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Adsorption and thermal treatments of 1-dodecene on Si(100) investigated by STM

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ABSTRACT

We investigate the atomic behaviour of long-chain 1-dodecene adsorbed on Si(100) using a scanning tunnelling microscope with an exposure of 30 to 2.4 Langmuirs. Unlike previous reports on short-chain molecules, remarkable self-ordered assembly of molecules is not observed at room temperature, which is possibly attributed to the asymmetric molecular structure with long chains of 1-dodecene. After annealing at 500~580 ºC, ordered patterns form with a *c*(4×4) structure, accompanied with thermal decomposition of molecules.

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1. Introduction

There is increasing interest in developing methods with organic-based structures for organic electronic applications such as organic thin film transistors (OTFTs), nonlinear optics, thin-film displays and nanolithography. Organic devices either completely organic or organic-inorganic hybrid are poised to enable advances where mechanical flexibility, low-temperature fabrication and low-cost manufacturing are desired. The Si(001) surface is technologically important as the starting point for most microelectronic devices. It has been known that for certain molecular films grown on various substrates (SiO_2, metals, polymers, and chemically modified Si(100)), the organic crystal size and molecular orientation vary greatly depending on the electronic and structural properties of the molecule-substrate interface, thus affecting the performance of devices.[1-5]

1-Dodecene ($C_{12}H_{24}$) is an alkene with the formula $C_{10}H_{21}CH{=}CH_2$, consisting of a chain of twelve carbon atoms terminated by a double bond. The full length of a molecule is as long as 1.4 nm. It has been used in the OTFT structure as a buffer layer between the organic (pentacene) film and the Si(100) substrate to modulate the film nucleation and growth, as investigated by low-energy-electron microscopy.[6] According to the common belief, a deposited self-assembled dodecene monolayer is densely packed and well ordered, as previously characterized by infrared spectroscopy, ellipsometry, and water contact angle measurements.[7] Despite the great technological importance of organic-based devices, there has been little work attempting to understand well-defined 1-dodecene films at the nanometre-scale. The surface chemistry of organic molecules on Si(100) has been widely studied for alkenes C_nH_{2n} using scanning tunnelling microscopy (STM),[8-12] but not for the long-chain molecules (C_nH_{2n}, $n \geq 8$).[13]

Motivated by Ref. [6], in this work we use STM to investigate 1-dodecene deposited on Si(100) substrate at room temperature followed with thermal treatments, in order to contrast the atomic behaviour of 1-dodecene with that of short-chain molecules.

2. Experimental section

The experiments were carried out in a home-built UHV-STM equipped with a field-ion microscope that is used to monitor and fabricate the tip.[14] The base pressure for STM is 1.8×10^{-10} torr. The silicon *p*-type

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Si(001) sample was annealed at 1200 °C to produce clean well-ordered surfaces exhibiting a (2×1) reconstruction. The 1-dodecene liquid (95%, Aldrich) was purified by multiple freeze-pump-thaw cycles, and then introduced in the system through a separate variable leak valve. The chemical was dosed onto the sample from the chamber background pressure. Exposure was measured in Langmuirs (L=1×10^{-6} torr·s) based on the pressure measured by an ion gauge.

3. Results and discussion

Alkenes react with silicon dimers to form pairs of C-Si bonds. The mechanism and products of this reaction have been the subjects of a number of experimental[8-11] and theoretical studies.[15-17] After reaction of C=C with the Si dimer, the C-C σ–bond and hydrogens remain intact and there is no additional product on the surface.

