Fizika Nizkikh Temperatur, 2003, v. 29, No. 3, p. 263–269

Low temperature electron transport on semiconductor surfaces

M. Lastapis, D. Riedel, A. Mayne, K. Bobrov, and G. Dujardin

Laboratoire de Photophysique Moleculaire, Batiment 210
Universite Paris-Sud, 91405 Orsay Cedex, France
E-mail: gerald.dujardin@ppm.u-psud.fr

Received October 2, 2002

The low temperature electron transport on semiconductor surfaces has been studied using an ultra high vacuum, variable temperature Scanning Tunneling Microscope (STM). The STM $I(V)$ spectroscopy recorded at various temperatures has enabled to investigate the temperature dependence (300 K to 35 K) of the surface conductivity of three different semiconductor surfaces: highly doped n-type Si(100), p-type Si(100), and hydrogenated C(100). Low temperature freezing of specific surface electronic channels on the higly doped n-type Si(100) and moderately doped p-type Si(100) surfaces could be achieved whereas the total surface conductivity on the hydrogenated C(100) surface can be frozen below only 180 K.

PACS: 72.20.Jv

1. Introduction

The operation of nanoscale electronic devices requires an efficient electronic decoupling from the substrate on which the devices have been built [1]. This can be best achieved either on insulating or on low temperature semiconducting substrates. For example, the electronic transport of gold nanowires deposited on a Si(111) surface has been recently measured at low temperature (4 K) [1]. At such a low temperature, all the measured current flows through the gold nanowire as long as the applied bias voltage is within the silicon electronic band gap. Indeed, the electronic channels through the silicon surface whose energy are located within the band gap are assumed to be frozen at such a low temperature. Low temperature semiconductor surfaces have several advantages over insulators. First, they can still be conducting at low temperature, when sufficiently doped [2]. This allows the use of experimental surface techniques requiring some surface conductivity such as the Scanning Tunneling Microscope (STM). Second, the preparation of high quality surfaces having few defects at the atomic-scale is much easier for semiconductors.

The low temperature electron transport properties of *bulk* semiconductors are rather well understood [2], mainly in terms of the decreased number of free carriers. However, when dealing with *surface* properties, the situation is much more complicated. Indeed, the interface between the semiconductor and the vacuum can produce specific surface (or sub-surface) electronic states inducing charges or holes confined at the surface [3,4], which may completely modify the low temperature electron transport properties.

The low temperature electron transport properties of semiconductor surfaces have never been investigated before at the atomic-scale, except a recent study of the Ge(111) surface [5]. In this paper, we report the temperature dependence of the electron transport properties of three different semiconductor surfaces: highly doped n-type Si(100), p-type Si(100), and hydrogenated C(100). We used the $I(V)$ spectroscopy using the STM performed at various temperatures to explore the conductivity of these surfaces. The observed behavior is very different in these three cases. It will be shown that specific surface conductivity channels can be frozen at low temperature for highly doped n-type Si(100) and p-type Si(100), whereas the surface conductivity is completely frozen at low temperature for hydrogenated C(100).

2. Experimental

The electron transport properties of semiconductor surfaces have been measured in an ultra high vacuum (UHV) chamber (base pressure $2{\cdot}10^{-11}$ torr) using a variable temperature Scanning Tunneling Microscope (STM). The sample can be cooled down to 30 K using a helium liquid flow cryostat.

© M. Lastapis, D. Riedel, A. Mayne, K. Bobrov, and G. Dujardin, 2003

Three types of semiconductor samples have been studied:

– *highly doped n-type* Si(100): the silicon sample (6×2×0.1 mm) was n doped with Arsenic (bulk resistivity of 0.004 to 0.007 $\Omega \cdot$ cm). Clean and well ordered Si(100)–(2×1) reconstructed surfaces were obtained by first outgassing for at least 12 hours at 700°C in UHV before flashing to 1080°C to remove the oxide layer. The duration of each flash was adjusted such that the pressure remained below $1{\cdot}10^{-9}$ torr (usually < $2{\cdot}10^{-10}$ torr).

– *p-type* Si(100): the silicon sample (6 × 2 × ×0.25 mm) was p doped with Boron (bulk resistivity 0.7 to 1.3 $\Omega \cdot$ cm). Clean and well ordered Si(100)–(2×1) reconstructed surfaces were obtained as described before.

