

Rectification behaviour of molecular layers on Si(111)

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Received 4 September 2006; received in revised form 12 January 2007; accepted 18 January 2007 by A. Pinczuk
Available online 23 January 2007

Abstract

Reproducible and strong diode-like behaviour is observed for molecular films of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) on n-type Si(111)- 7×7 surfaces studied by scanning tunnelling microscopy (STM) and spectroscopy (STS) at 77 K. The mechanism behind the rectification is likely to be related to the electron distribution at the molecule-silicon interface. We suggest that the adsorption of the molecular layer profoundly modifies the electronic structure of the Si(111)- 7×7 surface.

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PACS: 73.40.-c; 73.40.Ei

Keywords: A. Semiconductors; A. Thin films; A. Surfaces and interfaces; C. Scanning tunnelling microscopy

1. Introduction

Since today's electronics industry heavily relies on silicon technology, probably the next step towards molecular based electronics would be hybrid technologies, i.e., the incorporation of functional molecules into silicon-based electronics. Due to their large variation in properties, which can be carefully selected by a proper choice and design of the molecule, such as conductivity, absorption spectrum, chemical affinity, flexibility, size, shape, etc., organic molecules have the potential to enhance silicon technology and modify the interface properties of silicon systems [1–4].

Molecular rectification was first proposed in 1973 when Aviram and Ratner suggested that single molecules with proper asymmetry should have diode-like I(V) characteristics, and hence suggested a rectifier based on a single organic molecule [5]. The model molecule consisted of an electron donor part (D) and an electron acceptor part (A), separated by a σ -bond bridging the two parts while decoupling their molecular orbitals, to give a molecule with I(V) characteristics similar to a pn junction. Molecular rectification is defined by asymmetric

I(V) characteristics, with much higher current values at one voltage polarity than at the other. Theoretical arguments have explained that molecular rectification in tunnelling junctions is generally difficult to realize [6]. Though the first requirement of molecular asymmetry along the junction (i.e., lack of molecular inversion symmetry) is not too difficult to meet, an asymmetric electrostatic potential profile and a voltage drop across the molecule are also required. Thus the molecule must be rigid towards deformation by the applied electric field, which would otherwise cause an effectively symmetric voltage profile for the two bias directions. Asymmetric I(V) characteristics have been experimentally observed for different types of molecular junctions and explained by different mechanisms, such as true molecular origin in D-bridge-A systems [7,8], or asymmetric junctions [7,9,10].

In this paper we present scanning tunnelling microscopy (STM) and spectroscopy (STS) studies of molecular films of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) on n-type Si(111)- 7×7 surfaces performed at 77 K. TEMPO is an oxygen radical, which reacts with the dangling bonds of the Si surface to form a Si–O bond [11]. A schematic image of TEMPO is shown in Fig. 1, for simplicity drawn planar though it should be noted that this is a non-planar species [12]. Since TEMPO is a saturated organic molecule it is not expected to be sensitive to electron stimulated desorption [13,14]. Room temperature measurements of TEMPO on Si(100) surfaces have

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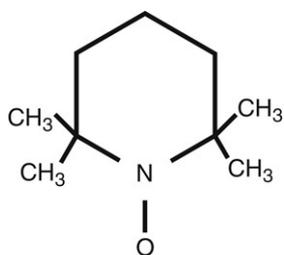


Fig. 1. Schematic of the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical.

reported negative differential resistance (NDR) for individual molecules, explained by resonant tunnelling between molecular and substrate levels [13,15,16]. For a full monolayer of TEMPO on Si(100) at room temperature the NDR effect was suppressed compared to the observations for single molecules, indicating that the local environment surrounding each molecule plays an important role in charge transport. It was suggested that the NDR effect is suppressed by the electrons tunnelling through more than one molecule [17]. In view of these previously published interesting results for TEMPO on Si(100) at room temperature, we decided to study the properties of TEMPO on Si(111)- 7×7 surfaces, which is an intriguing surface with several surface states, also within the bulk band gap [18]. Results on individual TEMPO molecules on Si(111)- 7×7 surfaces at room temperature and at 77 K have been published elsewhere [19].

2. Experimental details

The measurements presented in this paper have been performed using a commercially available low temperature scanning tunnelling microscope (LT-STM, Omicron GmbH). Chemically etched W tips were used. The Si samples were lightly doped n-type with resistivity 1.5–2.2 k Ω /cm. Prior to molecular dosing, the Si samples were cleaned by thermal annealing in UHV, by slow degassing at relatively low temperatures followed by flash annealing at higher temperatures. Flash annealing was repeated until a satisfactory clean and defect-free Si(111)- 7×7 surface was observed. Deposition of TEMPO was performed at room temperature, the STM/STS measurements were performed at 77 K. The organic species were deposited on the Si surface from the gas phase, in a preparation chamber connected to the STM chamber via a valve. After deposition the sample was transported to the STM chamber without breaking the vacuum.

