Negative differential resistance of TEMPO molecules on Si(1 1 1)

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Abstract

Negative differential resistance (NDR) has been observed for individual 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) molecules on Si(1 1 1) in ultra high vacuum (UHV) scanning tunneling microscopy (STM) and spectroscopy (STS) measurements at room temperature. NDR effects were observed exclusively at negative bias voltage using an n-type Si(1 1 1) sample. At 77 K no NDR effects were observed, but the $I(V)$ curves were similar in shape to those recorded on bare Si(1 1 1) sites. TEMPO was observed to adsorb preferentially at corner adatom sites of the Si(1 1 1)-7×7 structure. Although the Si(1 1 1)-7×7 reconstruction was conserved, local defects were frequently observed in the vicinity of the TEMPO adsorbates.

1. Introduction

Since today's electronics industry heavily relies on silicon technology, incorporation of functional molecules into silicon-based electronics might be the next step towards realizing molecule-based electronics. By the possibility of tuning the values of certain properties, such as conductivity, absorption spectrum, chemical affinity, flexibility, size, shape, etc. by a proper choice of molecule, incorporation of organic molecules have the potential to enhance silicon technology. In order to gain understanding of the properties of organic molecules on semiconductor surfaces, a range of different systems has been studied [1]. Another advantage of silicon over metal surfaces is the presence of a band gap, which offers possibilities for resonant tunneling devices [2].

In this paper, scanning tunneling microscopy (STM) and spectroscopy (STS) measurements of individual 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) on a lightly *n*-doped (resistivity 1.5–2.2 kΩ cm) Si(1 1 1) surface performed at room temperature and at 77 K are presented. The organic species were deposited on the Si-surface from the gas phase, at various exposure times. Below, results from room temperature measurements performed after, respectively, 10 and 50 s exposure at 10^{-8} mbar are presented. The 77 K data presented were obtained after 5 s exposure at 10^{-8} mbar, similar results were obtained also after longer exposures. TEMPO is a stable nitroxyl free radical, with an unpaired electron at the O atom, which can react with the dangling bonds of the Si surface to form a Si–O bond. A schematic picture of TEMPO is shown in Fig. 1. The dot on the oxygen atom indicates the unpaired electron. Although NDR effects have also been observed for conjugated molecules [3], saturated organic species have the advantage of stability against electron stimulated desorption, which has been observed for conjugated molecules [3,4].

The complex Si(1 1 1)-7×7 reconstruction, with its 19 dangling bonds located at 7 spatially inequivalent types of Si atoms (corner and centre adatoms and rest atoms at faulted and unfaulted halves and the corner hole atom) provides multiple reaction sites with different electronic structures and hence different reactivity [5–11]. Each rest atom or corner atom has a formal charge of −1, adatoms approximately +7/12, with slight differences between the faulted and the unfaulted halves of the 7×7 unit cell. Depending on the difference in electronegativity between the surface and the reactant, adsorption will take place at preferably corner atoms and rest atoms or adatom sites, respectively [11]. This multiplicity of

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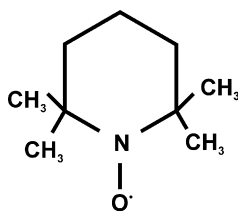E-mail address: H.J.W.Zandvliet@utwente.nl (H.J.W. Zandvliet).

Fig. 1. Schematic picture of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The dot on the oxygen atom indicates the unpaired electron.

spatially and electronically in-equivalent reactive sites indicates a diversity of reaction mechanisms for different organic molecules.

