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Full Length Article

Ordered array of CoPc-vacancies filled with single-molecule rotors

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ABSTRACT

We report the highly ordered array of CoPc-vacancies and the single-molecule rotors inside the vacancies. When CoPc molecules are deposited on Cd(0001) at low-temperature, three types of molecular vacancies appeared randomly in the CoPc monolayer. Annealing the sample to higher temperature leads to the spontaneous phase separation and self-organized arrangement of the vacancies. Highly ordered arrays of two-molecule vacancies and single-molecule vacancies have been obtained. In particular, there is a rotating CoPc molecule inside each single-molecule vacancy, which constitutes the array of single-molecule rotors. These results provide a new routine to fabricate the nano-machines on a large scale.

1. Introduction

In the past decade, strain attracted considerable interest because it plays an important role in controlling the structure and morphology of epitaxial films [1–5]. Several strain relaxation mechanisms have been found such as step bunching [6,7], faceting [8], and misfit dislocations [9–12]. In addition, there is an unusual mechanism that strain is released through the formation of periodic domain boundaries (discommensuration) [13–18]. For example, strain is relieved through the vacancy-like craters at the domain boundaries of Si(111)-5.5 × 5.5-Cu [18–22].

In fact, discommensuration takes place when the adsorbate–adsorbate interaction is comparable to the adsorbate–substrate interaction [17]. When the former is dominant, the adsorbates will adopt the incommensurate lattices. When the latter is dominant, the adsorbates will adopt commensurate lattices [23]. The discommensurate structure is neither commensurate nor incommensurate because it consists of periodic domain boundaries. Strain is built in the domains and is released at domain boundaries. If the adsorbate is compressed in the domains, it expands in the domain boundary and vice versa. Nevertheless, all the reported discommensurate structures were limited to the inorganic adsorbates such Cu, In, and Ga films grown on Si(111) or Ge(111) [13–16]. To our knowledge, there has been so far no report on the formation of organic discommensurate thin films. So it remains unclear whether the organic molecules can form the discommensurate structure or not. If yes, what kind of new features will be presented by the organic molecular films, which usually have large unit cells and numerous degrees of freedom?

Metal phthalocyanine (MPc) is a model system to study the interaction between metal–organic complexes and solid surfaces [24]. There have been many studies on the adsorption and self-assembly of MPcs on various solid surfaces such as Au [25,26], Ag [27–31], Cu [32–35], Pb [36], Bi [37], graphene [38], or NaCl [39]. In the present paper, we found a discommensurate structure in the monolayer of cobalt phthalocyanine (CoPc) grown on Cd (0001). Due to the strain relaxation, three types of CoPc-vacancies formed in the as-deposited CoPc monolayer. Annealing to higher temperature leads the spontaneous phase separation and vacancy array formation. In particular, inside the single-molecule vacancies, there is a rotating CoPc molecule due to the spare space, which is similar to the supramolecular rotors caged in the metal–organic network pores [40,41].

2. Experimental

The experiments were performed in an ultra-high vacuum low temperature scanning tunneling microscopy (STM) system (Unisoku, Japan) with the base pressure around 1.2×10^{-10} Torr. The smooth Cd(0001) thin film was prepared by depositing 10-monolayer (ML) Cd on the Si(111)-7 × 7 surfaces at room temperature (RT). After degassing at 650 K, CoPc molecules were deposited onto the Cd(0001) surface at liquid nitrogen (LN_2) temperature by means of thermal sublimation from a Ta boat. A polycrystalline tungsten wire was used as the STM tip. Before

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measurement, the tip was treated by electron-beam bombardment to get rid of the contamination and oxidation. All the topographic images were obtained in constant-current mode at 78 K or 4.7 K.

3. Results and discussions

Firstly, we deposited a small amount of CoPc molecules to the Cd(0001) surface at LN_2 temperature. The Cd(0001) surface exhibits the hexagonal lattices (lattice constant a ≈ 3.0 Å) (Fig. 1a). Fig. 1b shows an isolated CoPc molecule and a trimer chain. Each molecule exhibits a four-lobe shape, consistent with the chemical structure of CoPc. For the molecule marked by the dotted line, there are two opposing lobes deviating from the lattice directions of Cd(0001). For the other three molecules, there are two opposing lobes oriented to the lattice directions of Cd(0001). Hereafter we refer to the former and the latter as misoriented and oriented molecules, respectively. We have also measured *dI*/*dV* spectra for the isolated CoPc molecules on Cd(0001), which is displayed in Fig. S1. It is found the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are located at −0.74 eV, and +0.73 eV, respectively. The latter is very close to the reported LUMO of CoPc molecule adsorbed on graphene/Ir (111) [42]. The HOMO–LUMO gap is 1.47 eV, smaller than that of a free CoPc molecules (2.3 eV) [43], due to the considerable molecule–substrate interaction.