– *hydrogenated* C(100): the diamond sample (6×1×0.2 mm) is a natural single crystal of (100) orientation. It is a weakly Boron p-type doped sample. Prior to insertion into the UHV chamber, the diamond sample was ex-situ saturated with hydrogen in a microwave hydrogen plasma at 800°C for 1 hour. Details on the hydrogenation procedure can be found elsewhere [6]. Clean and well ordered hydrogenated C(100)–(2×1):H surfaces were obtained by outgassing in UHV for a few minutes at 300°C to remove any physisorbed species from the surface.

During the STM experiments, the edges of the sample were sandwiched between two molybdenum plates to which the voltage was applied.

Experiments were performed as follows at a given sample temperature between 30 K and 300 K. The sample surface was first imaged at a constant tunnel current with the STM. For some samples and some temperatures, no tunnel current could be established between the STM tip and the sample. In such cases, the STM tip crashed on the surface. Where the STM imaging was possible, the STM tip was located at fixed positions across the surface and $I(V)$ spectroscopy curves were recorded at a fixed tip-surface distance.

3. Results and discussions

Before we discuss the results, one should note that the $I(V)$ STM spectroscopy curves are usually considered to be due only to the STM junction conductivity. Indeed, the conductance between the electronic surface states located under the STM tip and the sample metallic holder to which the voltage is applied is assumed to be very high. In such a case, the $I(V)$ curves only reflect the coupling between the surface electronic states of the tungsten tip with those of the sample surface [3]. However, at low temperature, where the resistivity of the semiconductor sample cannot be neglected anymore, the analysis of the $I(V)$ curves is more complicated. The measured I/V conductivity is the combination of the STM junction conductivity itself, the coupling between the electronic surface states of the sample and the electronic channels through the sample and the conductivity of these electronic channels as far as the sample molybdenum holders. At this point, the electronic channels through the sample can be either surface or bulk electronic channels.

3.1. Highly doped n-type Si(100)

The highly doped n-type Si(100) surface could be easily imaged with the STM at any temperature between 30 K and 300 K under usual sample voltage (V = −1.5 V) and tunnel current (I = 0.5 nA) conditions (see Fig. 1). This is not surprising since such a highly doped silicon sample is known to have an almost constant conductivity in this temperature range [2]. More astonishing are the $I(V)$ curves recorded as a function of the temperature (Fig. 2). As seen in Fig. 2,*b*, the dI/dV curve at 300 K shows a narrow band gap of about 0.2 eV whereas the dI/dV curve at 35 K shows a band gap of about 1 eV, i.e., equal to the bulk electronic band gap of silicon [3]. This temperature effect cannot be explained by any freezing of the bulk conductance since such a highly doped silicon sample is known to have a bulk conductivity which is almost constant between 300 K and 35 K [2]. A similar opening of the surface band gap at low temperature has been observed previously on the Ge(111) surface [5]. It has been assigned to low

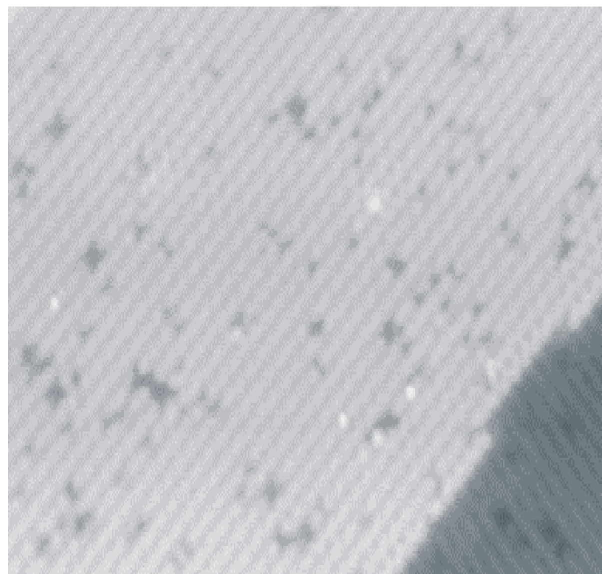

Fig. 1. Scanning Tunneling Microscope topography (390 Å by 240 Å) of the highly doped n-type Si(100)–2×1 surface recorded at 35 K. The sample voltage is V_S = −1.5 V and the tunnel current I = 0.5 nA.