Experiments performed on two different samples using two different tips are presented here. The first sample was prepared by exposure of Si(111)- 7×7 to TEMPO for 30 s at $5 \cdot 10^{-8}$ Torr (background pressure approximately $2 \cdot 10^{-10}$ Torr). After exposure the pressure in the preparation chamber was allowed to drop to $1 \cdot 10^{-9}$ Torr before carefully opening the valve to the chamber containing the STM. The pressure dropped only slowly, and the Si(111) sample was exposed to a 10^{-9} Torr TEMPO vapour for a time estimated at 5–10 min. The second sample was exposed to TEMPO for 2 min at a pressure of $1 \cdot 10^{-8}$ Torr followed by 3 min at $1 \cdot 10^{-7}$ Torr plus about

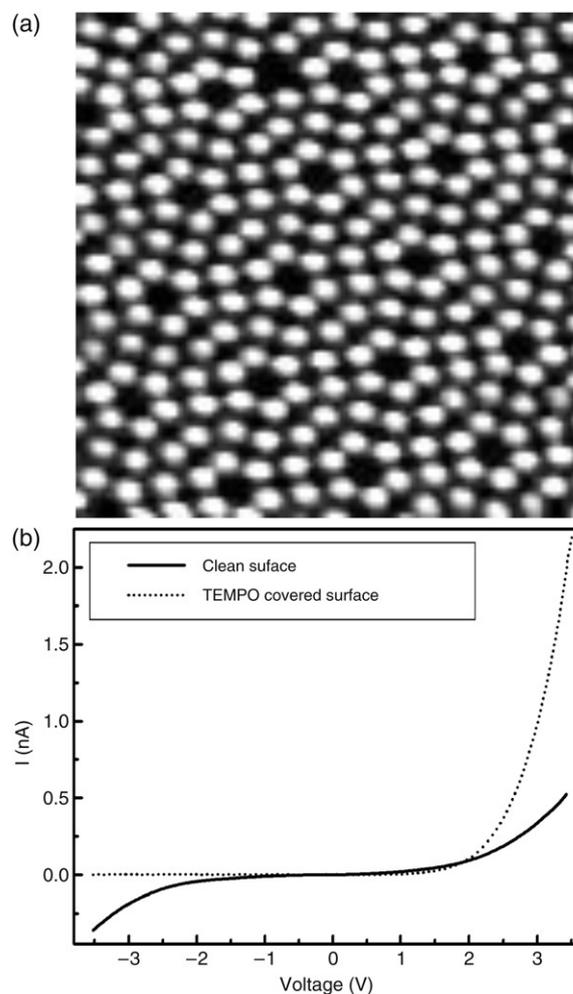


Fig. 2. Comparison of I(V) characteristics for the clean and the TEMPO covered Si surfaces. (a) Image of a clean Si(111)- 7×7 surface. Surface area 10 nm by 10 nm. Sample bias +1.8 V, tunnelling current 0.5 nA. (b) I(V) curves for the clean Si(111)- 7×7 surface (full line) and the TEMPO covered surface (dotted line).

1 min in the 10^{-8} Torr region during pressure decrease after closing the leak valve.

All spectroscopic data presented in this paper has been recorded with a set point tunnelling current of 0.1 nA at a bias voltage of +2.0 V. The tunnelling current was measured at voltage values between (–3.5, +3.5) V (Figs. 2 and 3) or (–4.0, +4.0) V (Fig. 4), and with an energy resolution of 14 meV (Fig. 3) or 17 meV (Figs. 2 and 4). All spectroscopic data has been averaged over curves recorded over surface areas of different sizes: 15 nm by 15 nm for Fig. 2, 10 nm by 10 nm for Fig. 3, and 100 nm by 100 nm for Fig. 4.

The molecular layer was easily removed by thermal annealing. High temperature flash annealing gave a reasonably clean surface, showing the 7×7 reconstruction with imaging possible at both bias polarities.

3. Experimental results

In this study, the Si(111)- 7×7 surface was fully covered with TEMPO molecules. In imaging at positive sample bias, no

