generated electron-hole pairs becomes lower and a surface photovoltage (SPV) shift will appear in the photoemission spectra. The positive charges (holes) generated by different light sources (synchrotron radiation, visible light, etc.) will move to the surface, compensating the negative charge and thereby reducing the band bending. As a consequence the whole photoemission spectrum will shift toward higher binding energy. In the case of a *p*-type sample the initial band bending is instead downward. The SPV effect will shift the photoemission spectra toward lower binding energy and as a consequence spectral features may appear above the Fermi level.[12,13] Obviously, the SPV shifts will cause an uncertainty in the determination of the absolute energy positions of spectral features at low temperature. As a further complication, the SPV shift may vary strongly with the light intensity, which could result in a variation of the energy position of the photoemission spectrum during the course of acquiring the data. Such shifts could result in substantial broadening of spectral features. There exist two methods to circumvent this problem, i.e., by shining intense visible light on the sample from an external light source or by completely blocking any external light. The first method is used in order to saturate the SPV shift to obtain a flatband condition. The SPV effect will be stable under these conditions and the shift will have its maximum value. The second method is used to minimize the SPV effect by strongly reducing the light exposure of the sample. This method will minimize the shift of the spectral energies. To obtain "true" binding energies, it is often required that the photon flux is highly reduced since even photons from the excitation source result in an SPV shift. Traditionally, one often uses core-level spectra (such as Si 2*p*) obtained at room temperature and at low temperature to determine the SPV shift. That value is then applied to the low temperature valence-band spectra. This method has been used in the literature, especially when discussing low temperature phase transitions. However, as demonstrated in this paper, the core-level and the valence-band spectra do not show the same SPV shift in general since they are often recorded at different photon energies and with different photon flux.

In this study, the SPV shift and its relation to the annealing temperature have been investigated in detail by core-level and valence-band photoelectron spectroscopies. The low temperature SPV shift on the 7×7 surface depends strongly on the sample annealing temperature and experimental light conditions. For annealing at 900–1050 °C, the n-type SPV shift increases from 0.47 to 0.7 eV when flooding the sample with visible light. After annealing in the range of 1050–1150 °C, the absolute value of the SPV shift is reduced to 0.05–0.1 eV depending on the light conditions. An interesting p-type SPV shift of $\sim$0.15 eV was observed after annealing the sample at 1250 and 1270 °C. The SPV shifts are discussed in terms of a change in the Fermi-level position near the surface due to a depletion of dopants and a formation of a p-type layer affecting the band bending under illumination.

II. EXPERIMENTAL DETAILS

The photoemission study was performed at beam line I311 at the MAX-lab synchrotron-radiation facility in Lund, Sweden. A large hemispherical analyzer (Scienta 200) was used and the photon flux on the sample was about $10^{11}-10^{13}$ photons/s. Si $2p$ (C $1s$) core-level spectra with an energy resolution of $\sim$20 (300) meV were recorded in normal emission with an acceptance angle of about 15°. Angle integrated valence-band spectra were obtained in normal emission with a total-energy resolution of $\sim$50 meV. The Fermi level was determined from spectra measured on a Ta foil in electrical contact with the sample. The n-type Si(111) samples were cut from a Czochralski Si wafer doped by Sb (3 Ωcm). These lightly doped samples have a carrier concentration of typically 1×10^{15} cm^{-3} at room temperature. The samples were preoxidized using the Shiraki method[3] and cleaned *in situ* by stepwise direct current heating up to 900 °C for 5 min after thorough out gassing at 600 °C. This procedure resulted in a well-ordered 7×7 surface, as evidenced by a sharp low-energy electron-diffraction pattern and strong surface-state emission. The room-temperature core-level and valence-band spectra after annealing at 900 °C did not show any SPV shift and they were used as reference spectra, i.e., their binding energies do not depend on light conditions. The high-temperature annealings were done in the following steps to keep the pressure lower than 5×10^{-10} mbar: 1 min at 950 °C, 30 s at 1000 °C, 15 s at 1050 °C, 8 s at 1100 °C, 4 s at 1150 °C, 2 s at 1200 °C, 2 s at 1250 °C, and 2 s at 1270 °C. All temperatures were measured by a pyrometer (model OS3708, Omega Engineering) with a spectral response of 0.78–1.06 μm and an emissivity value set to 0.63. The core-level SPV shifts were determined by comparing the energy position of the bulk Si $2p$ core-level at 100 K with that of the room-temperature reference. The valence-band SPV shifts were obtained by comparing the energy position of the S_2 surface state at 100 K with that of the room-temperature reference. To study the response of the SPV shift to the incident light we have applied two conditions: (1) Visible light was flooded onto the sample from an external light source. (2) External light was prevented from entering the UHV chamber (windows were covered, no filaments were on). The sample was thus only exposed to the synchrotron light.