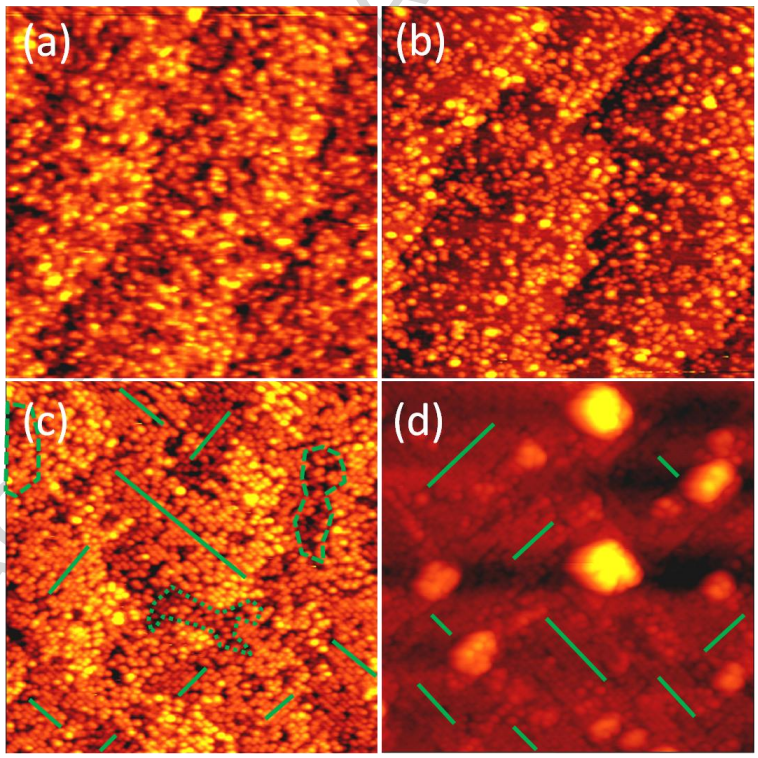

FIG. 1. Adsorption and thermal treatments of dodecene Si(100)-2×1 surface. All scan sizes are 50 nm × 50 nm. (a) Deposition at RT, 30 Langmuirs (1.0×10^{-8} torr for 30 s). V = -3.53 V, I_t = 16.4 pA. (b) Further annealing at 400 ºC. V = -3.74 V, I_t = 14.5 pA. (c) Additional annealing at 500 ºC. V = -4.19 V, I_t = 27.4 pA. (d) Final annealing at 580 ºC. V = -4.31 V, I_t = 25.5 pA. The green lines in (c) and (d) indicate the domain orientations. The structures in the region marked by the dashed green line in (c) are unordered.

1-Dodecene molecules are first deposited on a clean Si(100) surface at room temperature at 30 L. The

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dodecene-Si(100) surface is very disordered (Fig. 1(a)) though the underlying Si steps can be seen. We decrease the amount of deposited molecules by at least one amplitude to further investigate the initial adsorption of dodecene on Si(100) (not shown). The result shows that regardless of the coverage, when the molecules are deposited at RT, no ordered pattern forms. The poor packing density of 1-dodecene at RT is likely associated with steric effects from the long alkyl chain.

Our observation agrees with Weidkamp's X-ray photoelectron spectroscopy and photoemission electron spectroscopy data under similar experimental conditions.[6] They claim that the C/Si ratio of dodecene is as low as 0.15, and dodecene forms a self-terminating ML with a density of one molecule per-three to four dimers on the Si(100) surface, consistent with the estimated length of the alkyl chain.[6]

We suggest that the structural complexity of long-chain molecule could be the reason why it is difficult to observe the ordered pattern at the atomic scale, when the molecules are deposited at room temperature. A 1-dodecene molecule can be considered as a long carbon chain protruding from the surface with a strong Si-C bond at the interface.[6,18] For 1-butene attached onto a Si(100) surface, four spatially different orientations of the ethyl group can be distinguished.[18] A simulation of a similar long-chain molecule 1-hexadecence on Si(100)-2×1 shows that among all possible adsorption patterns, the following one should be optimal to lower the surface energy: looking perpendicularly to the C-C bond, it appears that the hydrogen atoms point toward hydrogen atoms on adjacent chains. However, looking along the C-C bond, the chains from each dimer row slant in two different, alternating directions and the hydrogen atoms on one chain interlace with hydrogen atoms on adjacent hydrocarbon chains.[18] Moreover, longer chains have more rotational degrees of freedom to orient themselves into their lowest energy configuration.[18]

Despite the lack of order seen after exposure at RT, thermal treatments of dodecene Si (001) result in the formation of ordered patterns. When the sample is annealed at ~400 ºC for 40 min, the molecules are still distributed individually, but the height on the surface becomes more even (Fig. 1(b)). Ordered patterns form (Fig. 1(c)) following further annealing of the sample at ~500 ºC for 20 min. When the annealing temperature is as high as ~580 ºC for 20 min, big particles form on the ordered structures (Fig. 1(d)). From Figs. 1(c) and 1(d), we can see that the molecular domains have two orientations, which are perpendicular to each other. The fact that two and only two orientations are present and that both orientations are commensurate with the

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Si-(2×1) lattice indicates that the grown layer is epitaxial. The optimal annealing temperature for ordering is in the narrow range of 500~540 ºC. We note that the regions marked with dashed lines between the boundaries of domains in Fig. 1(c) are still unordered.