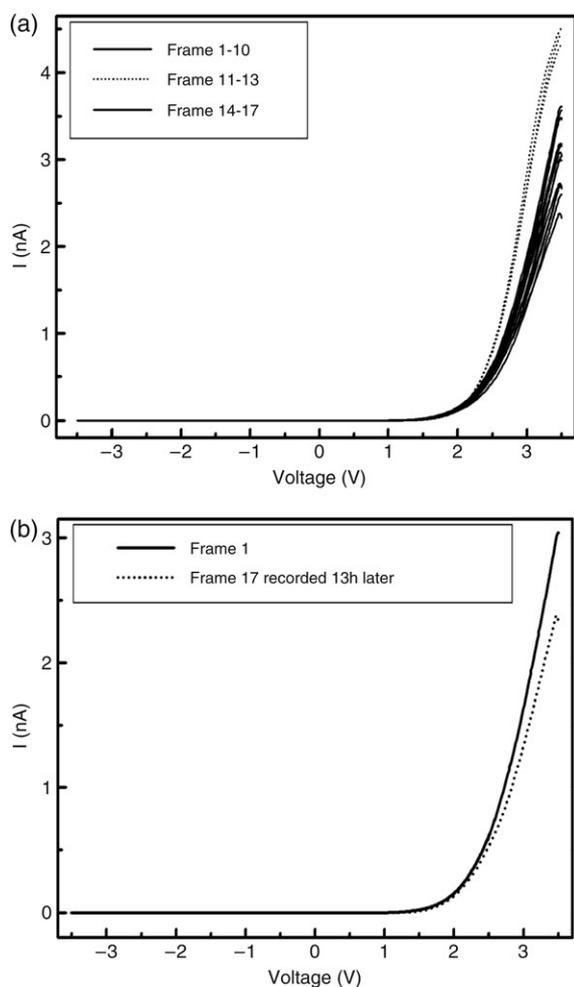


Fig. 3. I(V) data recorded during extended measurement of the same 10 nm by 10 nm surface area. In total, in this measurement series 17 data frames were recorded. (a) Average curves for each 17 data frames. (b) The first and the last I(V) curves of the measurement series.

structured molecular ordering could be observed. At negative sample bias electron tunnelling was not possible.

I(V) spectroscopy showed that there are indeed no surface states at negative bias voltage. When stepwise increasing the sample bias, starting from a negative value, electron tunnelling is hindered until the bias voltage reaches a value of approximately +1.5 V where the current suddenly increases rapidly. An example of this is shown in Fig. 2(b), together with an I(V) curve recorded on the clean Si(111)- 7×7 surface. Both curves have been recorded with similar measurement settings. Strongly rectifying behaviour was observed throughout many I(V) measurements on different areas of the TEMPO covered surface. Reversing the start and end points of the spectroscopic measurement (i.e., going from -3.5 V to $+3.5$ V or reversed) did not change the shape of the I(V) curve.

An image of the clean Si(111)- 7×7 surface is shown in Fig. 2(a). The full curve in the graph shown in Fig. 2(b) (clean Si(111)) shows an S shaped I(V) curve, with a band gap, typical for semiconductors, while the dotted curve (TEMPO covered surface) deviates strongly from this. Until the threshold around +1.5 V the current is suppressed, while for voltages higher than

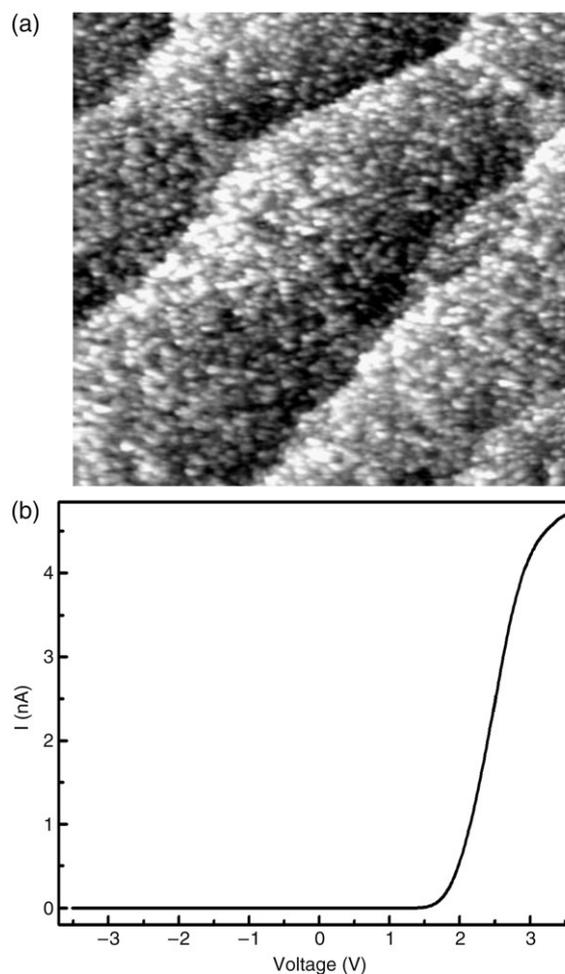


Fig. 4. (a) Fully TEMPO covered surface area which is relatively smooth, and with step edges visible. Surface area 100 nm by 100 nm. Sample bias +2.0 V, tunnelling current 0.1 nA. (b) I(V) curve recorded on the relatively smooth TEMPO covered surface.

