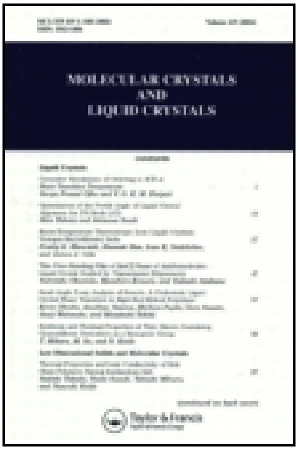

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Study on Charge Transport through a Molecule-Silicon Junction by Scanning Tunneling Microscopy

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The current-voltage (I-V) characteristics of organic molecules anchored covalently to silicon surfaces were studied with a scanning tunneling microscope in ultrahigh vacuum. It was found that molecules on silicon were not stable in the I-V measurement. Molecules were removed during the measurement, which was possibly induced by charge injection. Artificial negative differential resistance was sometimes recorded in the I-V plot. The origin of this event was explained by deformation and/or desorption of molecules induced by the charge injection during observation.

Keywords: molecular electronics; negative differential resistance; organic molecule; silicon; STM

INTRODUCTION

The molecular electronics has attracted interest as a candidate to break through the processing limit of inorganic semiconductor devices [1]. It has recently been demonstrated that simple molecular components

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exhibit interesting characteristics such as negative differential resistance (NDR) [2], rectifying [3], and switching [4]. Although the metal-molecule junction system, especially the Au–S bond, has been widely used to build molecular devices, the interface of the Au–S bond has not yet been well characterized. As a promising candidate in place of the Au–S junction, the hybridization of organic molecules and silicon substrates, the silicon-carbon (Si–C) junction, has recently been received considerable attention [5]. In recent studies, NDR has been discussed in I-V measurements on metal tip/vacuum/molecule/silicon systems using a scanning tunneling microscope (STM) [6,7]. NDR is one of the most challenging events in the molecular-scale electronics because of its application to the fast speed switching and the high performance oscillation circuits. The understanding of charge transfer and NDR event through the silicon-molecule system is, however, still insufficient. In this study, we show STM images and I-V characteristics through cyclopentene and 1,5-cyclooctadiene (COD) on Si(100)-2x1 surface using an ultrahigh vacuum (UHV) STM, and discuss the origin of NDR-like curves observed.

EXPERIMENTAL

All experiments were performed in the UHV STM (JEOL, JSPM-4500) system with the base pressure of 6.0×10^{-9} Pa. An electrochemically polished polycrystalline W wire with a diameter of 0.3 mm was used as an STM tip. Silicon substrates ($1 \times 7 \times 0.3\,\mathrm{mm}^3$) were cut from n-type Si(100) wafers (0.1–0.2 Ωcm). Silicon substrates were outgassed for 12 hours and flashed in the UHV chamber prior to use. Cyclopentene (Wako, 95%) and 1,5-cyclooctadiene (Wako, 98%) were introduced through a variable leak valve after degassing by the freeze-pump-thaw cycle. The silicon substrate after the exposure to molecules was transferred to a STM stage, and STM observation was carried out at room temperature. STM images were taken over the same area before, during, and after the I-V measurement of the molecule.

RESULTS AND DISCUSSION

Figure 1(a) shows a STM image before the I-V measurement of Si(100)-2×1 surface exposed to 0.01 langmuir (1 langmuir = exposure at 1×10^{-6} Torr for 1 sec) of cyclopentene molecules. Two cyclopentene molecules are recognized as blight spots. The sample bias (Vs) was set at -1.2 V and the tunneling current (It) was 0.5 nA. Almost the same images have been reported by several groups [7,8], in which the molecules were confirmed to anchor to Si(100)-2×1 surface via the $[2+2]$

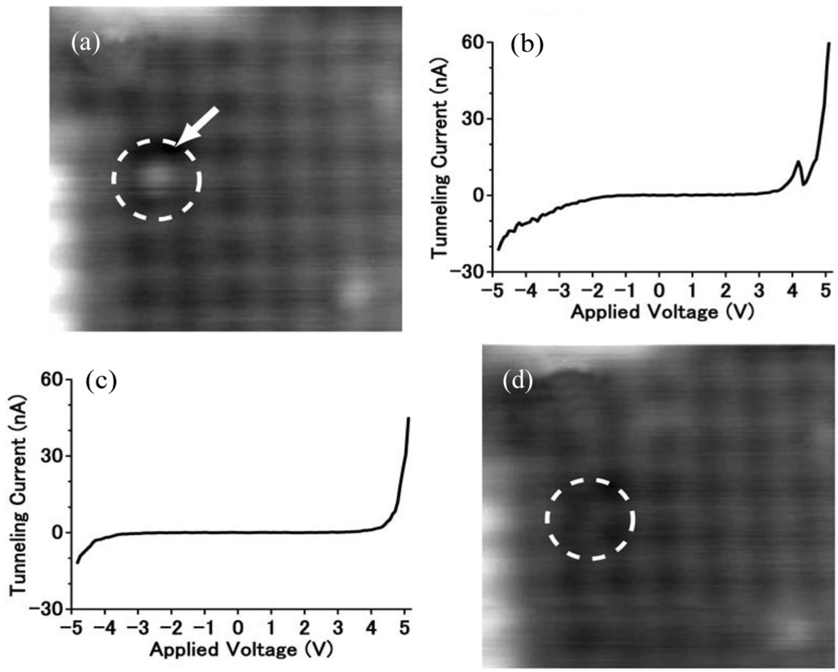

FIGURE 1 (a, d) STM images of Si(100)-2 × 1 surface with cyclopentene molecules before (a) and after (d) I-V measurement: $5 \times 5\,nm^2$, Vs = −1.2 V, It = 0.5 nA. (b, c) I-V plots taken over the molecule (b) and clean Si(100)-2 × 1 (c).