Annealing or a suitable substrate temperature is crucial for creating ordered patterns. A small dosage of 2.4 L 1-dodecene was deposited on Si (100) at 540 ºC and then annealed for 15 min. Its STM image (Fig. 2(a)) shows that some of the molecules still sit individually and many brighter clusters randomly distribute on the top. However, it can be clearly seen that the surface atoms become mobile enough to start assembling together. Figure 2(b) shows that the ordered patterns are growing up with longer annealing time. Figure 2(c) presents a typical STM image of an ordered pattern formed by annealing. A *c*(4×4) structure is marked by two arrows, in which the distance between two protrusions is 1.134 nm (Fig. 2(d)). The ordered structures remain stable at annealing temperatures from 500 °C up to about 580 °C.

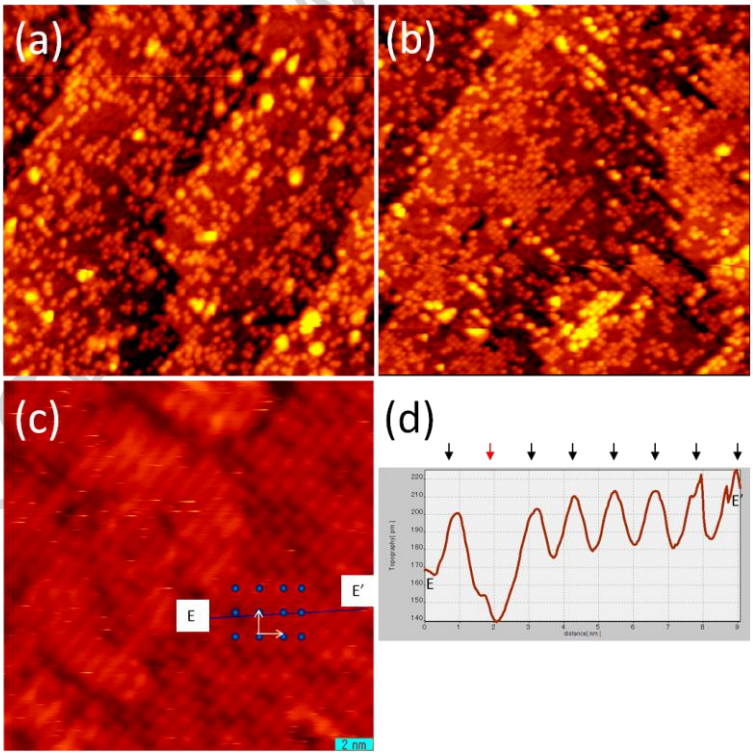

FIG. 2. (a) Exposure to 2.4 L of 1-dodecene at $T_{substrate}$=540 ºC, then annealing for 15 min. V = -3.27 V, I_t = 10.0 pA. (b) Further annealing the sample for another 15 min. V = -3.27 V, I_t = 24.0pA. (c) Dodecene deposited on Si(001) under $1x10^{-9}$ torr, subsequently annealed at 540 ˚C for 80 min. V = -2.51 V, I_t = 15.8 pA. (d) Section profile along the line EE' in (c). A *c*(4×4) structure is marked by two arrows in (c). The scan sizes are 50 nm × 50 nm for (a) and (b), and 20 nm × 20 nm for (c).

We expected that annealing is helpful to form ordered patterns of 1-dodecene molecules, which are

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densely packed and nearly perpendicularly standing. However, from the STM data it is difficult to determine what the ordered pattern is. Besides, we notice that the temperature range for the formation of ordered patterns and big particles agree with previous reports on the thermal decomposition and the SiC particle formation of ethylenene.[11,19-21]As reported by Yoshinobu *et al.*,[19] chemisorptions of unsaturated hydrocarbons can occur at the relatively low temperature of 80 K. By heating at 650 K, ca. 40% of ethylene is desorbed, while the remainder is decomposed into CH, CH_2 and SiH species. By heating up to 1000 K, the H adatoms are completely desorbed, and SiC is formed on the Si(100) substrate.[19] Their conclusion is supported by their results on the adsorbed state of ethylene on the Si(100) surface studied by electron energy loss spectroscopy, low-energy electron diffraction, and Auger electron spectroscopy.[19,22] Li *et al.* also observed the creation of SiC particles with a restoration of the Si(100)-2×1 structure next to the clusters, and the metastable *c*(4×4) Si(100) structures between the clusters, by annealing C_2H_2 on Si(100).[11]