+2.0 V the current gains much higher values on the TEMPO covered surface than on the clean Si(111)- 7×7 surface. The exact details of the electronic properties near the Fermi energy cannot be extracted from the general shape of the I(V) curve, as pointed out in the discussion section below.

Similar results were obtained for the second Si(111) sample. Topography and I(V) spectroscopy were measured at different locations on the surface, all showing similar rectifying behaviour. Results from I(V) measurements on the same area over 13 h are shown in Fig. 3. In Fig. 3(a) average curves are shown for each of the 17 data frames recorded during the measurement. In Fig. 3(b) only the I(V) curves of the first and the last data frames (time difference 13 h) are shown. In all frames similar rectification behaviour is observed, with some variations in the slope of the I(V) curve at high positive bias. Although the curve averaged over the last data frame shows lower current values than the curve of the first frame, more studies are necessary in order to draw conclusions regarding the time stability of this molecular rectifier.

Fig. 4(a) shows the Si(111) surface after saturation with TEMPO molecules. The surface is relatively smooth, and step edges of the Si substrate are still visible at positive sample

bias. Clearly, all available dangling bonds of the Si(111) surface have reacted with TEMPO molecules, resulting in a densely packed TEMPO layer. At negative sample bias tunnelling is not possible, and I(V) measurements show rectification behaviour similar to that previously observed. Fig. 4(b) shows an I(V) curve which is similar in shape but more smooth, to those recorded at more rough areas.

4. Discussion

The highly reproducible diode-like behaviour, with I(V) curves very similar to those characteristic for pn junction diodes, observed for the molecular films of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) on n-type Si(111)-7 × 7 at 77 K, might be explained by the interaction between the TEMPO molecules and the Si(111)-7 × 7 surface and by the asymmetry of the junction.

The rectification behaviour might be explained by the molecule-surface interaction, and the (lack of) availability of free surface charge carriers. At negative sample bias, electrons tunnel from occupied states of the surface to the tip. Hence, free electrons need to be available at the surface in order for tunnelling to take place. While this is possible for the clean Si(111)-7 × 7 surface (see e.g. Fig. 2(b) full line), adsorption of TEMPO will profoundly modify the electronic structure of the clean Si(111)-7 × 7 surface [18,20], as shown in e.g. Fig. 2(b) (dotted line). This can be explained by the TEMPO molecules attracting electrons due to their unpaired electron, i.e., they can be thought of as lacking one electron. Adsorption of TEMPO molecules will cause saturation of the dangling bonds and hence cancellation of the metallic surface state within the band gap of the Si(111)-7 × 7 surface. Thus, for a Si(111)-7 × 7 surface covered with TEMPO molecules up to saturation, there are no free electrons available at the surface. It should be pointed out here that the uptake of electrons by the TEMPO molecules results in an increase of the band bending (for clean Si the bands already bend upwards).

At positive sample bias, electrons tunnel from the tip to unoccupied states of the surface. The drastic increase of tunnelling current at positive voltages can be explained by the lack of electrons and thus the huge amount of holes in the space charge region.

Another relevant aspect, which might have an effect on symmetry of the IV-curve is the asymmetry of the junction and the lack of inversion symmetry of TEMPO itself [21]. The STM junction is clearly asymmetric, containing on one side the Si surface with the adsorbates, and as second electrode the metal tip. As can be seen in Fig. 1, the molecule obviously lacks inversion symmetry.

An interesting question is the structure (molecular ordering and molecular orientation) of the molecular film. The molecular arrangements within the layer might influence the I(V) properties, as has been demonstrated for the rectifying properties of phthalocyanine layers on n-type Si(111)-7 × 7 [21]. Unfortunately, the experimental equipment used in

these measurements does not allow for a determination of the molecular arrangements in the layer, though, it would constitute an interesting further study. However, the fact that the surface is relatively smooth and that substrate step edges can be seen, as shown in Fig. 4(a), indicates that the TEMPO molecules form a relative flat film on the Si(111)-7 × 7 surface.

Further research, experimentally and also theoretically, is necessary to reveal which mechanism is responsible for the strongly rectifying behaviour. Since the arrangement within the molecular layer might influence the I(V) behaviour, this would be interesting to study, as well as the time stability of the rectifier.

In summary, we have shown that fully TEMPO covered Si(111) surfaces exhibit strong and reproducible rectification in their I(V) characteristics. We suggest that this is caused by the molecule-surface interface and the modification of the electronic structure of the Si(111)-7 × 7 surface by adsorption of the TEMPO molecules.

Acknowledgements

This work (VIDI.TTF.5847) is financially supported by NWO (Nederlandse Organisatie voor Wetenschappelijk Onderzoek) and STW (Stichting Technische Wetenschappen).

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