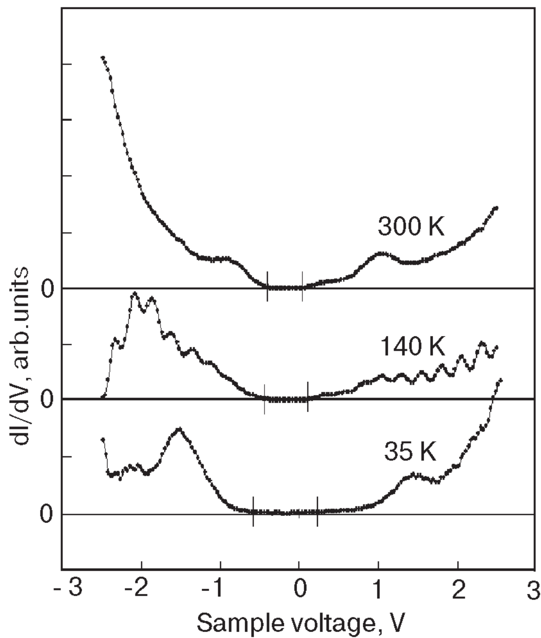

Fig. 2. dI/dV curves recorded on the highly doped n-type Si(100)–(2×1) surface at various temperatures. The scanning conditions for recording these curves are V_S = = −1.5 V and I = 0.5 nA.

temperature freezing of specific surface electronic channels whose energies are located within the electronic bulk band gap [5]. Recent measurements of the total surface conductivity of the Si(100) surface [7] have shown that, on the contrary, the surface conductivity increases at low temperature. One cannot completely exclude that the conductivity of the specific surface electronic channels whose energies are located within the bulk band gap would decrease at low temperature whereas the total surface conductivity would increase. However such an explanation seems very unlikely. Therefore, another explanation needs to be considered as illustrated in Fig. 3. At room temperature, the tunnel current flowing through occupied surface states located within the bulk band gap requires some transport of electrons from the bulk conduction band (CB) to the occupied surface states (SS). This can be achieved by the combination of two effects, (i) the electron transport through the energy barrier of the upward surface band bending caused by the «pinning» of the surface states at the Fermi level [3] and (ii) the release of electron energy to reach the lower lying surface states. This latter effect would require some coupling between electrons and phonons. Considering that the transmission over the energy barrier as well as the phonon population are thermally activated, both effects are expected to be much less efficient at low temperature, thus explaining the freezing of the electronic channels through the surface states located within the bulk band gap.

