Energy gap revealed by low-temperature scanning–tunnelling spectroscopy of the Si(111)-7 × 7 surface in illuminated slightly doped crystals

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Abstract
Physical properties of the Si(111)-7 × 7 surface of low-doped n- and p-type Si samples are studied in the liquid helium temperature region by scanning–tunnelling microscopy and spectroscopy. Conduction required for the study is provided by illumination of the surface. Application of illumination completely removes the band bending near the surface and restores the initial population of the surface states. Our results indicate the existence of the energy gap $2\Delta = 40 \pm 10$ meV in the intrinsically populated Si(111)-7 × 7 surface.

1. Introduction
Si(111)-7 × 7 is one of the most extensively studied crystal surfaces of semiconductors. It has a relatively high surface density of states with the Fermi level sitting inside one of the surface zones. The latter must lead to the metallic character of Si(111)-7 × 7 [1]. Experimental studies have demonstrated, however, contradictory behaviour. Some authors report metallic properties of Si(111)-7×7 [2], whereas others observe the dielectric gap with the value varying between 70 meV [4] and 1 eV [5]. Non-metallic behaviour is also found in the transport measurements [7]. Revealed contradictions have resulted in a significant increase of the number of publications devoted to physical properties of the Si(111)-7 × 7 surface.

In general, low-temperature scanning–tunnelling microscopy (STM) and spectroscopy (STS) studies of the Si(111)-7 × 7 surface are carried out using heavily doped Si (typical resistivity $\rho \sim 0.01-0.001$ Ω cm). Such a high doping level is necessary to provide a reasonable conduction, especially in the low-temperature range. But the effect of doping on the surface concentration of current carriers is not negligible. As will be argued below, a typical variation of the surface current carrier concentration is of the order of its value in heavily doped crystals. Thus, in principle the effect of doping may be responsible for variation of physical properties of the Si(111)-7 × 7 surface obtained by different groups, so it deserves a special consideration.

Here we report the results of our STS study of the energy spectrum of the Si(111)-7 × 7 surface in slightly doped n- and p-type Si at temperatures of 5 and 78 K under illumination, which was used to remove band bending near the surface and provide STM measurements at 5 K. We also demonstrate the possibility of STM and STS measurements in nominally dielectric Si samples in a new mode when the external circuit contacts the crystal surface. The results confirm the existence of the dielectric gap $2\Delta = 40 \pm 10$ meV in the low-temperature region on p-type and n-type crystals, in qualitative agreement with the earlier observation [4].

2. Experimental details
We studied n- and p-type Si with $\rho = 1$ Ω cm. Such crystals are insulating in the low-temperature region. Conduction required for STS and STM study can be achieved by illumination of the surface by light with the photon
energy above the Si energy gap. A relatively lower doping level provides smaller band bending with respect to the heavily doped Si usually studied, and a larger lifetime for non-equilibrium carriers excited by a general white light LED with the estimated light intensity \( \sim 10^{-4} \, \text{W cm}^{-2} \) at the sample position. The illumination can also be used for additional flattening of the band structure near the surface (see below).

High-quality Si(111)-7 \times 7 surfaces were prepared in situ with the standard procedure of 10 h degassing at \( T \approx 900^\circ \text{C} \) DC followed by flashing up to 1250°C for 10 s and slow computer-controlled cooling down. All the experiments were performed in an LT UHV Omicron STM at a base vacuum level below 10^{-10} \, \text{Torr}. We used cut platinum and electrochemically etched tungsten STM tips cleaned with a focused electron beam in ultra-high vacuum conditions. We made measurements on several p- and n-type silicon samples with different Pt and W tips, to obtain reproducible results.

The relatively low conduction of studied surface does not allow us to use a fast voltage sweep, so we use 500 voltage points in each voltage sweep direction and 40 ms signal integration time for each voltage point. With such a setting no noticeable hysteresis between back and forth voltage sweeps was observed. The \( I-V \) curves presented here were measured over the adatom in the centre of a side of the Si(111)-7 \times 7 unit cell and averaged over series of measurements consisting of ten individual cycles for survey curves and 50 for detailed curves. Similar results were obtained in the measurements performed over the corner adatom and the corner hole positions. Finally, it took about half an hour to collect the data for a single detailed curve. The drifts at liquid helium temperature are insignificant and the STM tip is stable at one point during one measurement. Differential conduction was calculated numerically from the resulting \( I-V \) curve.

