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# Double Decoration of a Si(111)-7 × 7 Surface at Room Temperature by Chemisorption of an Organic Salt

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This work describes the chemisorption of an organic salt, which is constituted by an iodide anion and a pyridinium-based cation, on the Si(111)-7 × 7 surface at room temperature. The adsorption of both iodide anion and organic cation has been justified by the study of the STM images polarity dependency. The regioselectivity of the chemisorptive process is explained by the electrostatic interactions between substrate and ionic species.

## Introduction

The investigation of molecular adsorption on silicon surfaces is of great industrial and fundamental scientific interest.<sup>1</sup> One important motivation for exploring the silicon surface chemistry is to tune with precision the electronic properties of silicon surfaces. Attaching molecules<sup>2–4</sup> or halogens atoms<sup>5–7</sup> onto specific sites of silicon surfaces requires us to have the necessary control over the electron transfer efficiency through interfaces. Most of the work related to the functionalization of the Si(111)-7 × 7 surface by organic molecules is usually explained by dissociation or chemisorption of precursors<sup>8</sup> except when adsorbate–substrate interactions can be overridden by an electrostatic shielding of the molecules,<sup>9,10</sup> by supramolecular interactions,<sup>11</sup> or by passivation of the surface due to the insertion of doping elements.<sup>12,13</sup> The chemical reactions between halogens and silicon surfaces have been intensively investigated because halogen atoms can be used to passivate the dangling bonds of semiconductor surfaces or halogen-containing gases are used in semiconductor etching processes. The deposition of inorganic iodo derivatives such as I<sub>2</sub>,<sup>14</sup> ICl,<sup>15</sup> or IBr<sup>16</sup> on a silicon surface leads to the adsorption of halogen atoms, which has been supported by experimental data as well as by theoretical simulations. However, the adsorption of organic iodo compounds on semiconductors has been less investigated than other halogeno-derivatives adsorption.<sup>2,11,17,18</sup> The deposition of alkyl iodide leads to the adsorption of hydrogen and iodine atoms on the surface via a dissociative process of the organic precursor, which implies the loss of the carbon skeleton.<sup>19,20</sup> All of these phenomena have been completely elucidated thanks to the emergence of ultrahigh vacuum scanning tunneling microscopy (UHV-STM), which has played a key role in understanding the mechanisms of adsorption for adsorbate–surface systems. However, to the best of our knowledge, only the STM investigations of empty states on the iodine–semiconductor systems have been described in the literature. This is surprising because many features can be obtained by the study of the filled states of adsorbate–surface systems.

In this Article, we report the first example of the adsorption of an organic salt, of the type iodide pyridinium-based salt, leading to the grafting of iodine atoms and organic molecules on a Si(111)-7 × 7 surface at room temperature. The adsorption sites have been elucidated thanks to the polarity-dependence investigations of STM images in both filled and empty states.

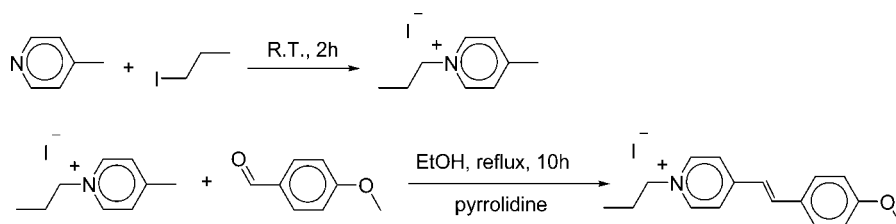
## Experimental Methods

**Synthesis of 4-Methoxy-*N*-propylstilbazolium Iodide.** 4-Picoline was treated at room temperature with a large excess of iodopropyl, leading to crystalline 4-methyl-(*n*-propyl)pyridinium iodide, which was used for the subsequent reaction without further purification. To a solution of 4-methyl-(*n*-propyl)pyridinium iodide in 15 mL of anhydrous ethanol were added 1 equiv of the 4-methoxybenzaldehyde and a catalytic amount of pyrrolidine. The mixture was heated under reflux for 10 h and then cooled to 0 °C. The precipitated product was filtered and washed with ether. The intense yellow solid was purified by column chromatography (silica gel, acetone, *R<sub>f</sub>* close to 0.5). The pure 4-methoxy-(*n*-propyl)stilbazolium iodide (MPSI, Scheme 1) was isolated as an intense yellow powder after evaporation of the solvent. MPSI molecules have been synthesized in accordance with the method previously described by Nicoud et al.<sup>21</sup> MPSI is unambiguously characterized by mass spectroscopy (MS), satisfactory elemental analysis data, as well as <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data, which are listed next.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.93 (t, <sup>3</sup>J = 7.3 Hz, 3H), 1.97 (hex., <sup>3</sup>J = 7.3 Hz, 2H), 3.76 (s, 3H), 4.62 (t, <sup>3</sup>J = 7.3 Hz, 2H), 6.85 (d, <sup>3</sup>J = 8.7 Hz, 2H), 7.05 (d, <sup>3</sup>J = 16.2 Hz, 1H), 7.59 (d, <sup>3</sup>J = 8.7 Hz, 2H), 7.69 (d, <sup>3</sup>J = 16.2 Hz, 1H), 8.03 (d, <sup>3</sup>J = 6.7 Hz, 2H), 8.99 (d, <sup>3</sup>J = 6.7 Hz, 2H). MS (ESI): *m/z* 254 [M<sup>+</sup>]. Anal. (%) Calcd for C<sub>17</sub>H<sub>20</sub>INO (381.06): C, 53.56; H, 5.29; N, 3.67. Found: C, 53.54; H, 5.32; N, 3.70.