The occurrence of NDR effects for organic molecules on silicon surfaces has been a matter of debate recently. Previous STM and STS studies on TEMPO adsorbed on Si(1 0 0) surfaces have reported multiple NDR effects for individual TEMPO molecules, occurring at a specific voltage polarity dependent on the substrate doping. For n-type Si(1 0 0) NDR occurred at negative voltages, for p-type at positive voltages. This has been argued to be consistent with resonant tunneling between the Si band structure and the molecular orbitals of the adsorbed molecule, the molecular levels being driven off resonance with the bulk Si band edges of degenerately doped Si and driven into the band gap [2,3,12]. Hence, according to this model the NDR is determined by the bulk band edge structures of silicon. However, the model could not explain the position of the peaks, although these seem to be influenced by the distance between the molecule and the STM tip. The magnitude of the current at the NDR peak position was seen to be dependent on both the tip-molecule distance and the amount of doping of the substrate [12]. However, contrary to the theoretical predictions, the necessity of a high negative bias voltage for the onset of NDR at n-type Si was not observed experimentally. Instead NDR effects were observed at bias values comparable to the bias values at which NDR occurred at the p-type substrate, which could not be explained theoretically [12]. Calculations and experiments showed that TEMPO binds to the Si substrate by a covalent bond formed by the unpaired electron and a Si dangling bond [13]. For a full monolayer of TEMPO on Si(1 0 0) the NDR effect was suppressed compared to the observations for single molecules. This lead to the conclusion that the local environment surrounding each molecule plays an important role in charge transport. It was suggested that the suppression of the NDR effect is caused by electrons tunneling through more than one molecule [14]. The polarity at which NDR occurred was still determined by the substrate doping. However, a recent publication has presented evidence that NDR-like peaks in $I(V)$ curves observed for styrene and cyclopentene on Si(1 0 0) [3,14] is not likely to be due to resonant tunneling via alignment of molecular levels with Si bands but rather to originate in random molecular processes, such as molecular rearrangement, desorption or decomposition, induced by inelastic scattering of the tunneling electrons [15]. Based on STM measurements on the reversible passivation of dangling bonds by TEMPO [16,17] on hydrogen terminated silicon surfaces, H–Si(1 0 0) and H–Si(1 1 1), which showed that TEMPO can be removed from these surface by scanning at voltages greater than 3.5 V, the authors argue that NDR observed for TEMPO on clean Si(1 0 0) would also originate in molecular desorption rather than true resonant tunneling NDR.

A point to note already here is that the results presented in this paper cannot be directly compared to the resonant tunneling model presented in [2,3,12], since that model was based on a degenerately doped sample while in our measurements a lightly doped (n-type) sample was used. Another point of caution is the metallic-like surface properties that have been reported for the Si(1 1 1)-7 × 7 surface [18]. The presence of surface states within the band gap will indeed decrease the likelihood of NDR due to resonant tunneling.

2. Experimental

The room temperature measurements were performed in ultra high vacuum (UHV), at a pressure of 1.3×10^{-10} mbar, in a commercially available scanning tunneling microscope (Omicron GmbH). The low temperature measurements were performed in a low temperature STM (LT-STM, Omicron GmbH), in UHV at a pressure in the 10^{-11} mbar region. Electrochemically etched W tips were used.