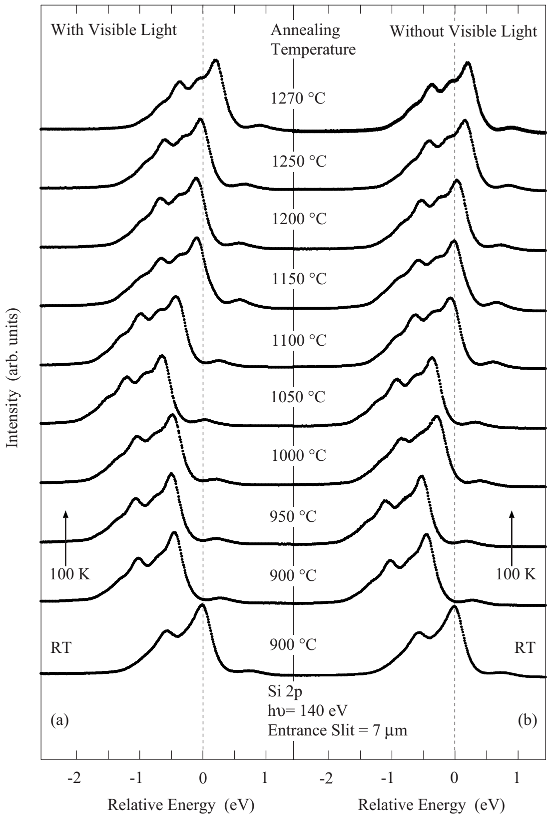


FIG. 1. High-resolution Si $2p$ core-level spectra recorded at a photon energy of 140 eV at 100 K for different sample annealing temperatures. Left (a) and right panel (b) show spectra obtained with and without external visible light, respectively. The dashed lines indicate the Si $2p_{2/3}$ bulk position at room temperature. The deviation in the energy position from that of the reference spectrum represents the SPV shift.

III. RESULTS AND DISCUSSION

Figure 1 shows a set of high-resolution Si $2p$ core-level spectra obtained after annealing at different temperatures as indicated in the figure. The spectra were recorded in normal emission using a photon energy of 140 eV. The room-temperature Si $2p$ core-level spectrum recorded after annealing at 900 °C was used as a reference. Annealing at 1050 °C or higher resulted in better resolved core-level spectra indicating a higher quality of the 7×7 surface. In earlier studies, the Fermi-level pinning position for the 7×7 surface was found at 0.65 eV above the VBM.[10,11] In Fig. 1(a), the spectrum of the 900 °C annealed surface is shifted by 0.47 eV to higher binding energy at 100 K. The bulk Fermi level of the lightly doped sample is around 70 meV below the conduction-band minimum (CBM) at 100 K. Since the band