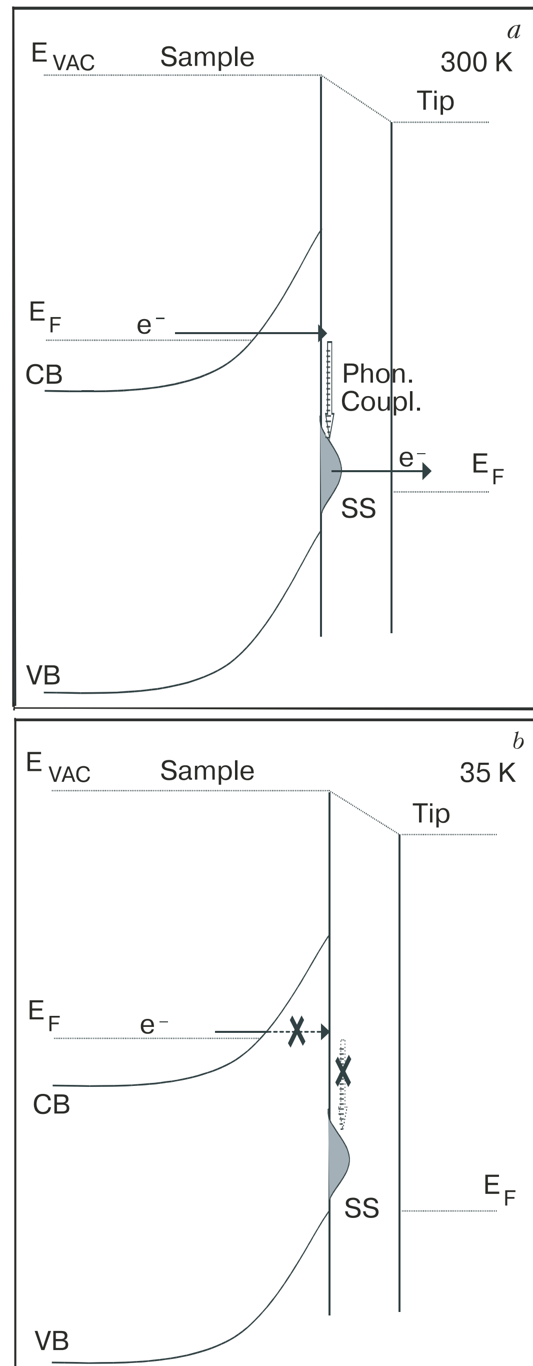

Fig. 3. Schematic energy diagram of electrons flowing from the highly doped n-type Si(100)–(2×1) sample to the STM tip. At 300 K (a), the thermal energy can (i) activate the transport of electrons from the sample Fermi level E_F through the sub-surface barrier due to the upward band bending and (ii) activate the coupling with phonons and surface states (SS). At 35 K (b), the loss of thermal activation freezes the electron current.

3.2. p-type Si(*100*)

At room temperature, the *p*-type Si(100) sample shows a STM topography and $I(V)$ spectroscopy curves similar to the highly doped *n*-type Si(100) (see Fig. 4). However, as soon as the sample temperature is lowered to about 180 K, both the STM topography and $I(V)$ curves are markedly modified. At 180 K, stable STM topographies with atomic resolution can hardly be obtained. At room temperature, STM topographies could easily be obtained at relatively small negative (−2 V, I = 0.5 nA) sample voltages. At 180 K, STM topographies could be obtained only at high negative sample voltages (−5 V, I = 0.5 nA) (see Fig. 4) and were found to be very unstable, suggesting some local charging occuring after a few minutes of tunneling. The $I(V)$ curves are also strongly modified (see Fig. 5), with a much reduced conductivity at negative sample voltages. At 35 K, it was impossible to obtain any STM topography at any negative sample voltage and the

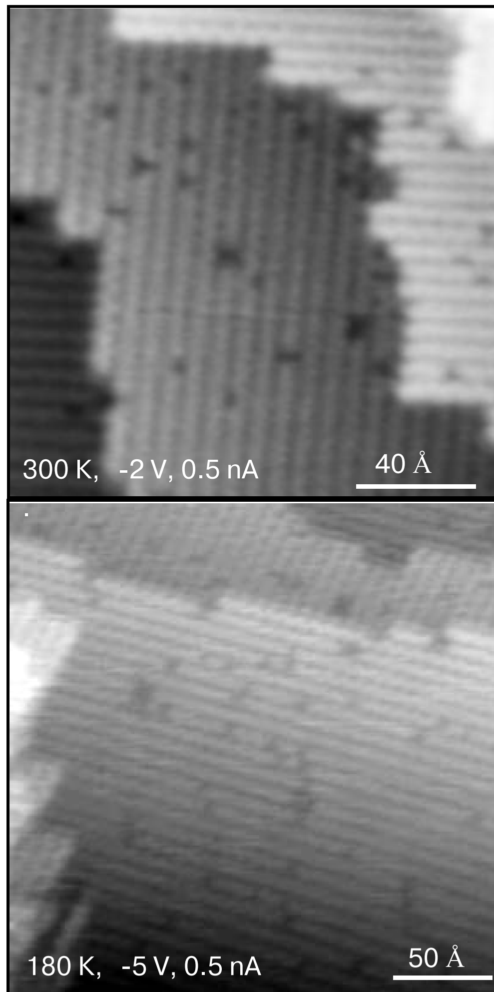

Fig. 4. Scanning Tunneling Microscope topographies of the *p*-type Si(100) surface at 300 K (top − 160×160 Å) and 180 K (bottom − 250×250 Å).