3. Results

Figure 1 shows an STM image of an illuminated Si(111)-7 \times 7 surface obtained at the helium temperature. The middle part of the image was taken without illumination. It is clearly seen that switching the illumination off results in destruction of the reconstruction (image centre), which was absent before this procedure. This indicates the impossibility of STM study of low-doped Si samples without an additional conduction-improving action. Thus, illumination extends the range of doping level appropriate for STM study.

Typical low-temperature \( I-V \) and \( dI/dV \) curves of illuminated Si(111)-7 \times 7 surfaces of p- and n-doped crystals are shown in figure 2. The curves indicate the presence of the energy gaps at non-zero voltage positions. The results allow us to determine the midgap positions: they are shifted from zero voltage by \( V_{\text{ph}} = 0.6 \) and \(-0.4 \, \text{V} \) for p type and n type respectively, due to the effect of surface photovoltage. A detailed explanation is given in section 4.

Figure 3 provides a more detailed view of the gap regions measured with 1 mV voltage resolution. The gap edges are relatively sharp; the gap values in both cases are the same, 2\( \Delta = 40 \pm 10 \, \text{meV} \). Figure 3(c) shows a set of \( dI/dV \) curves measured at different surface–tip distances \( Z \). It is clearly seen that the shape of the curves does not change in the way reported by Modesti et al [4], who observed an increase of the gap at small \( Z \) due to the contribution of the surface–sample holder circuit resistance. The resistance of illuminated samples is much smaller the resistance of the tunnelling barrier and does not affect the measured energy gap value.

In addition, we studied the energy spectrum of an Si(111)-7 \times 7 sample with the surface partially covered by In. The procedure of In deposition was the following. The STM tip was placed 10 nm from the surface, thus creating a shadow mask; the STM feedback circuit was switched off. Then a small amount of In was deposited on the surface at 5 K, the STM feedback circuit was switched on and the STM returned into a normal regime. The In film thickness obtained from the STM profile data was \( \sim 10 \, \text{nm} \). As a result, a fragment of clean Si(111)-7 \times 7 surface surrounded by an In layer was prepared. We found that such a procedure provides enough surface conduction for STM/STS study of the clean fragment of the surface even without illumination. Illumination, however, enables further conduction increase and facilitates observation of the energy gap. Such a coverage provides an electrical contact to the Si(111)-7 \times 7 surface and eliminates the effect of surface photovoltage. The results are presented in figure 4.

At \( T = 78 \, \text{K} \) the effect of illumination on the \( I-V \) curves is many orders smaller and does not affect the shape of the \( I-V \) curves. At this temperature the energy gap disappears and the Fermi level sits inside the surface band, providing thereby the metallic conduction of the surface (figure 5), in agreement with the general results [1].
Figure 2. $I-V$ and $dI/dV$ curves of illuminated Si(111)-7×7 surface ((a) p type, $\rho = 1$ Ω cm; (b) n type, $\rho = 1$ Ω cm) at $T = 5$ K. The energy gap for both samples shifted by photovoltage is clearly seen in the $dI/dV$ curve. Positive voltage means positive potential of the sample.

Figure 3. $dI/dV$ curves of the illuminated Si(111)-7×7 surface in the gap region at $T = 5$ K. (a) p type, $\rho = 1$ Ω cm; (b) n type, $\rho = 1$ Ω cm; (c) set of $dI/dV$ curves measured at different surface–tip distances $Z$ for p-type sample, $\rho = 1$ Ω cm. $\Delta Z = Z - Z(V_0, I_0)$ is the STM tip shift to the surface with respect to the set point. The set point is $V_0 = 2$ V and $I_0 = 100$ pA. The curves are shifted in the vertical direction for clarity.

4. Discussion

The Fermi level is strongly pinned for both p- and n-type Si(111)-7×7 surfaces due to a substantial density of states near the Fermi level [8]. The pinning position lies near the middle of the bulk band gap at 0.65 eV above the valence band maximum [8]. Pinning of the Fermi level is provided by a variation of surface electron concentration required to screen the electric field produced by charged impurities in the space charge region, shown schematically in figure 6. The variation of the surface current carrier concentration can be estimated as the total charge density of the space charge region per unit
surface area

$$\Delta Q \approx dN_a$$

(for p-type silicon), where $N_a$ is the bulk concentration for acceptor atoms, depending on doping level, and $d$ is the depletion layer thickness. In its turn $d$ can be estimated as