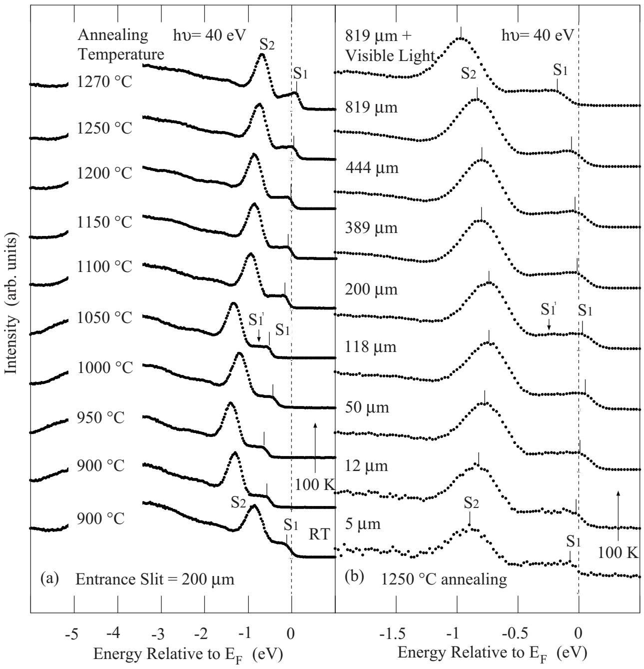


FIG. 2. Normal emission valence-band spectra recorded with a photon energy of 40 eV at 100 K. The SPV shifts as function of annealing temperatures (a) and slit widths (b) are evident from the figure. The slit was set to 200 μm in (a) and the only light source was the synchrotron itself. The spectra in (b) were obtained after the sample was annealed at 1250 °C.

gap of Si is around 1.17 eV at 100 K, the estimated Fermi pinning position is 0.63 eV above the VBM. This value is quite close to the one in Ref. 11, indicating a consistent result with this earlier study of the 7×7 surface. However, after the sample had been subjected to annealing at higher temperatures the Si $2p$ spectra shifted dramatically, as shown in Fig. 1.

The Fermi level of the 7×7 surface cuts through the low binding-energy side of the S_1 peak that corresponds to emission from the adatom surface state, as shown in the valence-band spectra in Fig. 2 (due to charge transfer from the adatoms to the rest atoms and the corner hole atom, there remain five electrons to be shared by the 12 adatoms). One can calculate the depletion-layer width and the surface charge concentration needed for a band bending of 0.47 eV. The estimated depletion-layer width is 6400 Å and the surface charge concentration corresponds to an additional electron concentration of about 1×10^{11} cm^{-2} at the surface. Compared to the electron concentration due to the five adatom electrons in the 7×7 unit cell (8×10^{13} cm^{-2}) this is only an increase by 0.12%. Such a small increase indicates that the Fermi position is very stable on the 7×7 surface. Thus, the dramatic shift of the Si $2p$ core-level spectra must originate from a change of the Fermi level of the subsurface layers. From 950 up to 1050 °C, the SPV shift of the Si $2p$ spectrum changes from -0.47 to -0.66 eV. For higher annealing temperatures, from 1050 to 1250 °C, the Si $2p$ core-level spectra move back toward the room-temperature energy position [Fig. 1(a)]. An unusual shift is observed after the 1270 °C anneal. The spectrum exhibits a shift to lower binding energies compared to the room-temperature spectrum (positive SPV shift). The magnitudes of the SPV shifts do not only depend on the annealing temperature but they also vary with light conditions. The spectra in Fig. 1(a) were obtained when the sample was flooded with light from an external visible-light source, while the sample was only exposed to the synchrotron light when the spectra in Fig. 1(b) were recorded. Except for the 950 °C annealing step, the spectra in Fig. 1(b) are shifted to lower binding energies compared to those in Fig. 1(a). As a consequence, also the 1250 °C spectrum shows a clear positive SPV shift when the light is reduced.