**STM Experiments.** The Si(111) substrate was heated under ultrahigh vacuum by direct current. Clean surfaces were obtained by repeated cycles of heating at 1200 °C and slow cooling to room temperature. Deposition of the molecules from a Mo crucible was performed at 390 K onto the sample maintained at room temperature. All STM experiments were performed with an Omicron microscope and were carried out in an ultrahigh vacuum chamber with a pressure lower than 2 × 10<sup>−10</sup> mbar. STM images were acquired in the usual constant-current mode at room temperature.

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**SCHEME 1: Synthesis of 4-Methoxy-(*n*-propyl)stilbazolium Iodide (MPSI)****Results**

The 4-methoxy-(*n*-propyl)stilbazolium iodide (MPSI) has been chosen because this salt possesses an iodide anion that is not linked with a carbon atom by a covalent bond. Therefore, the well-known dissociative process<sup>19,20</sup> (i.e., H- $\beta$  elimination) could not occur in this case, and the grafting of both iodide anion and organic cation on the semiconductor surface could be possible.

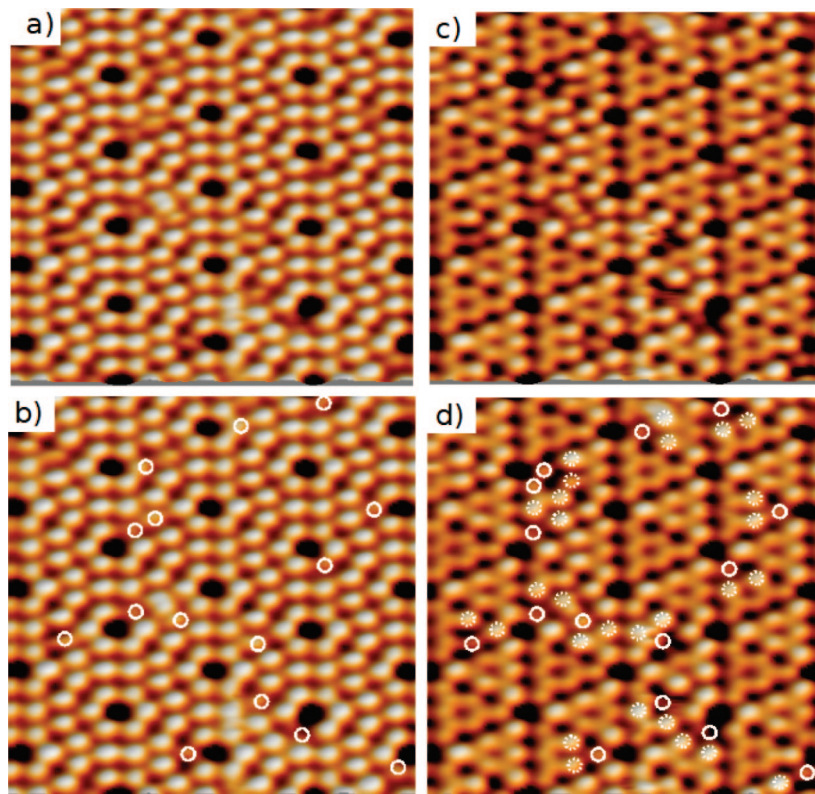
The high-resolution STM images polarity dependency of adsorbed MPSI molecules on Si(111)- $7 \times 7$  surface at room temperature has been investigated at  $-1.8$  and  $+1.8$  V<sub>s</sub> (Figure 1).

