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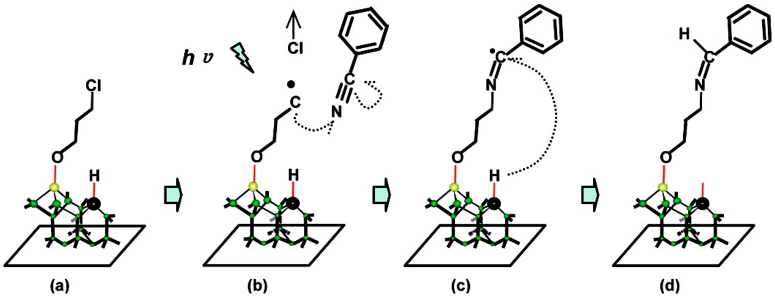

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Photoinduced Construction of a Second Covalently Bonded Organic Layer on the Si(111)-7 × 7 Surface

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The incorporation of organic functionalities to the semiconductor surface has potential applications in fine-tuning the chemical, physical, and mechanical properties of the organic-semiconductor interface, which would lead to the development of molecular devices, biosensors, and nanotechnologies.[1] Due to the importance of silicon in the semiconductor industry, molecular attachment chemistry of silicon surfaces is a subject of great interest. The interactions of organic functionalities with vacuum-prepared Si(111) and Si(100) surfaces have been extensively studied, and many molecular templates with unique properties have been developed.[2] Specifically, many studies have focused on the interactions of multifunctional organic molecules with silicon surfaces to develop molecular templates that may be used for further modifications and functionalizations. However, in contrast to the growth of an organic multilayer on silicon surfaces in solution,[3] vacuum-based methods are still facing great challenges.[4] The difficulties in constructing an organic multilayer under vacuum conditions are usually due to the relatively low reactivities of organic molecules with the remaining functionalities of the first molecular monolayer.

In this paper, we report the successful photochemical construction of a second organic layer covalently bonded to the Si(111)-7 × 7 surface at low temperature (cooled by liquid nitrogen). The Si(111)-7 × 7 surface was routinely prepared by repeated Ar-ion bombardment and annealing to 1200 K in an ultrahigh vacuum (UHV) chamber. The clean Si(111)-7 × 7 surface was exposed to 3-chloro-1-propanol ($HO-CH_2CH_2CH_2-Cl$) at 110 K and subsequently annealed to 250 K to desorb the physisorbed organic molecules. In this way, the Si(111)-7 × 7 surface was saturated with the first chemically attached organic layer ($Si-O-CH_2CH_2CH_2-Cl$) with terminal C−Cl bonds extending into the vacuum through the dissociation of the −OH group. Subsequently, benzonitrile molecules (C_6H_5-CN) were then physisorbed on the 3-chloro-1-propanol modified Si(111)-7 × 7 surface at 110 K. Upon irradiating the surface with photons at 193 nm (generated by an ArF excimer laser with an intensity of 0.04 W/cm^2 to minimize thermal effect), the photoinduced cleavage of the C−Cl bond produces a reactive radical site to react with the benzonitrile molecule via the cyano group, resulting in the formation of the second covalently bonded organic layer.

Figure 1a shows the HREELS spectrum obtained after multilayer physisorption of 3-chloro-1-propanol on the Si(111)-7 × 7 surface. The energy loss peaks at 654, 1067, 1285, 1431, 2958, and 3237 cm^{-1} can be readily observed, in excellent agreement with the FT-IR spectrum for liquid 3-chloro-1-propanol.[5] Among them, the vibrational peak at 3237 cm^{-1} is assigned to the O−H stretching mode, and the loss at 654 cm^{-1} is attributed to the C−Cl stretching mode.[6] In comparison, the vibrational spectrum for the chemisorbed species, obtained after annealing the above sample to 250 K to drive away the physisorbed molecules, is shown in Figure 1b. Upon chemisorption, the O−H stretching mode at about 3237 cm^{-1} disappeared, and meanwhile, the Si−H stretching mode at 2120 cm^{-1} was clearly observed, suggesting the dissociation of the O−H bonds and the formation of new Si−H bonds.[7] The C−Cl stretching mode at about 654 cm^{-1}, on the other hand, remains after the surface reaction. Collectively, the HREELS results indicate that 3-chloro-1-propanol adsorbs on the Si(111)-7 × 7 surface through the dissociation of the O−H bond at an adjacent adatom−rest atom site and with the C−Cl bond unperturbed (Figure 2a).