The valence-band spectra show SPV shifts of similar magnitudes to those of the core-level spectra. Figure 2(a) shows a set of normal-emission spectra where the only light source was the synchrotron radiation itself. Except for a gradually more pronounced S_1 structure after each annealing step all spectra are quite similar. In these spectra, two surface states, S_1 and S_2, originating from the adatoms and the rest atoms are clearly resolved. One may notice that another surface state, S_1', just below S_1, is barely visible after annealing at 1050 °C and above.[7] As already mentioned above, if a large change of the SPV shifts was caused by a change in the Fermi pinning position on the 7×7 surface, one would expect a significant change in the shape of the S_1 surface state. Obviously, this is not the case. The rigid shift of the entire valence-band spectra and the more or less constant S_1 intensity indicate a rather stable surface Fermi pinning position. At low temperature (100 K), a downward shift of the valence-band spectrum by -0.46 eV obtained from the 900 °C annealed surface fits well with the SPV effect that straightens out the band bending. Consistent with the core-level measurements, adding visible light shifts the valence-band spectra to even higher binding energy. The largest SPV shift, -0.7 eV, was found for the 1050 °C annealed surface when flooded with visible light. In Fig. 2(a), the unexpected p-type SPV shifts for the n-type substrate are particularly evident after annealing at 1250 and 1270 °C since S_1 appears above the Fermi level.

The occurrence of photoemission features above the Fermi level can be explained by the formation of a p-type layer near the surface.[12–17] This will give an SPV shift in the positive direction, i.e., the spectra will shift upward. If the shift is large enough, the upper part of the spectra may even appear above the Fermi level as for the 1250 and 1270 °C annealed surfaces. The SPV shift was also found to vary with the synchrotron light intensity. Figure 2(b) shows how the valence-band spectra shift as a function of the width of the slit between the monochromator and the spectrometer for the 1250 °C annealed surface. The change in the SPV shift has been studied for slit widths from 5 up to 819 μm by monitoring the position of the S_1 and S_2 surface states. In Fig. 2(b), S_1 starts out just below the Fermi level and moves to a position of $\sim$0.1 eV above for a slit width of 118 μm. When the slit is opened further, the spectra shift downward and S_1 is found close to the initial position using an 819 μm slit. There is a further downward shift to $\sim$0.13 eV below the Fermi level when the sample is also flooded with visible light.

Figure 3 shows a summary of the SPV shifts obtained from the Si $2p$ core-level and the valence-band spectra. Evi-