Figure 1a and c shows STM images ( $20 \times 20$  nm<sup>2</sup>) at a low molecular covering, obtained in the two polarities over the same area. All of the adatoms of the Si(111) are still visible, and the  $7 \times 7$  reconstruction is preserved. In the case of empty states (Figure 1a), 15 adatoms of the surface appear as darker spots (highlighted with white circles, Figure 1b). In the filled states (Figure 1c), the 15 darker adatoms are still observed at the same place. Moreover, 15 rest-atoms appear as darker spots, and 28 abnormal brighter center adatoms are revealed (dashed circles, Figure 1d).<sup>22</sup> Moreover, almost all dark rest-atoms are adjoining two bright protrusions.

**Discussion**

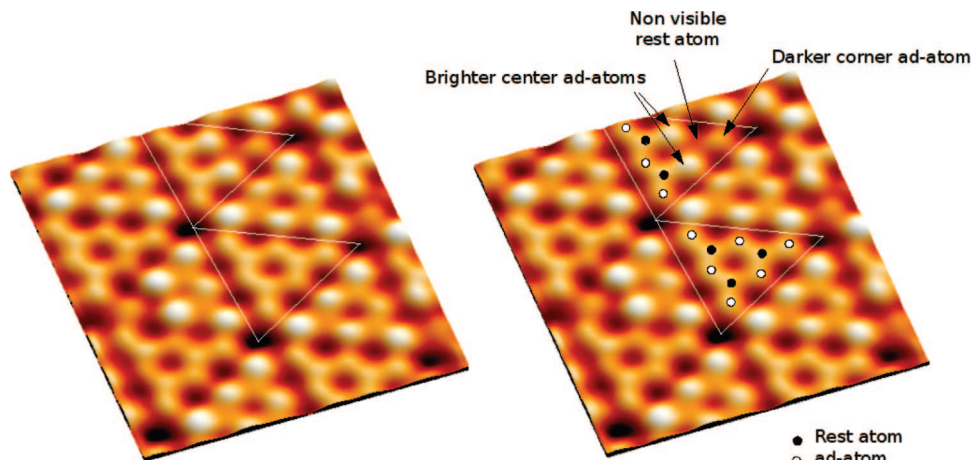
To the best of our knowledge, the iodine grafting on silicon surface has never been discussed on the basis of both STM filled and empty states images. In empty states, our STM images are similar to those described in the literature after the deposition of iodo derivatives.<sup>15</sup> Consequently, the observed dark spots can be attributed to the reacted Si adatoms, due to the elimination of their dangling bond by the formation of a Si-I bond. The same zone observed in the filled states shows dark spots located at the same positions (i.e., silicon adatoms). As the dark spots are unchanged by the polarity inversion, they are assigned to the iodine atoms grafted on the silicon adatoms of the surface. These darker spots are located equivalently atop corner or center silicon adatoms of the  $7 \times 7$  reconstruction (see Figure 2). This phenomenon can be explained because silicon adatoms have a quite similar electrophilic character,<sup>5,14,23</sup> leading to an identical electrostatic interaction with iodide anions. In summary, the iodide anions grafted on the Si(111)- $7 \times 7$  appear as darker adatoms in the two polarities.

In the filled states, the rest-atoms neighboring to reacted adatoms are darker than the clean rest-atom sites, indicating their participation in surface reaction. As the rest-atoms are negatively charged,<sup>23</sup> the 4-methoxy-(*n*-propyl)stilbazolium

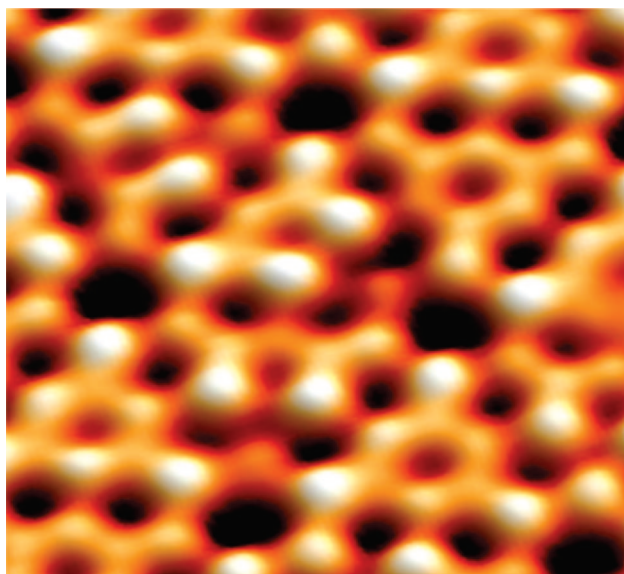


**Figure 1.** (a,b) STM images in empty ( $V_s = +1.8$  V) and (c,d) filled ( $V_s = -1.8$  V) states of MPSI adsorbed on Si(111)- $7 \times 7$  interface at room temperature ( $20 \times 20$  nm<sup>2</sup>,  $I_t = 0.22$  nA; darker adatoms, white circles; dashed circles, brighter center adatoms).