$$d \approx \sqrt{\frac{2e\epsilon_0\Delta E}{e^2N_a}}$$

where $\Delta E = E_p - E_a$, $E_p$ is the pinning position of the Fermi energy on the surface, $E_p = 0.65 \pm 0.05$ eV for Si(111)-7 × 7 [8], $E_a$ is the bulk Fermi level, which is approximately the bulk acceptor energy level, 0.045 eV (both $E_p$ and $E_a$ are shown here with respect to the top of the valence band), and $\epsilon$ = 11.7 is the relative permittivity of Si. The Si(111)-7 × 7 surface has five electrons per unit cell [6], thus the surface current carrier concentration can be estimated as $N_s \approx 8 \times 10^{13}$ cm$^{-2}$. For heavily doped silicon samples widely used in low-temperature STM/STS studies, with typical resistivity $\rho \sim 0.01–0.001$ $\Omega$ cm, the impurity concentration $N_a$ is an order of $10^{19}–10^{20}$ cm$^{-3}$ [3]. The respective surface charge concentration change can be estimated as $\Delta N_s \approx 0.9 \times 10^{13}–3 \times 10^{13}$ cm$^{-2}$, which amounts to 10–40% of the nominal value. For slightly doped silicon with $\rho \gtrsim 1$ $\Omega$ cm, this change is $\Delta N_s \approx 8 \times 10^{10}$ cm$^{-2}$, smaller than 1%.

Thus, the effect of variation of surface carrier concentration in heavily doped crystals may be strong and should be taken into account. As will be shown below, external illumination removes the effect of surface carrier concentration change and allows us to investigate the intrinsic properties of the Si(111)-7 × 7 surface.

Illumination-induced changes of the energy band structure near the surface for slightly doped silicon are shown schematically in figure 6. In the dark, pinning of the Fermi level at the surface leads to formation of the Schottky barrier with the respective band bending $\Delta E$. Non-equilibrium carriers produced by illumination are separated by the electric field near the surface, thereby reducing this field. At sufficiently large illumination intensity the field is almost completely suppressed and the bands are practically flat. The surface potential is shifted by $\Delta E$, the band bending without illumination (i.e. without the Schottky barrier), and the initial current carrier concentration is restored.

The surface photovoltage shifts the whole $I$–$V$ curve by $V_{ph} \leq \Delta E/e$, where $e$ is the elementary charge, in a positive
direction $\Delta E = E_p - E_a$, $\Delta E \approx 0.6$ eV, for p-type samples, and in a negative direction $\Delta E = E_g - E_p - E_d$, $\Delta E \approx 0.47$ eV, for n-type samples, where $E_p$ is the Fermi surface pinning level for $7 \times 7$ structure (0.65 eV) [8], $E_a$ and $E_d$ are acceptor and donor energy levels for B and P dopants and $E_g$ is the silicon bulk gap, 1.17 eV at $T = 5$ K. The observed values of the photovoltage shifts (+0.6 eV for p-type and −0.4 eV for n-type samples) practically coincide with the estimated ones (+0.6 eV and −0.47 eV). This means that illumination almost completely suppresses the Schottky barrier.

An odd number of electrons per unit cell implies metallic conduction of the Si(111)-7 × 7 surface. Observation of the energy gap at the Fermi level testifies to the importance of electron–electron correlations, as already discussed in numerous papers (see e.g. [2, 4, 6] and references therein). Note that a small suppression of the energy gap upon tip approach (see figure 3(c)) is consistent with local screening of the Coulomb interaction by the conducting tip surface. Possible scenarios of gap opening include a Mott–Hubbard mechanism assisted by electron–phonon interaction [4], formation of a two-dimensional Wigner crystal or density waves (for a review see [9] and references therein). Note that the energy gap value of the Si(111)-7 × 7 surface is the same in slightly doped p- and n-type samples, but is almost two times smaller than the gap value reported in [4] for heavily doped samples. In most scenarios the smaller gap value corresponds to a bigger bare electron density of states of the Si(111)-7 × 7 surface at the Fermi level. An additional contribution of random potential caused by doping impurities into the gap value cannot be excluded. Further study is necessary to distinguish different possibilities.

5. Conclusion

In conclusion, we have studied the low-temperature energy structure of the Si(111)-7 × 7 surface. We argue that physical properties of the surface should depend essentially on the doping level; therefore, we performed our measurements on low-doped Si samples. Illumination allows us to extend the range of doping level appropriate for STM study, removes almost completely the band bending near the surface and reveals intrinsic properties of the studied surface. Our results indicate the existence of the energy gap $2\Delta = 40 \pm 10$ meV in the Si(111)-7 × 7 surface at $T = 5$ K for both p- and n-type low-doped silicon crystals.

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