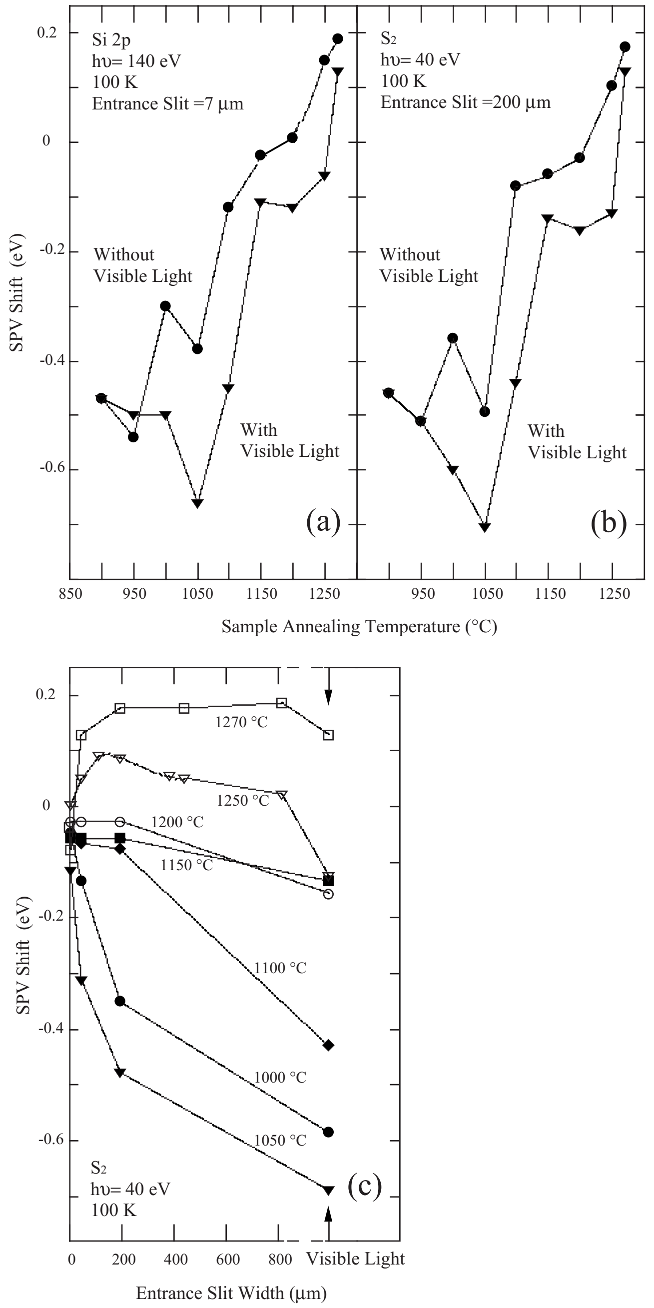


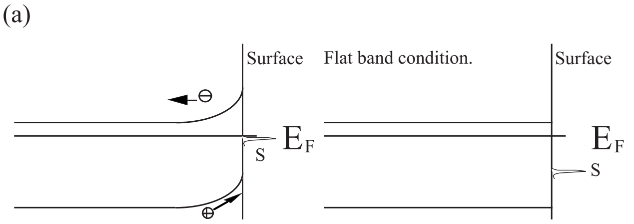
FIG. 3. Summary of SPV shifts under various conditions. (a) Si 2*p* shifts versus sample annealing temperatures obtained from Fig. 1. (b) As (a) but for the S_2 surface state in the valence-band spectra. (c) SPV shifts as a function of light intensity (slit widths and external light).

dently, the Si 2*p* core-level and the valence-band spectra do not show the same SPV shifts. This discrepancy is related to the fact that the experimental conditions (photon energy and flux) were different. A difference of 50–100 meV is frequently observed when comparing the two sets of SPV shifts. Both the Si 2*p* and valence-band spectra show the same tendency of the SPV shifts for the high-temperature annealings. For the 900 °C annealed surface, we find the same SPV shift (−0.47 eV) with or without external light. This means that the SPV effect is already saturated by the synchrotron light itself. The largest absolute value of the SPV shift, 0.7 eV, was observed after annealing at 1050 °C under the light flooding condition [Fig. 3(b)]. Based on a Fermi level at 0.63 eV above the VBM, the apparent band bending value of 0.7 eV would require a Fermi level in the bulk at 1.33 eV above the bulk VBM. This value is 0.16 eV larger than the band gap. The sample thus behaves as if it was degenerately *n* doped. The position of the Fermi level corresponds to a doping concentration of about 3×10^{20} cm^{-3}. An accumulation of the Sb dopant would in principle explain this behavior, but it is considered less likely. At annealing temperatures of 1050 °C a depletion of the dopant is the more realistic scenario,[15,18] leaving the exceptionally large SPV shift unexplained at this point. We may only speculate that vacancies injected into the crystal and quenched by the fast cooling process are involved in getting this high doping level.

A dramatic reduction in the SPV shifts is quite clear for the 1100 and 1150 °C annealing steps. A depletion of the dopants would shift the Fermi level of the subsurface layers well below the CBM, resulting in a decrease of the band bending. For a complete depletion one can expect that the Fermi level of the near surface layers approaches the intrinsic level, which is near the middle of the band gap. At 100 K this value is about 0.59 eV above the VBM. In that case, the Fermi level of the subsurface layers would be nearly aligned with the Fermi level of the 7×7 surface. After annealing at 1150 °C, both Si 2*p* and valence-band spectra show very small SPV shifts, −30 and −60 meV, respectively, without external light. In Figs. 3(a) and 3(b), a plateau appears between 1150 and 1200 °C corresponding to a small variation of the SPV shift. The *p*-type SPV shift appears on the 1250 °C annealed surface without any external light. A *p*-type SPV shift is also observed for the 1270 °C annealed surface, in both core-level and valence-band spectra irrespective of the light conditions. We attribute the results after the 1250 and 1270 °C anneals to the formation of a *p*-type layer in the near surface region. The existence of a *p*-type layer after the 1270 °C anneal was also confirmed by so-called hot-probe measurements, showing hole conduction in the near surface region.