Deposition of TEMPO on the surface was in both cases performed at room temperature. The Si sample was lightly n-type doped with resistivity 1.5–2.2 kΩ cm. Before room temperature measurements the sample was cleaned by sputtering with Ar ions and thermal annealing cycles, by sending a direct current through the sample. Before low temperature measurements the sample was cleaned through thermal annealing only. The TEMPO molecules were commercially purchased from Sigma–Aldrich Chemie GmbH, with 98% purity. The TEMPO species, which are in solid phase at room temperature (melting point 36 °C), are loaded into a small vessel (under ambient conditions), which is connected to the vacuum system via a leak valve. Prior to loading, the vessel was connected to the vacuum system and baked out to remove contaminations of the inner walls. Since TEMPO has a high vapor pressure, the vapor can be introduced into the vacuum chamber by opening the leak valve, no heating of the vessel is necessary. Before opening the leak valve to the vacuum system the vessel is shortly pumped, in order to remove contaminations in the vapor. The vessel was connected to the load lock chamber of the room temperature STM, which has a base pressure of 2×10^{-9} mbar, exposure of the Si(1 1 1) sample to TEMPO is performed at a pressure in the middle of the 10^{-8} mbar range, measured by an ion gauge. Measurements were performed for exposure times of the clean sample to the organic species successively increasing from 5 to 100 s (5, 10, 50, 100 s). For the low temperature measurements the vessel was connected to the preparation chamber of the LT-STM, which has a base pressure in the low 10^{-10} mbar region. Exposure was performed at times varying from 5 s to 2 min at 10^{-8} mbar.
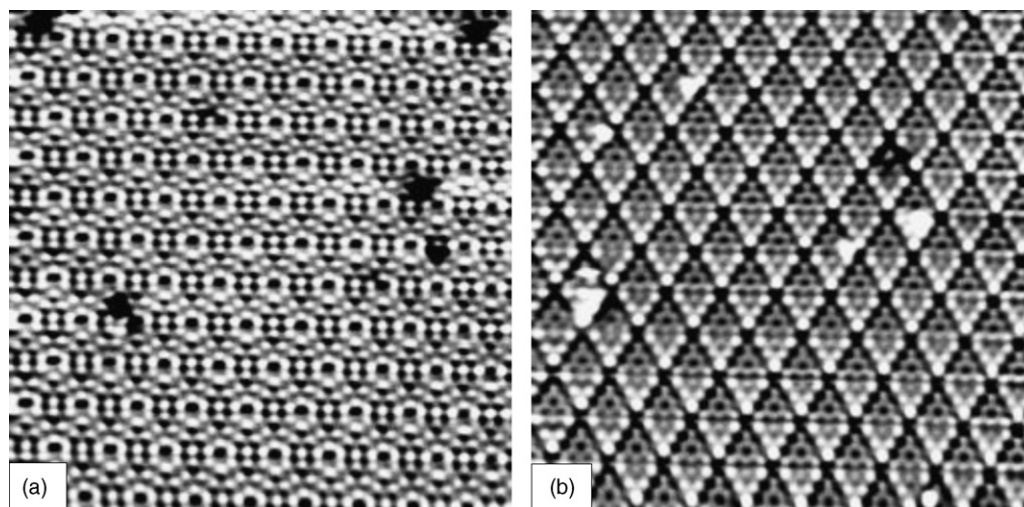
Fig. 2. Si(1 1 1) cleaned by sputtering and annealing. The images, recorded at room temperature, show the empty and the filled states, respectively, of the same 25 nm × 25 nm area. Tunneling current 0.23 nA, sample bias: (a) +1.93 V and (b) −1.93 V.

3. Results and discussion

Before exposure of the sample to TEMPO the sample was cleaned by sputtering for 20 min at 3×10^{-5} mbar Ar pressure followed by thermal annealing at approximately 1500 K. An image recorded on the clean surface is shown in Fig. 2.

After imaging the cleaned sample it was transferred to the load-lock chamber of the room temperature STM where it was exposed to TEMPO for 10 s at a pressure of 10^{-8} mbar. Fig. 3 shows an image recorded after exposure. Single point $I(V)$ measurements have been recorded on the surface adsorbates within circles and squares and on several places at the bare Si surface. On the white features not circled or squared, no $I(V)$ data were recorded. Topographical data were recorded with a tunneling current of 0.10 nA and simultaneously at sample biases of −2.0 and +2.0 V in the two topological channels, respectively. Spectroscopic data were recorded by performing single point spectroscopy during imaging. In single point

spectroscopy a specific point on the image is selected during imaging. After finishing the current image line, the STM tip is moved to the selected point, the feedback loop is turned off and the bias voltage is ramped while recording the current. Spectroscopic data was recorded with an acquisition time of 640 μs at each voltage value and a delay time of 200 μs between each acquisition. The $I(V)$ curves presented in Fig. 4 below were recorded in the voltage range (−2.54 to +2.50) V with an energy resolution of 25 meV.