We thus attribute the ordered patterns shown in Figs.1(c), 1(d) and Fig. 2 to the carbon-related structures formed at elevated temperature, which is necessarily accompanying the thermal decomposition of the long-chains. Previously researchers claimed that the *c*(4×4) phase is one of the intrinsic Si(100) reconstructions without any foreign element,[23] but such a claim has been rebutted by recent studies and the existence of C is generally accepted.[20,21,24] The latter one is supported by our experimental results. The model of carbon-induced Si(100)-*c*(4×4) atomic structure proposed by Simon *et al*. consists of a dimer network involving both C-Si and Si-Si dimers (two pairs per unit cell).[20] Theoretically the *c*(4×4) superstructure formation is a way to accommodate C atoms in bulk Si.[20]

As a reference, we measured the height (not real length but affected by local density of states) from the pattern top to the underlying layer from several probed areas. The measured values vary with the exact positions and the treatment conditions. Recalling the calculated structural parameters of C_2H_2/Si(100): Si-C (1.88 Å), C-C (1.34 Å), C-H (1.09 Å), and Si-Si (2.36 for dimerized model and 4.13 for cleaved model)[25], at 520 ^{o}C we observe a few typical heights (1.04~1.1 Å, 1.5 Å), which are consistent with the lengths of C-H and C-C bonds. The largest height (1.8~1.9Å) is found for the flashed dodecene/Si(100). This agrees with the Si-C bond length, and is more fit to the dimerized model in theoretical calculations[17] and previous STM observation of C_2H_2/Si(100).[11] We should point out that this comparison only applies for the perpendicular

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bonding case. If the bonding is tilted the apparent height should be shorter than the bonding length.

The high-resolution bias-dependent STM images of dodecene at exposure 3 L at RT are illustrated in Fig. 3. It can be seen that there is practically no difference between the surface morphology at lower and higher biases. Bright features roughly the size of the Si dimers are observed (Fig. 3(a)). At the sample biases of +1.55 V (Fig. 3(b)), -2.05 V (Fig. 3(c)) and -1.55 V (Fig. 3(d)), the images have protrusions, indicating the molecular adsorption sites. In Fig. 3a, at a more positive sample bias of +2.05 V, the molecules look like "transparent" on the Si surface. Our results are unlike cyclopentene and cyclooctadiene, whose images contrast involve both a reduced barrier for tunnelling through the molecules and the alteration of the silicon surface by bonding, leading to images strongly bias-dependent and changing from mounds to depressions as the sample bias is changed from -2.5 to -1.0 V.[26] This difference is probably caused by the molecular adsorption status: chemisorbed, like in the present case, or physisorbed.

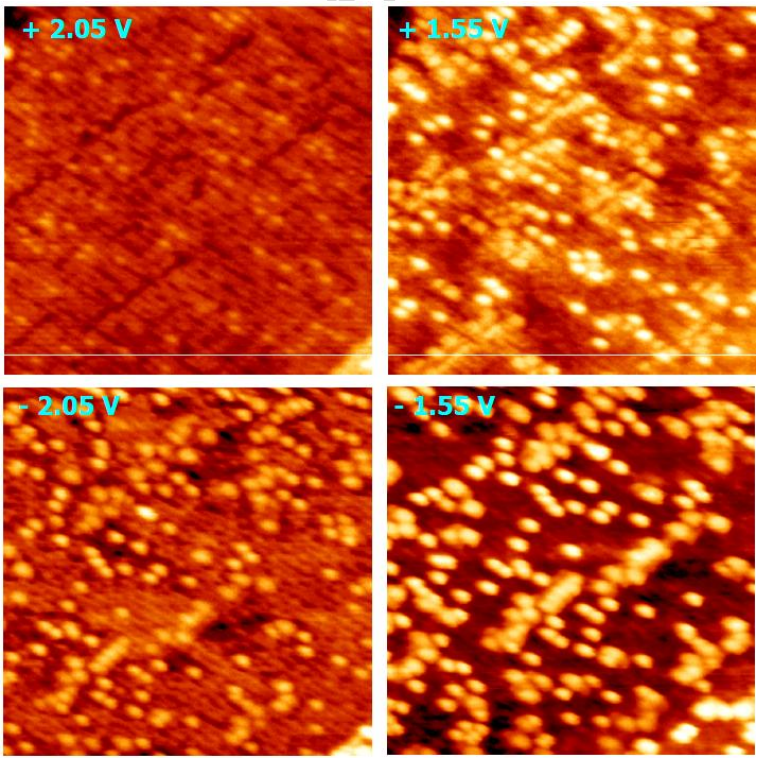

FIG. 3. Bias-dependent STM images of dodecene on Si(100) after exposure to 3 L at RT. All images are 25 nm × 25 nm with I_t = 20.0 pA, and taken approximately from the same area on the surface.