cycloaddition reaction. Figure 1(b) shows the I-V characteristics measured over a cyclopentene molecule indicated by an arrow in Figure 1(a). The sample bias voltage was swept from −5 V to +5 V and the I-V plot was recorded with 128 points. It is noted that a NDR-like peak was observed at the bias of around +4 V in the I-V plot. NDR-like peaks were sometimes observed at the negative bias in I-V plots, while no noticeable peaks were detected for bare Si(100) as shown in Figure 1(c). Figure 1(d) shows a STM image of the same area taken after the I-V measurement with Vs = −1.2 V and It = 0.5 nA. It is noticed that a molecule was removed from the original position. Similar effect was frequently observed in I-V measurements of cyclopentene on the Si(100)-2 × 1 surface [7]. The molecule was desorbed due to the I-V measurement.

Figure 2(a) shows a STM image of Si(100)-2 × 1 surface exposed to 0.03 langmuir of COD molecules with Vs = −1.2 V and It = 0.3 nA. Four COD molecules are recognized as blight spots. Similar images have been reported in previous studies [5]. Figure 2(b) shows a STM

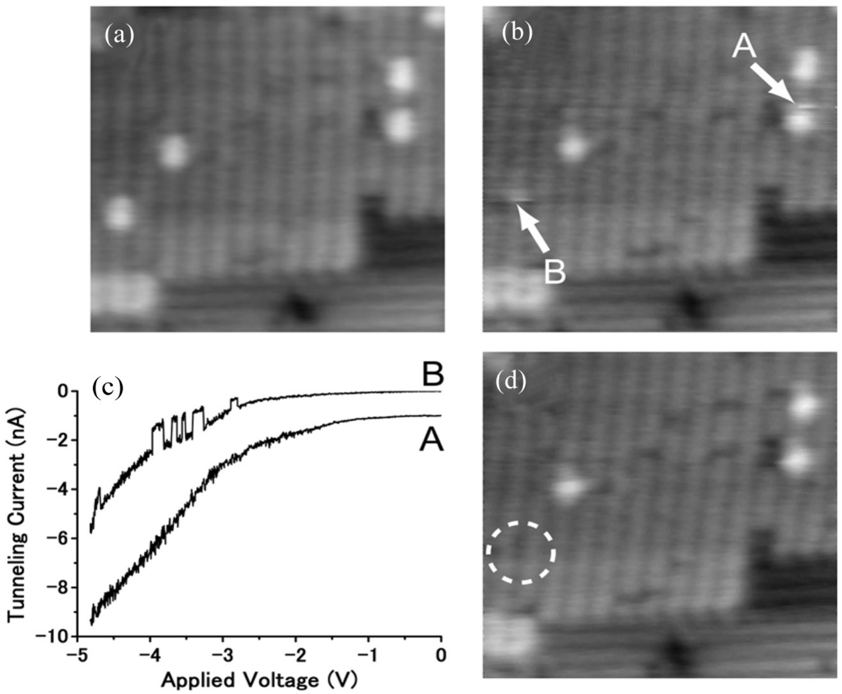

FIGURE 2 (a, b, d) STM images of Si(100)-2 × 1 surface with COD molecules before (a), during (b) and after (d) I-V measurement: $10 \times 10\,\mathrm{nm}^2$, $Vs = -1.2\,V$, $It = 0.3\,nA$; (c) I-V plot taken over molecules "A" and "B" shown in Figure 2(b).

image of COD on Si(100)-2 × 1 with $Vs = -1.2\,V$ and $It = 0.3\,nA$, in which, during the scanning, the I-V measurement was carried out on the molecules labeled "A" and "B". It should be noted that a molecule "B" was decomposed just after the I-V measurement. No noticeable change was observed for the molecule "A" in the image. Figure 2(c) shows the I-V characteristics measured over COD molecules labeled "A" and "B". The sample bias voltage was swept from 0 V to −5 V and the I-V plot was recorded with 1024 points. Noticeable changes in current were randomly appeared on the I-V curve taken over a molecule "B", while significant changes were not observed for a molecule "A". Figure 2(d) shows a STM image after the I-V measurement of Si(100)-2 × 1 surface with $Vs = -1.2\,V$ and $It = 0.3\,nA$. The desorption of the molecule "B" from the Si(100)-2 × 1 surface was confirmed in comparison to the image in Figure 2(a). The desorption of molecule from Si(100)-2 × 1 through the Si−C bond breaking is thought to play a key role to generate NDR-like events as demonstrated in Figure 2. NDR-like events could be explained not by a resonant tunneling model but by decomposition and/or desorption of molecules. The sharp increase/decrease in the tunneling current was thought to be due to the inelastic electron scattering within organic molecules which induces the Si−C bond breaking as pointed out by Pitters *et al*. [7].

In summary, we confirmed that the cyclopentene and COD molecules anchored to Si(100)-2 $\times$ 1 surfaces were not stable against the I-V measurement. The NDR-like event was induced by deformation and/or desorption of molecules following the carrier injection.

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