In the empty state image of Fig. 3b many defects, in the form of missing adatoms, of the surface lattice are visible. Of the seven features for which $I(V)$ data have been recorded, five showed NDR effects (indicated by circles). Of these, three are adsorbed at corner adatom sites, one at a centre adatom site, and one in a highly distorted area. Of the two squared features, both invisible at positive bias, one is placed at a corner adatom site, the other is so large that it covers almost half a unit cell. Examples of $I(V)$ curves recorded on molecules (A, B) and on
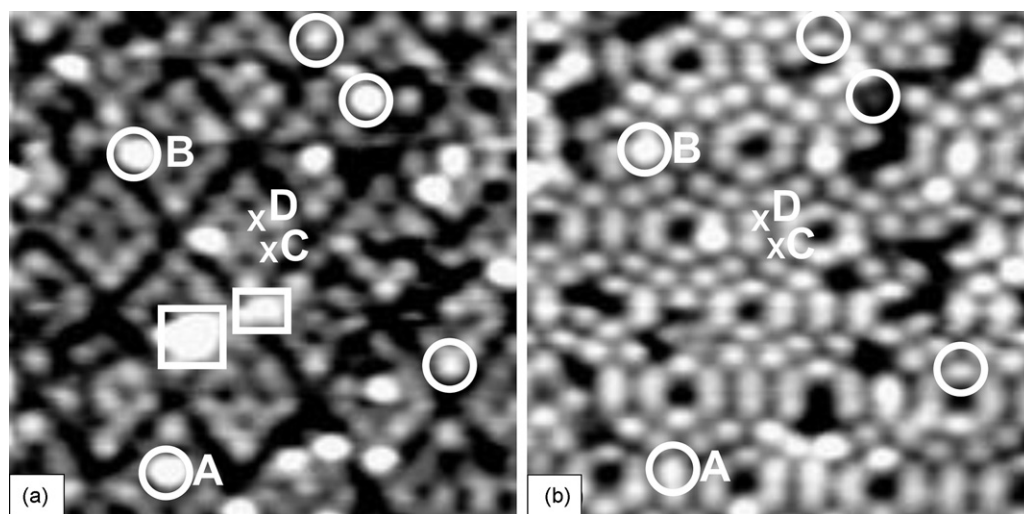

Fig. 3. Circles indicate features where NDR effects have been observed at room temperature. $I(V)$ data was also recorded on several bare Si sites. See for the labels A–D the text and Fig. 4. Surface area 10 nm × 10 nm. Tunneling current 0.10 nA, sample bias: (a) −2.0 V and (b) +2.0 V.
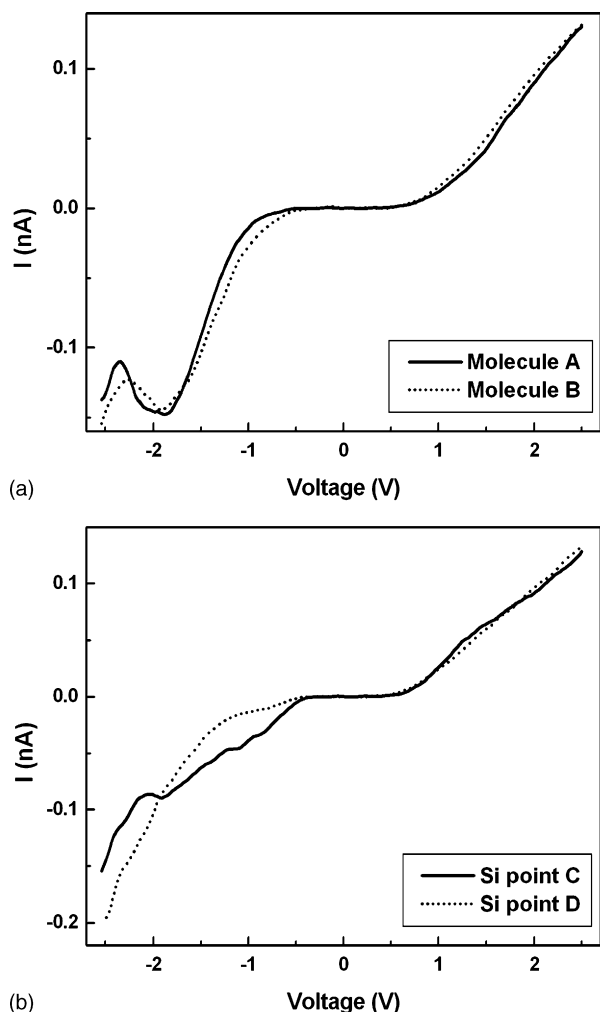
(a)

