

Title	シリコン(001) 2×1表面上に配向した個々の4,4"-ジアミノpターフェニル分子の走査型トンネル顕微鏡によるナノスケール解析
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Title: Nanoscale analysis of alignment of individual 4,4'-diamino-*p*-terphenyl molecules deposited on Si(001)-2×1 observed by scanning tunneling microscopy.

Keywords: molecule; diamino-*p*-terphenyl; silicon; butterfly bonding; scanning tunneling microscopy

Abstract

Organic molecular electronics has attracted much interest to fabricate innovative products with high performance at low cost, and furthermore to open novel architecture for future device processes. To improve their characteristic performance, the conformational alignments and bonding states of individual organic molecules in the devices are crucial. Selection and preparation of molecule-binding substrates also dominate the performance, and a wide-ranging survey for the molecule-substrate combination is indispensable.

In this study scanning tunneling microscopy (STM) observation was conducted for 4,4'-diamino-*p*-terphenyl (DAT) molecules deposited on a clean reconstructed Si(001)-(2×1) surface at room temperature (RT). The Si surface can be a good candidate for a substrate to examine molecular adsorption. In this study, the linear but twisted π -conjugated framework of DAT, were mostly revealed to lie down laterally on the surface, which has a linear framework consisting of a central benzene ring and two phenyl rings (terphenyl) terminated with two amino groups at both ends.

The DAT was evaporated by heating a crucible containing the DAT at a temperature ranged from 418 to 433 K, which was below the DAT melting temperature of ~510 K. The depositing amount of the DAT molecules on the Si(001) surface was controlled by changing the opening time of a mechanical shutter over the crucible, ranging from a few seconds to a few minutes.

The majority of DATs were tilted laterally at about 17° with respect to the direction of a Si dimer row on the surface, though a variety of DAT configuration with different angles was found by STM. The histograms of the tilted angles at low coverages (0.04 molecule/nm²) showed that the most frequent angle was 17°. The DATs tilted at 17° looked hollow at the center and their apparent height was lower than that of other configurations of DAT in STM images. This indicates that the DAT tends to take a double arched shape at the tilted angle of 17° in a stable conformation with butterfly-like bonding through the central ring to a Si dimer as well as the two amino groups bonded to respective Si atoms on the dimer row.

The DAT molecules adsorbed on the Si(001) surfaces at low coverages were annealed at 523 K for 1 min, and the surfaces were examined by STM. The number at 17° increased from 50% to about 80%, while the number of molecules at a tilted angle of 8° and 0° decreased less than 15%, and the number at other angles diminished within our total counting of about 250 protrusions. It is probable that the protrusion at 17° was the most stable irrespective of annealing, corresponding to a chemical configuration of DAT absorbed on the Si(001)-(2×1) surface. The deposition amount of DAT was increased to 0.24 molecule/nm² and annealed at 523 K for 1 min. STM images showed that the DAT at high coverages (0.24 molecules/nm² or more) turned out to be linearly ordered structure running to the direction of about 22° with respect to the Si dimer row.

The results obtained in this study showed that the amino groups of molecules interacted with Si surfaces at RT, and phenyl rings also interacted with Si dimers between their π state electron orbitals. The well-defined Si surface exhibited to hold the proper characteristics to reveal the interaction with the molecules. The results also showed the potential for the DAT and Si system leading to a fundamental layer to grow the overlayer with their well-defined configuration for future molecular electronics.