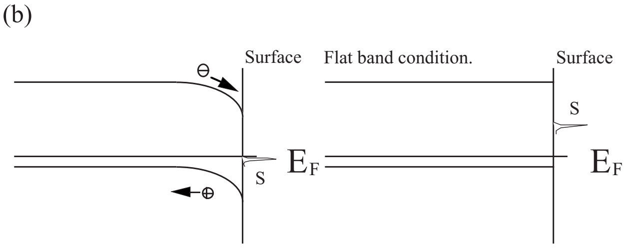
Figure 3(c) shows the SPV shifts obtained from the valence-band spectra using different slit widths for the synchrotron light. For the smaller slit widths, the SPV shifts obtained after the various annealing steps all reduce toward zero with decreasing slit width. Except for this common feature, the curves showing the SPV shifts vs. slit widths are quite different. Compared to the 1000 °C step, a more rapid change of the SPV shift is evident for the 1050 °C annealed surface. A more or less flat curve appears after the 1150 and 1200 °C annealing steps, while a *p*-type SPV shift is observed after the 1250 and 1270 °C anneals. It is interesting to note that the SPV shift first increases to a maximum value, and then decreases as the slit is opened further. (In the case of the 1270 °C anneal the decrease does not occur until the sample is flooded with visible light.)

As mentioned above, the Fermi position of the 7×7 surface is pinned by S_1 at 0.63 eV above the VBM.[10] For a normal *n*-type sample, this means an upward band bending since the electrons from the bulk will occupy the unfilled part of the S_1 surface band so that the bulk and surface Fermi



n-type sample with upward band bending.

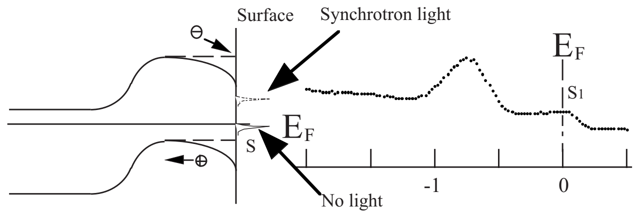
n-type sample with SPV shift to higher binding energy at low temperature.



p-type sample with downward band bending.

p-type sample with SPV shift to lower binding energy at low temperature.

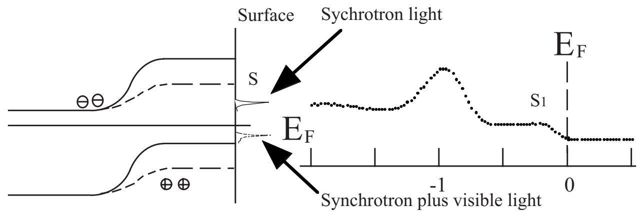
(c) 1250 °C annealed surface.



n-type bulk, p-type layer

S_1 is above the Fermi-level.

(d) 1250 °C annealed surface.



n-type bulk, p-type layer

S_1 is below the Fermi-level.

FIG. 4. SPV shifts and band bending. (a) *n*-type sample. (b) *p*-type sample. (c) *n*-type sample with a *p*-type layer near the surface, exposed to synchrotron light only. (d) *n*-type sample with a *p*-type layer near the surface, exposed to synchrotron light plus external visible light.