(b)

Fig. 4. (a) I(V) curves recorded on surface adsorbates, both exhibiting strong NDR effects. Molecule A is adsorbed at a centre adatom site, molecule B at a corner adatom site. (b) I(V) curves recorded on bare Si sites. While the solid curve exhibit strongly features not related to Si surfaces, the dotted curve is close to the S shape typical for semiconductor surfaces. All curves have been recorded at room temperature.

bare Si sites (C, D) are shown in Fig. 4. Molecules A and B show similar I(V) curves, both exhibiting an NDR peak below −2 V, molecule A is adsorbed at a centre adatom site, molecule B at a corner adatom site. Of the curves recorded on bare Si sites, the curve recorded at point D show the S shape typical for semiconductor surfaces, the one recorded at point C deviates distinctly from this S shape.

In a subsequent data frame measured on the area shown in Fig. 3, I(V) data was recorded in the voltage range (−3.0, +3.0) V. In this frame the features in squares, which did not show NDR effects in the data recorded in Fig. 3, now show NDR effects, while the second molecule from above, that showed NDR features in Fig. 3, does no longer. Feature B shows NDR effects in both data frames. This, as well as the non-Si like features in I(V) curves recorded on bare Si sites, indicates that a TEMPO molecule might attach to the STM tip during imaging. Note that deposition was performed in a chamber separated from the STM chamber and hence the STM tip was not directly exposed to the TEMPO.

In Figs. 5 and 6, results from room temperature STM and STS measurements performed after exposure of the sample to TEMPO for 50 s at 10^{-8} mbar are shown. Topographical data of the 15 nm × 15 nm area was recorded with a tunneling current of 0.10 nA and simultaneously at sample biases of −1.8 and +1.8 V, respectively. Similar to the measurements described above, spectroscopic data were recorded with an acquisition time of 640 μs and a delay time of 200 μs. I(V) measurements were performed in the voltage range (−3.5, +3.5) V, with an energy resolution of 25 mV. Fig. 5 shows an image containing relatively many features exhibiting NDR effects. Half of the molecules in Fig. 5, for which I(V) data have been recorded, exhibit NDR effects, indicated by circles. Of these, nine are adsorbed at corner adatom sites, two at centre adatom sites. Of the features exhibiting shoulders and/or plateaus (squares), four are positioned at corner adatom sites, four at centre adatom sites. In the vicinity of all these features the surface structure is defected, i.e., one or more adjacent
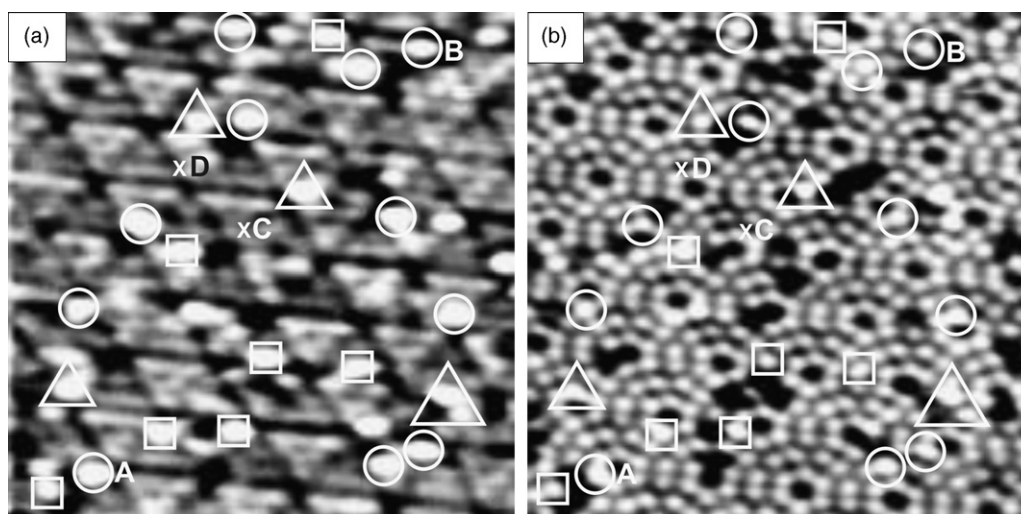