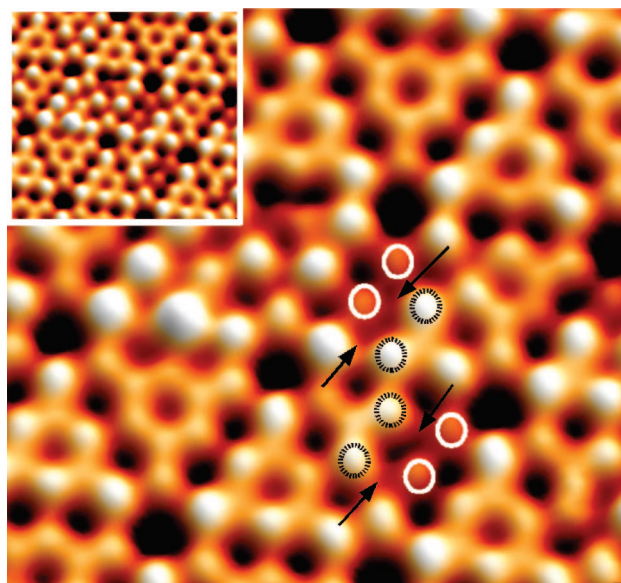




**Figure 2.** High-resolution STM images in filled states of MPSI adsorbed on Si(111)- $7 \times 7$  interface at room temperature ( $6.5 \times 5 \text{ nm}^2$ ,  $V_s = -1.8 \text{ V}$ , and  $I_t = 0.22 \text{ nA}$ ).



**Figure 3.** High-resolution STM image at room temperature in filled states showing adsorbed MPSI on faulted or unfaulted half-cell of Si(111)- $7 \times 7$  interface ( $5 \times 5 \text{ nm}^2$ ,  $V_s = -1.8 \text{ V}$ , and  $I_t = 0.22 \text{ nA}$ ).



**Figure 4.** High-resolution STM images at room temperature in filled states of half-cells of Si(111)- $7 \times 7$  interface including two adsorbed MPSI ( $7.5 \times 7.5 \text{ nm}^2$ ,  $V_s = -1.8 \text{ V}$ , and  $I_t = 0.22 \text{ nA}$ ).

cations are adsorbed on them, thanks to stabilizing electrostatic interactions. Moreover, the involvement of rest-atoms in the surface reaction leads to a redistribution of dangling bond electrons, leading to a decrease in the image intensity and to an enhancement of the brightness of the two neighboring unreacted center adatoms.<sup>24</sup> This phenomenon explains the presence of 28 abnormal brighter center adatoms in Figure 1c,d.

The adsorption of MPSI on Si(111)- $7 \times 7$  is a new example of the localized atomic reaction (LAR) as described by Polanyi et al.<sup>25</sup> In the case of LAR, the adsorption is a concerted mechanism where the broken and formed bonds involve adjacent atoms. In our case, the adsorption of the salt is atomically guided by the salt/substrate electrostatic interactions, and the cations and the anions are adsorbed on adjacent adatoms and rest-atoms. However, in our case, no covalent bond is broken because the cation and the iodide anion are linked via an ionic bond in the salt. Moreover, cations and anions are always adsorbed on neighboring adatoms and rest-atoms, and they are grafted on faulted or unfaulted half-cells of the  $7 \times 7$  reconstruction (Figure 3). These two effects indicate that anions and cations cannot diffuse at room temperature on the surface.

In the STM images of the filled states, a few half-cells possess two dark adatoms and two dark rest-atoms (Figure 4), proving that the grafting of two anions and two cations is possible in a unique half-cell, despite steric hindrance of cations attached to the rest-atoms.

## Conclusion

The adsorption of an organic salt on a Si(111)- $7 \times 7$  surface has been investigated by STM experiments at room temperature. The polarity dependence of the STM images has been used to fully account for the deposition of 4-methoxy-(*n*-propyl)stilbazolium iodide on a Si(111)- $7 \times 7$  surface at room temperature. The iodide anions, appearing as dark spots in the two polarities, are adsorbed equivalently on the electrophilic center or corner adatoms, whereas the cations are adsorbed onto the closest rest-atoms. The stability of the system, even at room temperature, and the regioselectivity of the deposition can be explained by the stabilizing electrostatic interactions between adsorbed species/substrate. This is, to the best of our knowledge, the first report of the grafting of an organic cation and an iodide anion pair onto a semiconductor. The deposition of organic salt seems

to be a new convenient way to build up an organic/inorganic assembly on semiconductors at room temperature.

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