levels become aligned [Fig. 4(a)]. The visible light (or synchrotron light) generates electron-hole pairs in the surface region. At room temperature, the recombination rate is high and there is no effect on the band bending. At low temperature, however, when the recombination rate is reduced, the electrons and holes will become physically separated. An upward band bending forces the electrons to move into the bulk while the holes move to the surface. The holes will compensate the negative surface charge associated with the upward band bending, thereby inducing a change toward a flat band condition. Thus the photoemission spectra will shift toward higher binding energy at low temperature [Fig. 4(a)]. For a *p*-type sample the band bending and the shift are just in the opposite directions [Fig. 4(b)] and the S_1 state will therefore move above the Fermi level. Evidently, the 900 °C annealed sample shows a normal *n*-type SPV shift. The 1250 °C surface shows a mixed behavior. Initially it acts as a *p*-type sample, but as the light flux is increased the positive SPV shift decreases and it turns to a negative shift as expected for an *n*-type sample. The mixed behavior clearly points to a *p*-type subsurface layer with a buried *pn*-junction underneath. Figure 4(c) shows a schematic drawing of a likely band bending scenario for the 1250 °C annealed surface with an *n*-type bulk below a *p*-type layer near the surface. Due to the *p*-type layer, the bands are bent upward to align the Fermi levels of the *n*-type bulk and *p*-type layer. Close to the surface there is a downward band bending determined by the Fermi-level position at the surface. With synchrotron light, the positive SPV shift caused by the *p*-type layer near the surface is dominating [Fig. 4(c)]. With increasing light exposure the shift due to the *pn*-junction becomes apparent and leads eventually to a negative *n*-type SPV shift as expected for an *n*-type sample [Fig. 4(d)].

Figure 5 shows a series of C 1*s* spectra after the different annealing steps. On the initial, 900 °C annealed surface a small C 1*s* component was detected. Also the C 1*s* spectra show the SPV effect when measured at low temperature (100 K). It is, however, difficult to make absolute comparisons with the SPV shifts from the Si 2*p* and valence-band spectra since the chemical shift of the C 1*s* component may differ throughout the annealing series. In Fig. 5 one can follow the reduction in the C 1*s* signal as the annealing temperature is increased. The carbon signal reduces rather slowly from the 4% reduction after the 1000 °C anneal up to the 40% reduction found in the 1200 °C spectrum. The following step, the 1250 °C anneal, has a more dramatic effect and it results in a 90% reduction compared to the initial C 1*s* signal. This strong decrease in the intensity of the C 1*s* component coincides with the switching to a *p*-type SPV shift. After the 1270 °C anneal no C 1*s* component is detectable.

It should be pointed out that the annealing series in this study were recorded in order to obtain detailed information on the SPV shifts during high-temperature annealing, but the different annealing steps are not crucial for the development of a *p*-type layer. For instance, a *p*-type layer may also be formed by flashing above 1200 °C, directly after an initial cleaning around 900 °C. We have also observed large changes of the SPV shifts (0.70–0.85 eV) on Si(100) samples after high-temperature annealing (1200–1260 °C). Thus, the formation of a *p*-type layer also occurs on Si(100) samples. This implies that the formation of a *p*-type layer is a general property of silicon, not limited to a specific surface orientation or surface reconstruction.

It is of general interest to find out what causes the *p*-type layer since this issue has not yet been settled. In previous studies,[14–17] three origins of the *p*-type formation on *n*-type samples were proposed, i.e., B contamination from borosilicate windows of the UHV systems,[15] or from glass beakers in the Si cleaning process, Si vacancies,[16] and in-diffusion of