Fig. 5. Circles indicate features that show NDR effects, squares features that have shoulders and plateaus in their I(V) curves. Features in triangles do not exhibit any of these effects. The curve recorded on point C, a bare Si site, exhibits shoulders, while the curve recorded on point D, also bare Si, shows the S shape typical for semiconductor surfaces. Surface area 15 nm × 15 nm. Tunneling current 0.10 nA, sample bias (a) −1.8 V, (b) +1.8 V.
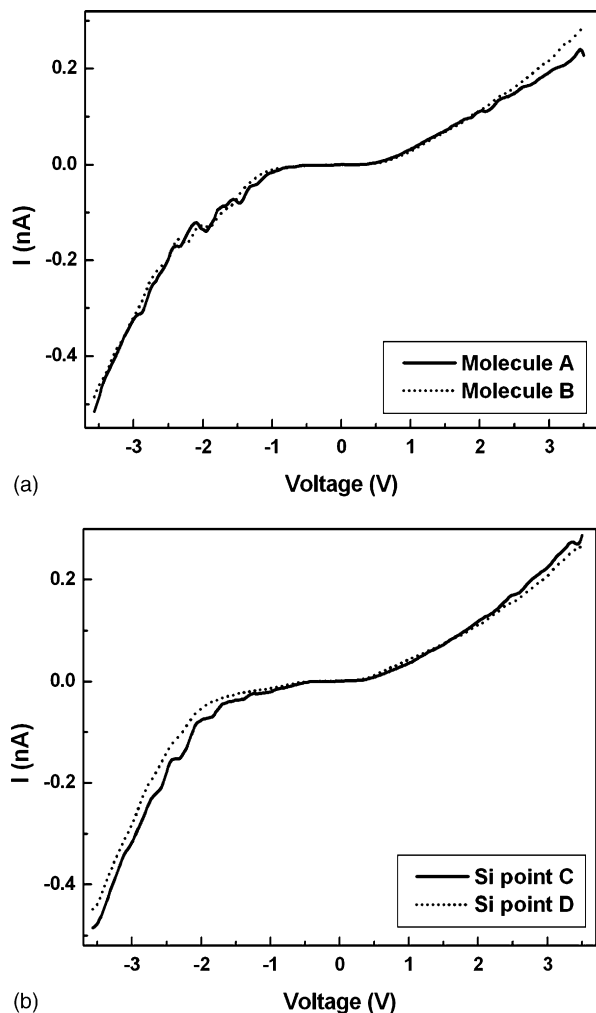
(a)

(b)