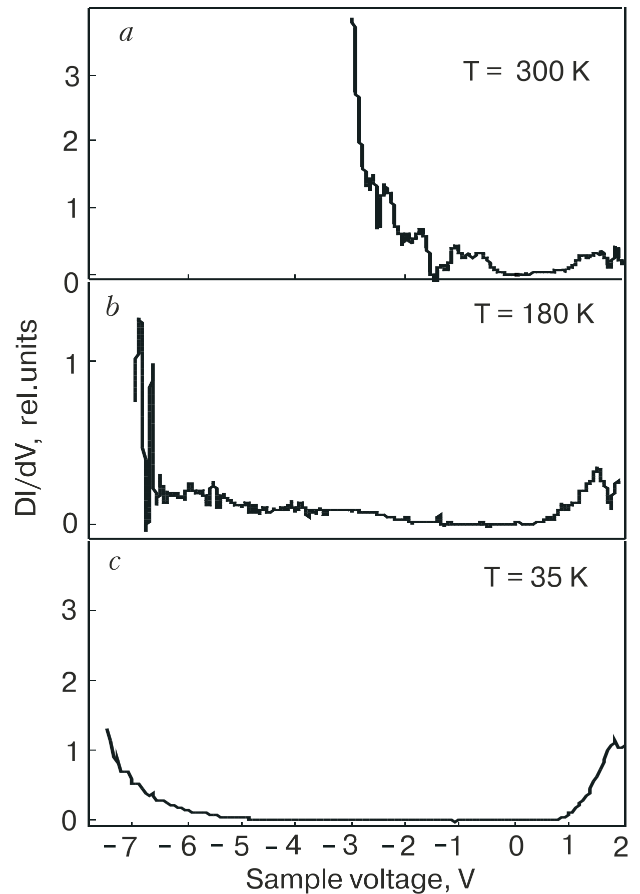

Fig. 5. dI/dV curves recorded on the *p*-type Si(100)-2×1 surface at various temperatures. The scanning conditions for recording these curves are (*a*) −2 V, 0.5 nA; (*b*) −6 V, 0.5 nA; (*c*) − 7 V, 0.5 nA.

$I(V)$ curves show a weak conductivity extending at even larger negative sample voltages (see Fig. 5). The conductivity is zero for sample voltages between −3 V and +1 V.

These results are somewhat surprising since they cannot be simply ascribed to the temperature dependence of the bulk conductivity of *p*-type Si(100). Indeed, from 300 K to 180 K, the conductivity of the sample is considered to increase [2]. Obviously this cannot explain the shift from −2 V to −5 V of the sample voltage for imaging, since this shift (associated with a tunnel current of 0.5 nA) would correspond to a spreading resistance of $6\cdot10^9$ Ω. In fact, these results can be well understood by considering a tip induced band bending as schematically shown in Fig. 6. The «pinning» of the surface states at the Fermi level produces a downward band bending [3]. At negative sample bias, charge carriers (h^+, holes) are prevented from flowing from the tip to the sample by the downward band bending of the valence bands. At room temperature, the holes can acquire enough thermal energy to overcome this energy barrier. However, at low temperature the hole

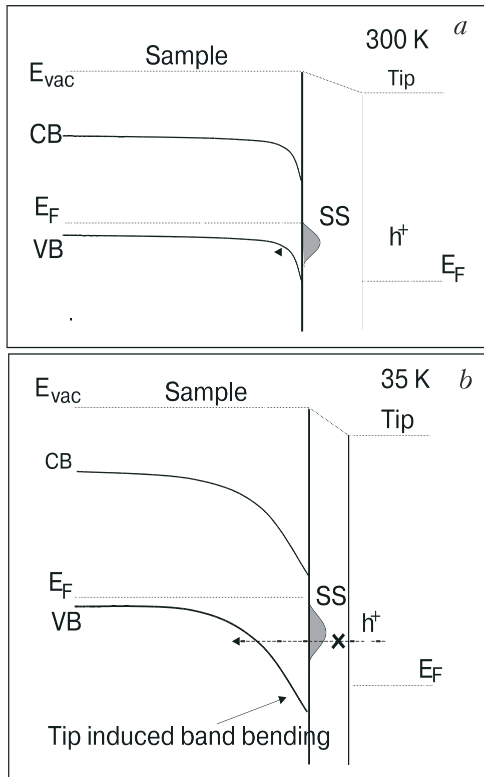

Fig. 6. Schematic energy diagram of electrons showing the flow of positive holes (h^+) from the STM tip to the p-type Si(100) sample. At 300 K (a), the thermal energy can activate the transport of holes through the energy barrier due to the surface state induced band bending. At 35 K (b), the tip induced band bending is too large to allow the flow of hole current.