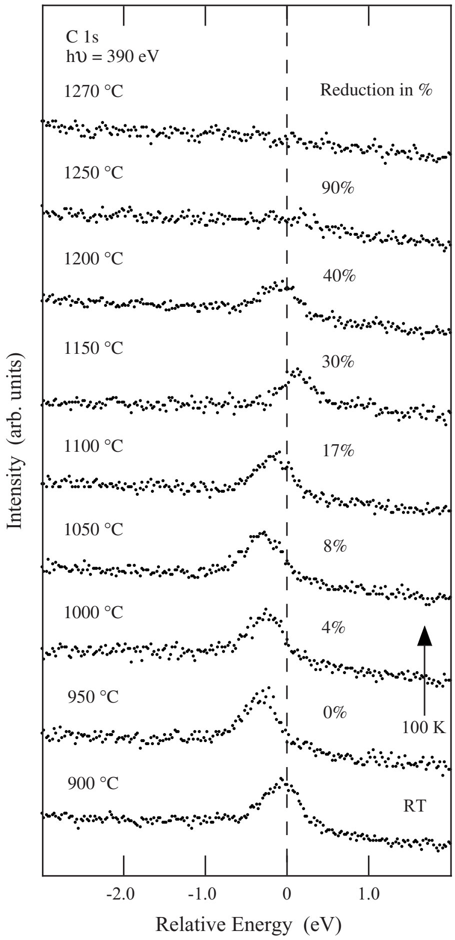


FIG. 5. C 1*s* core-level spectra recorded at a photon energy of 390 eV at 100 K for different sample annealing temperatures. The only light source was the synchrotron itself. The reduction in the C peak intensity is indicated after each annealing step.

carbon.[17] On the initial 900 °C annealed sample, we detected a tiny B 1*s* signal. The B peak started to reduce at 1000 °C and had vanished after the 1150 °C annealing, where the small plateau is found in Figs. 3(a) and 3(b). Since boron can act as an acceptor in Si, it is tempting to explain the *p*-type layer formation by surface boron diffusing into the sample. However, we have also observed the formation of a *p*-type layer on an initially B-free *n*-type sample after annealing at 1260 °C. Thus, our photoemission data do not support the idea that boron contamination is causing the *p*-type layer. On the B-free sample, the C peak vanished during the 1260 °C anneal, a point at which the SPV shift entered into the *p*-type region. The main difference between the B-contaminated and B-free samples is found for annealing temperatures below 1150 °C. Except for the extreme value of the SPV shift at 1050 °C, Figs. 3(a) and 3(b) show the general trend that the absolute values of the SPV shifts decrease up to the plateau at 1150 °C. The boron free surface shows a quite different SPV curve in this temperature range. The SPV shift is constant between 900 and 1050 °C, and between 1050 and 1200 °C the absolute value of the SPV shift increases. After this point there is a rapid change from the maximum *n*-type shift to a *p*-type shift. The gradual change toward a *p*-type behavior in the 950–1050 °C range, observed on the boron-contaminated surface, may very well be related to acceptor levels due to boron diffusing into the near surface layers. However, the change to a *p*-type SPV shift occurs both with and without an initial boron contamination and we therefore correlate it with the disappearance of carbon from the surface.

In an earlier study,[16] an increase in acceptor levels on an *n*-type sample was observed at 700 °C and was found to be saturated at 1050 °C. The *p*-type formation was explained in terms of Si vacancies. These results and conclusion are hard to discuss in the context of our results since the *p*-type layer formation starts at significantly higher annealing temperature in our case. Apart from the data presented in this study, we have in many other cases observed that the *p*-type SPV shift appears with the disappearance of the C peak from the surface. Thus we conclude that carbon is related to the *p*-type layer formation. It has been suggested that carbon may enter into the subsurface layers to act as a donor, or that silicon-carbide related structural defects could induce acceptor states.[17]

IV. CONCLUSIONS

The relation between annealing temperature and the low temperature SPV shifts has been studied by core-level and valence-band photoelectron spectroscopies. Clearly, high-temperature annealing (1150–1270 °C) results in higher quality spectra of the Si(111)7×7 surface. The SPV shift was found to depend strongly on the annealing temperature and the photon flux. Between 900 and 1250 °C the sign of the SPV shift is that expected for an *n*-type sample, but the magnitude shows a strong variation (0–0.7 eV). After annealing at 1250 °C, the SPV shift changes sign. This unexpected situation can be explained by the formation of a *p*-type layer in the near surface region. Based on our core-level data we have gained conclusive information regarding the role of boron and carbon contamination for the formation of the *p*-type layer, which has been discussed in the literature. Since the *p*-type shift was observed on boron contaminated as well as boron free surfaces we conclude that carbon contamination alone is sufficient to create the *p*-type layer. Our results show that the strong influence of the annealing temperature on the effective doping level in the near surface region can have a very large effect on the determination of binding energies in photoemission spectra obtained at reduced sample temperature. This is especially crucial when phase transitions, occurring at low temperature, are studied.

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