Fig. 6. (a) Two examples of $I(V)$ curves recorded on molecules showing multiple NDR effects. (b) $I(V)$ curves recorded on bare Si sites. The solid line exhibits shoulders, which might indicate that a molecule is attached to the STM tip, whereas the dotted line exhibits the S shaped typical of semiconductor surfaces. All curves were recorded at room temperature.

adatoms appear missing. It is not clear whether the defects are present already before adsorption or are induced by the adsorption process. The features in triangles exhibit neither NDR effects nor shoulders. The curve recorded on point C, which is a bare Si site, exhibits shoulders, while the curve recorded on point D, also bare Si, shows the S shape typical for semiconductor surfaces. Examples of $I(V)$ curves recorded on surface adsorbates and bare Si sites, respectively, are shown in Fig. 6. Molecules A and B exhibit multiple NDR events between −1 and −3 V, point C (bare Si) exhibit multiple steps in the $I(V)$ curve, and point D shows the typical S shaped curve.

Similar measurements have been performed at 77 K, after exposure for different times at room temperature. All $I(V)$ spectra recorded on surface adsorbates at 77 K show curves very close to curves recorded on bare Si sites, with no indication of NDR peaks or even shoulders in the $I(V)$ curves. A typical example is shown in Fig. 7. Spectroscopic data were recorded with an acquisition time of 1280 μs and a delay time of 1000 μs. $I(V)$ measurements were performed in the voltage range (−5.0, +5.0) V, with an energy resolution of 20 mV.

4. Conclusions

In summary, together with topographical imaging $I(V)$ measurements have been performed on individual 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) on a lightly doped n-type Si(1 1 1) surface. At room temperature many of the surface adsorbates for which $I(V)$ curves were recorded exhibit more or less pronounced NDR effects or shoulders and eventually plateaus. In agreement with references [3,14] these effects occur at negative bias voltage at the n-type surface. The specific voltage at which this occurs, as well as how pronounced this NDR effect or shoulder is, vary between different curves. NDR effects or shoulders in the $I(V)$ curve are sometimes measured at bare Si sites, which indicates that TEMPO can attach to the STM tip during measurements. The latter is concluded from the fact that deposition was performed in a chamber separated from the STM chamber. This might also cause NDR effects in curves recorded on white features that are not related to adsorbed TEMPO.
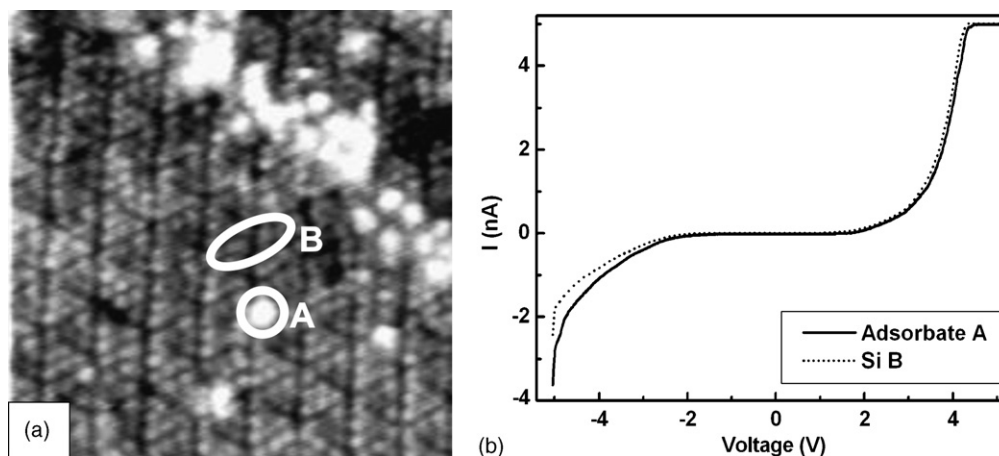

(a)

(b)

Fig. 7. Data recorded at 77 K. (a) Surface area 20 nm × 20 nm. Sample bias +2.0 V, tunneling current 0.10 nA. Exposure time 5 s. (b) $I(V)$ curves recorded on the adsorbate indicated by the circle and on bare Si sites indicated by the ellipse, respectively.