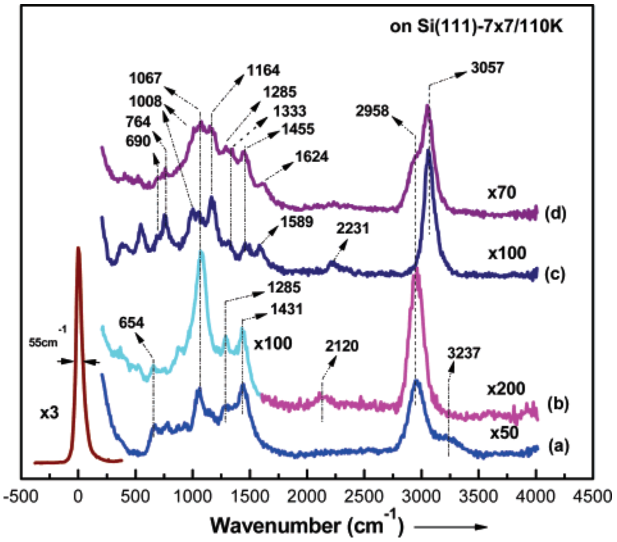

Figure 1. HREELS spectra obtained at 110 K on the Si(111)-7 × 7 surface (a) for the condensed 3-chloro-1-propanol multilayer, (b) for the chemisorbed 3-chloro-1-propanol, (c) for the condensed benzonitrile multilayer on the 3-chloro-1-propanol modified Si(111)-7 × 7 surface, and (d) after irradiating the sample for (c) using a 193 nm laser (∼0.04 W/cm^2) for 30 min followed by annealing to 300 K. The primary electron beam with an energy of 5.0 eV impinges on the surface at 60° from the surface normal. The scattered electrons were detected at the specular direction. The resolution of the spectrometer (fwhm) is 6−7 meV.

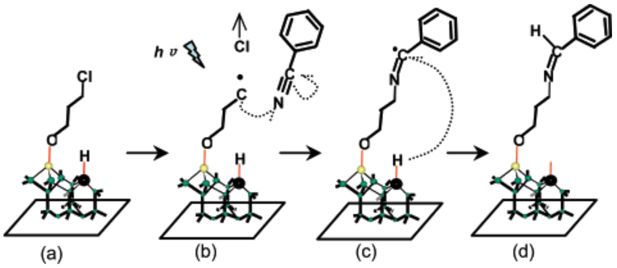

Figure 2. Schematic model for (a) chemisorbed 3-chloro-1-propanol on the Si(111)-7 × 7, (b) photodissociation of 3-chloro-1-propanol followed by interaction of the radical with the cyano group of physisorbed benzonitrile, (c) H abstraction by the −N═C•− radical from an adjacent rest atom site, and (d) the second covalently bonded organic layer.

To attach a second layer of organic molecules, the physisorbed multilayer of benzonitrile molecules was first formed on the 3-chloro-1-propanol modified Si(111)-7 × 7 surface before laser

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irradiation. The HREELS spectrum of this surface is shown in Figure 1c. The loss features at 690, 764, 1008, 1164, 1333, 1455, 1589, 2231, and 3057 cm^{-1} can be clearly identified, in good agreement with the IR spectrum of liquid benzonitrile and the HREELS spectrum of condensed benzonitrile on the Si(111)-7 × 7 surface.[8] It is important to note that the intense peak at 3057 cm^{-1} is ascribed to the sp^2 C−H stretching mode of the aromatic ring, and the energy losses at 1333, 1455, and 1589 cm^{-1} are assigned to the characteristic C−C stretching modes of the phenyl ring.[8,9] The above sample was subsequently irradiated by a 193 nm laser for 30 min, followed by annealing to 300 K to desorb the unreacted benzonitrile molecules. Dramatic spectral changes appear in Figure 1d. Besides the energy loss peaks of chemisorbed 3-chloro-1-propanol, the vibrational features of the sp^2 C−H stretching mode at about 3057 cm^{-1} can be clearly identified, together with the appearance of phenyl ring stretching modes at about 1455 and 1333 cm^{-1} and CH bending modes of phenyl ring at about 1164, 1008, and 764 cm^{-1}, indicating that the intact phenyl rings were covalently linked to the 3-chloro-1-propanol modified Si(111)-7 × 7 surface.[8,9] Furthermore, the absence of C≡N (2231 cm^{-1}) and C−Cl bond stretching peaks in Figure 1d compared to Figure 1c and 1b suggests that the grafting of benzonitrile on the 3-chloro-1-propanol modified Si(111)-7 × 7 surface is through the reaction of the C≡N group in benzonitrile with the radical site on the chemisorbed 3-chloro-1-propanol produced by photoinduced C−Cl cleavage. As illustrated in Figure 2, the reaction process is proposed to be that the radical site attacks the nitrogen atom of the cyano group, resulting in the transformation of the N≡C− bond to the $-N{=}C^{\bullet}-$ bond, and in turn, the new radical site on the $=C^{\bullet}-$ atom of $N{=}C^{\bullet}-$ group abstracts one H atom from the nearby rest atom, similar to the mechanism proposed by Wolkow for the adsorption of styrene on the H-terminated Si(100) surface.[10a] The H abstraction is probably enabled through the suitable conformations of the chain radical.[10b] In addition, the physisorption of benzonitrile ensures the close proximity between its cyano group and surface H atom. This reaction would lead to the formation of C═N double bonds and the elimination of Si−H bonds, which are evidenced by the appearance of the C═N stretching peak at 1624 cm^{-1} and the disappearance of the Si−H stretching mode at about 2120 cm^{-1} in Figure 1d.