We found that the low coverage of the molecules changes the step shapes of Si(100)-2×1 (Fig. 4(a)). In general the clusters tend to adsorb at step edges on terraces with the dimer rows perpendicular to the step edge, *i.e.*, type "*B*" steps, allowing the zigzag shape of Si steps to be further magnified possibly by selective

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etching. This observation is consistent with the previous experimental results of C_2H_2 absorption on Si(100) studied by the same group.[11] Moreover, when the 1-dodecene adsorbed Si(100) samples are flashed, several types of defects (A-, B- and C-)[27] appear on the Si(100) surface at both bias polarities, but type C defects are more frequently observed for the empty surface states, as shown in Fig. 4(b). These defects do not exist before the molecular deposition, indicating that the C-incorporation effect cannot be fully removed by flashing.

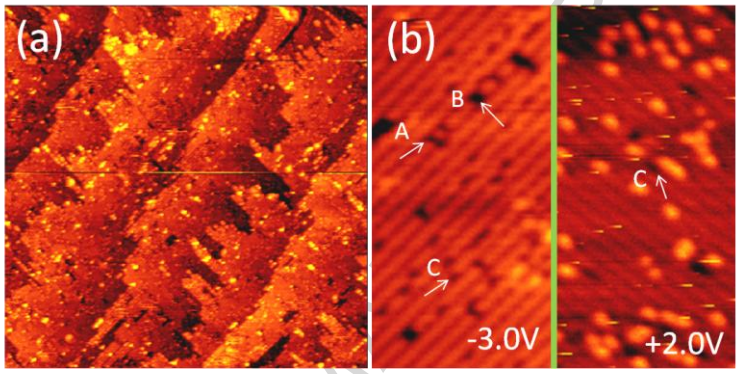

FIG. 4. Molecular effects of 1-dodecene on the Si(100) substrate. (a) The experimental condition is the same as in Fig. 2(b). The scan size is 100 nm ×100 nm. V = -3.62 V, I_t = 17.2 pA. (b) A-, B- and C- type defects appear on a flashed Si(100) surface.

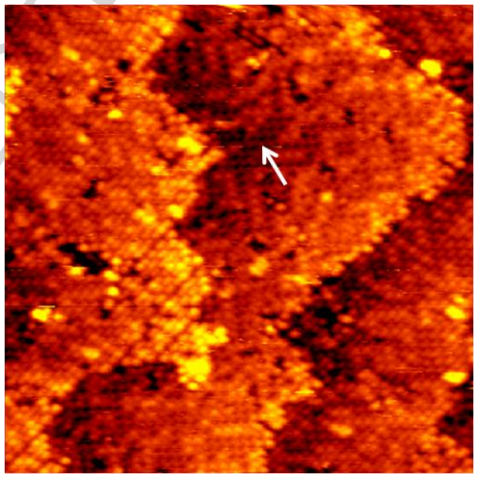

FIG. 5. Exposure to ~0.5 L 1-dodecene at T_s=540 ºC and further annealed for 20 min. A c(4×2) structure may form (marked by an arrow). The scan size is 50 nm ×50 nm. V = -3.26V.

In our experiment, *c*(4×4) is the predominant structure for the ordered patterns. However, we note that when depositing a small amount of dodecene (~0.5 L) on Si(100) at 540 ºC and further annealing for 20 min, a *c*(4×2) structure appears from the original Si(100)-*p*(2×1) structure, as shown in Fig. 5. It is possibly induced by carbon[28] or due to the asymmetric double bond-end of 1-dodecene,[18] which facilitates the dimer

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reconstruction of Si (100) to be asymmetric, *i.e.* twisting and tilting, by minimizing the surface energy.[29] Yet, the mechanism is unclear.

4. Conclusions

We investigated for the first time a long-chain 1-akelene (1-dodecene) growth on Si(100)-2×1 surface in UHV condition. Unlike for the short-chain molecules, we did not observe ordered patterns when the molecules are deposited at room temperature. The temperature range for ordering is narrow (500 to 580 °C).

Acknowledgments

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Highlights:

- STM investigation of long-chain 1-dodecene deposited on Si(100) substrate.
- Remarkable self-ordered assembly of molecules not observed at room temperature.
- After annealing ordered patterns form with a *c*(4×4) structure, accompanied with thermal decomposition of molecules.