As mentioned above, some surface adsorbates show NDR effects in one measurement but not in the other. This might be due to several reasons. The orientation of the molecule as well as the position of the STM tip above the molecule might influence the spectra. It is plausible that different bonding configurations or different tilt angles are possible for TEMPO molecules on the Si(1 1 1)-7 × 7 surface, and that this influences the $I(V)$ spectra and the possibility for molecular motions. Another explanation would be that, due to drift during scanning, the single point $I(V)$ curves may not be recorded at the intended site. Also, as just mentioned, TEMPO might attach to the STM tip, which could cause NDR effects to be measured at sites were no TEMPO is adsorbed, either bare Si sites or surface contaminations. If the TEMPO detaches from the tip, in the following $I(V)$ measurement of course no NDR will be observed.

At 77 K no trace of NDR effects was observed. This is contrary to a NDR behavior due to a shift of molecular energy levels relative to the Si energy bands, which would be expected to result in sharper NDR peaks at lower temperatures. This supports the findings presented in [15], that the non-linear features in the room temperature $I(V)$ spectra have their origin in molecular motions or rearrangements, if thermal in nature rather than tip induced as suggested by [15]. Thermal motions should be less at lower temperatures, whereas tip-driven processes need not be influenced by temperature. The irregularities of the NDR behavior observed at room temperature might also support this explanation. Another explanation could be the lower amount of free surface charge carriers available at low temperature. To conclude, the measurements presented in this paper give indications that the peaks in the room temperature $I(V)$ spectra can be caused by molecular motions or configuration changes rather than resonant tunneling. More experiments, similar to those presented in [15], are needed in order to reveal this issue, namely measurements of the tunneling current above surface adsorbates as a function of time at constant applied voltage which would indicate the presence of molecular rearrangements or conformation changes at constant bias voltage, and imaging at higher applied voltages in order to reveal bias induced molecular rearrangements. These complementary measurements need to be performed at both room temperature and at 77 K. Also the influence of the amount of substrate doping as well as the type of doping are interesting issues.

Next to their $I(V)$ characteristics, one important issue is the adsorption site of TEMPO on the Si(1 1 1)-7 × 7 surface. Since the TEMPO radical has one unpaired electron it most likely binds to a rest atom or a corner atom of the Si(1 1 1)-7 × 7, which have a formal charge of -1, which would give a bonding pair, while the adatoms have a formal charge of +7/12. As seen above, although some adsorbates at centre adatom positions exhibit NDR effects, the main part of the features on which NDR effects were observed are adsorbed on Si corner adatom sites. The corner adatom site might be preferred due to its more spacious surrounding, giving easier access to the corner atom in the underlying layer than is the case for access to a rest atom via a more centered place in the Si(1 1 1)-7 × 7 unit cell. Although the faulted and the unfaulted halves of the Si(1 1 1)-7 × 7 unit cell have differences in electron density, from our measurements no preference for the faulted or the unfaulted half as adsorption site for TEMPO could be deduced. The vast majority of the features exhibiting NDR effects have missing adatoms in their vicinity. These apparent defects in the vicinity of the TEMPO adsorbates might be due to adatoms really missing, or a change in the surface electronic structure making these adatoms appear missing at the bias voltage used for imaging. While on the large scale the 7 × 7 reconstruction is conserved, upon adsorption of TEMPO to the surface a local surface strain is induced, eventually leading to the ejection of adatoms. These Si atoms will then diffuse over the surface and form clusters, which preferably attach at surface defects such as antiphase boundaries of the 7 × 7 reconstruction or pre-existing steps. In our measurements, decoration of adsorbates along surface antiphase boundaries has been observed.

Acknowledgements

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