transport through this energy barrier is frozen. Since the conductivity decreases, the STM tip tends to approach the surface to maintain the tunnel current constant. As a consequence, the electric field between the STM tip and the surface is strongly increased, inducing a more pronounced downward band bending as shown in Fig. 6. This explains the large shift from −2 V (300 K) to −5 V (180 K) for imaging the surface as well as the shape of the $I(V)$ curves (Fig. 5). One should also mention here the possible influence of the surface states on the penetration of the electric field into the silicon sample. Indeed, the reduced charge population of the surface states at low temperature may decrease the screening effect and thus facilitate the penetration of the electric field produced by the tip. This tip-induced band bending was not observed with the previously studied n-type sample due to its high concentration of dopants which prevents the electric field from penetrating inside the sample.

3.3. Hydrogenated C(*100*)

At room temperature, the hydrogenated C(100) diamond surface can be imaged at the atomic-scale with the STM at both positive (V = +1.5 V, I = 1 nA) (see Fig. 7) and negative (V = −1.5 V, I = 1 nA) sample bias. The corresponding $I(V)$ curve is shown in Fig. 8. When lowering the sample temperature, the I/V conductivity decreases, especially at positive sample bias (see Fig. 8), so that below 180 K no STM imaging is possible anymore. Around 150 K, the $I(V)$ curve becomes «metallic» in form, i.e. linear. For temperatures below 150 K, no tunneling current could be established whatever the sample bias. This behavior is quite different from the two previous cases of the silicon surface and requires a specific explanation.

The clean natural (weakly doped) C(100) diamond surface is known to be insulating [8]. However, when hydrogenated, the C(100) diamond surface becomes conductive and STM imaging in the usual tunneling mode can be performed [9]. It has been demonstrated recently [9] that this surface conductivity requires the presence of both the hydrogen atoms on the surface and sub-surface oxygen and hydrogen. These sub-surface species, which are produced during the preparation procedure of the hydrogenated sample, result in an upward surface band bending (see Fig. 9) and a concentration of holes in the sub-surface region. As seen in Fig. 9, this enables a flow of holes at both negative and positive sample bias. When reducing the

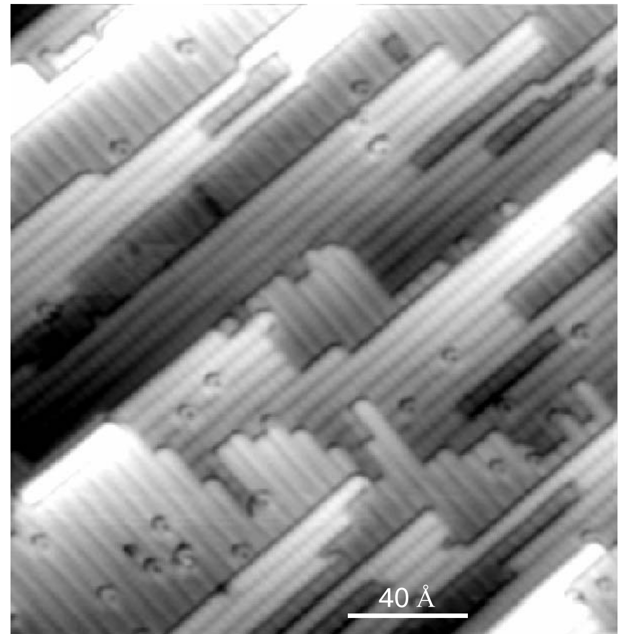

Fig. 7. 175×175 Å statement topography of the diamond C(100)-2×1 surface recorded at room temperature (V_S = = +1.5 V, I = 1.5 nA)