In the monolayer regime, close packing has not been observed from the deposited CoPc molecules, instead three types of CoPc-vacancies appeared in the monolayer (Fig. 1c). The largest is the trigonal three-molecule vacancies; the second largest is the linear two-molecule vacancies; the smallest is the round single-molecule vacancies containing a fuzzy protrusion, which cannot be imaged clearly at LN_2 temperature. From the close-up view in Fig. 1d, it is found that the three-molecule vacancies are surrounded by six oriented molecules (marked by green arrows) and three misoriented molecules; the two-molecule vacancies are surrounded by four oriented and four misoriented molecules; the single-molecule vacancies are surrounded by six molecules, which are all oriented to the lattice directions of Cd(0001).

Annealing the sample to RT for several hours leads to the structural transition of the three mixed vacancies. The three-molecule vacancies vanished from the monolayer and the spontaneous phase separation takes place between the two-molecule vacancies and single-molecule vacancies. Fig. 2a shows a pure domain of two-molecule-vacancies with periodic arrangements. The vacancies can be regarded as the organic discommensuration (domain

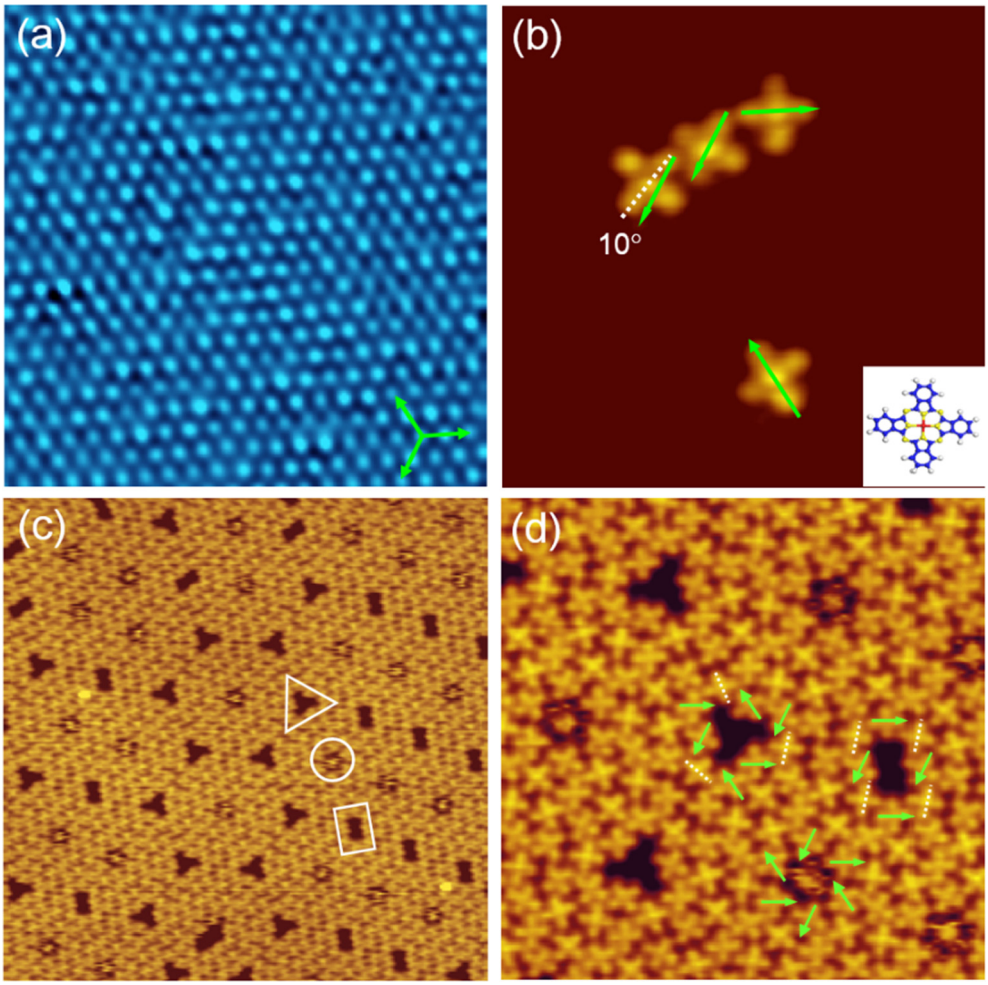

Fig. 1. Topographies of the as-deposited CoPc molecules and monolayer on Cd(0001). (a) Atomic-resolution STM image of the Cd(0001) surface, 6 nm × 6 nm, 0.5 V. (b) STM image of an isolated molecule and a trimer chain, 10 nm × 10 nm, 0.75 V. Inset shows the chemical structure of CoPc molecule. (c) STM image of the as-grown CoPc monolayer, 50 nm × 50 nm, 1.5 V. The triangle, rectangle, and circle mark the three-molecule vacancy, two-molecule vacancy, and single-molecule vacancy, respectively. (d) Close-up view of the three types of CoPc vacancies, 20 nm × 20 nm, 1.5 V. The green arrows and white dots lines mark the oriented and misoriented CoPc molecules, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)