Further experiments were also conducted to gain more insight into the grafting of a second covalently bonded organic layer. The dissociative binding mode of 3-chloro-1-propanol on the Si(111)-7 × 7 surface via the OH bond dissociation was confirmed by XPS study (refer to Supporting Information). The down shift of the O1s binding energy by about 1 eV from 533.3 eV (physisorption) to 532.3 eV (chemisorption) implies that the −OH group dissociates to form the Si−O species. The C1s XPS peak for the chemisorbed species can be deconvoluted into two peaks with an intensity ratio of about 2:1 in favor of the peak with higher binding energy (286.6 eV), suggesting that the electronegative Cl and O atoms are still connected to the C atoms. This is consistent with the Cl $2p_{3/2}$ XPS peak position of the chemisorbed 3-chloro-1-propanol at 200.5 eV, comparable to the value for physisorbed 3-chloro-1-propanol and a typical value for the C−Cl species.[11]

In order to confirm that the covalent grafting of benzonitrile molecules on the 3-chloro-1-propanol modified Si(111)-7 × 7 surface was triggered by photons, a physisorbed multilayer of benzonitrile molecules was condensed on the 3-chloro-1-propanol modified Si(111)-7 × 7 surface (same exposure as that for Figure 1c), followed by annealing the surface to 300 K without laser irradiation. Complete desorption of benzonitrile was found, suggesting that benzonitrile molecules do not react with the chemisorbed 3-chloro-1-propanol on the Si(111)-7 × 7 surface in the thermal annealing process after laser irradiation.

The critical role of the photons in the construction of the second covalently bonded organic layer is to produce radical sites by cleaving the C−Cl bonds in the chemisorbed 3-chloro-1-propanol. In the HREELS spectrum shown in Figure 1d, the presence of the vibrational features that correspond to the phenyl ring and the C═N group implies that benzonitrile does not dissociate in the photoreaction process. On the other hand, the photoinduced dissociation of the C−Cl bonds in the chemisorbed 3-chloro-1-propanol by 193 nm photons was confirmed in a separate study. After the irradiation of the 3-chloro-1-propanol modified Si(111)-7 × 7 surface using 193 nm photons for 30 min, the C−Cl stretching mode disappeared while other vibrational features (including the Si−H stretching mode) remained unchanged in the HREELS spectrum (not shown), indicating the cleavage of the C−Cl bond and remaining of the C−C−C skeleton, as well as the Si−H species on the Si(111)-7 × 7 surface after laser irradiation.

In summary, benzonitrile molecules can be covalently grafted to the chemisorbed 3-chloro-1-propanol molecules on the Si(111)-7 × 7 surface using photochemical method to form a second covalently bonded organic layer. In this process, the photoinduced C−Cl bond cleavage produces a reactive radical site, which subsequently reacts with the C≡N group of the physisorbed benzonitrile molecule to form the −C−N═C− covalent linkage. Therefore, the potential of photochemical methods as powerful tools for organic modification of the silicon surfaces has been demonstrated in this work.

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Supporting Information Available: XPS data of the adsorption of 3-chloro-1-propanol on Si(111)-7 × 7. This material is available free of charge via the Internet at http://pubs.acs.org.

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