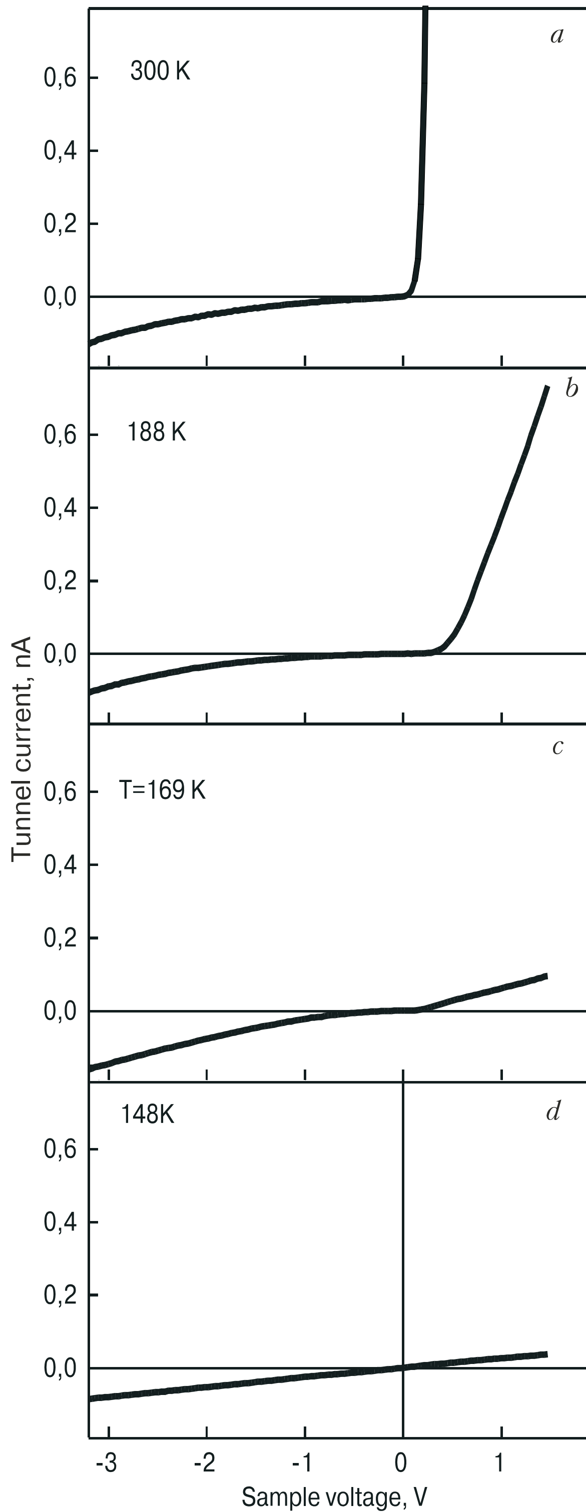

Fig. 8. $I(V)$ curves recorded on the diamond C(100)–(2×1) surface as a function of the temperature. The scanning conditions for recording these curves are $V_S = -2$ V, $I = 0.1$ nA.

sample temperature, the activation as dopants of the sub-surface species should rapidly decrease if their activation energy is high enough, of the order of 0.6 eV. This explains the much reduced surface conductivity. Around 150 K, the sub-surface conductivity is so low that the STM tip needs to be in full contact with the sample, thus leading to a «metallic» $I(V)$ curve. In summary, the freezing of the sub-surface conductivity explains why the hydrogenated diamond surface becomes fully insulating below 150 K.

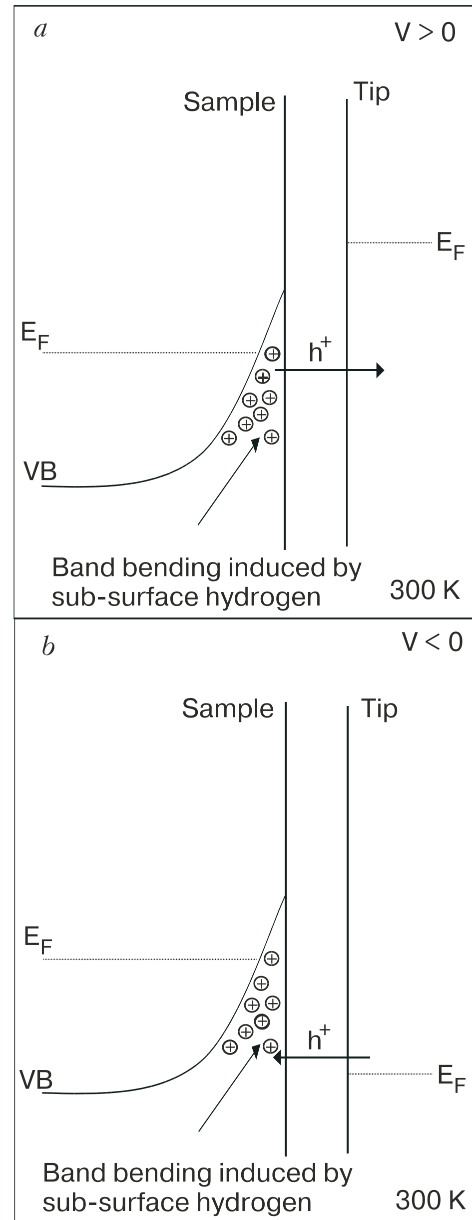

Fig. 9. Schematic energy diagram of electrons showing the flow of positive holes (h^+) for two polarities of the voltage on the diamond C(100)–(2×1) surface.

4. Conclusions

Investigating the low temperature conductivity of semiconductor surfaces with the STM is a very interesting problem since a large variety of phenomena can be encountered.

For highly doped *n*-type Si(100), lowering the sample temperature down to 35 K enables the freezing of the electronic channels whose energies are within the bulk band gap. Other electronic channels (outside the bulk band gap) seem to be accessible at low temperature, enabling the STM imaging of the sample down to 35 K. Due to the high concentration of dopants, tip-induced surface band bending can be neglected.

For moderately doped *p*-type Si(100), the surface band bending also freezes electronic channels at negative sample voltages. This effect is amplified by tip-induced surface band bending which freezes at low temperature all the electronic channels from −2 V down to −5 V at 35 K.

For hydrogenated C(100), the surface conductivity is due to the presence of sub-surface species (oxygen and hydrogen). The whole surface conductivty is strongly dependent on the temperature since below 180 K, the hydrogenated C(100) surface becomes fully insulating.

These three examples offer an interesting range of applications for nanoelectronics. The highly doped *n*-type Si(100) surface can be advantageously used at low temperature to decouple the electronic channels of a nanoscale device from the substrate only in the energy range located within the bulk band gap. The advantage is that the substrate is still conducting and STM imaging can still be performed at such a low temperature (35 K). The hydrogenated C(100) surface can be used, below room temperature at T = 180 K, to fully decouple the electronic channels of a nanoscale device from the substrate. However, in this case, the substrate is completely insulating and STM imaging is no longer possible. The moderately doped *p*-type Si(100) surface offers another potentially interesting application where surface tip-induced band bending can be used at low temperature (35 K) to freeze all the electronic channels across the surface whose energy is between −5 V and +1 V.

We wish to thank the European IST-FET «Bottom-up-Nanomachines» (BUN) and the European «Atomic and Molecular Manipulation; a new tool In Science and Technology» (AMMIST) network.

1. U. Ramsperger, T. Uchihashi, and H. Nejoh, *Appl. Phys. Lett*. **78**, 85 (2001).
2. S.M. Sze, *Physics of Semiconductor Devices*, John Wiley and Sons, **26** (1981).
3. J.A Stroscio and R. M. Feenstra, in : *Scanning Tunneling Microscopy*, J.A. Stroscio and W.J. Kaiser (eds.) Academic Press **27** (1993).
4. W. Mönch, *Semiconductor Surfaces and Interfaces*, Springer-Verlag **15** (1993).
5. G. Dujardin, A.J. Mayne, and F. Rose, *Phys. Rev. Lett*. **89**, 36802 (2002).
6. K. Bobrov, H. Shechter, M. Folman, and A. Hoffman, *Diamond Relat. Mater*. **7**, 170 (1998).
7. K. Yoo and H.H. Weitering, *Phys. Rev. Lett*. **87**, 026802 (2001).
8. K. Bobrov, A.J. Mayne, and G. Dujardin, *Nature* **413**, 616 (2001)
9. K. Bobrov, A.J. Mayne, G. Comtet, G. Dujardin, L. Hellner, and A. Hoffman, *in preparation*.