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Self-assembled C_{60} layers on incommensurate Cu/Si(111)'pseudo-5 × 5' surface

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ABSTRACT

Self-assembled growth of C_{60} monolayers on the pristine and Ge-modified Cu/Si(111)'pseudo-5 × 5' surfaces was studied using scanning tunneling microscopy observations. The pristine Cu/Si(111)'pseudo-5 × 5' surface shows up as an incommensurate reconstruction on Si(111) substrate, while Ge-modified surface shows up as an array of Ge atomic clusters grown on the Cu/Si(111)'pseudo-5 × 5' template. It has been found that C_{60} fullerenes are highly mobile on the both surfaces, hence at the early growth stages fullerenes are accumulated along the atomic steps forming their quasi-one-dimensional molecular stripes. With further C_{60} deposition, almost ideal two-dimensional close-packed molecular monolayers are formed. The layers are modulated as evidenced by developing quasi-periodic pattern of dim and bright fullerenes displaying 2 × 2 periodicity. Contrast difference between dim and bright fullerenes is supposed to have a topographical origin, namely, bright fullerenes reside higher than dim fullerenes. Dim fullerenes were concluded to occupy centers of hexagons which constitute honeycomb-like structure of the Cu/Si(111)'pseudo-5 × 5' surface. For the Ge-modified surface, this means that adsorbing C_{60} fullerenes displace Ge atoms from their original positions to the interstitial sites in the molecular monolayer. Ge atoms were found to terminate rotational motion of selected fullerenes in the layer.

1. Introduction

Interaction of fullerenes with reconstructed crystalline surfaces has been found to present a number of fascinated phenomena both at the initial stage of molecular island nucleation and growth as well as at the final stage of monomolecular layer completion followed by multilayer growth. Some of these phenomena are related to diversity of the adsorption sites which fullerenes can occupy on the reconstructed surface. At the stage of island growth, difference in C_{60} adsorption energy for different sites can be utilized to improve spatial ordering of the molecular islands [1–4] and to sharpen their size distribution [1,5]. When extended C_{60} arrays are formed, difference in C_{60} adsorption geometries leads to developing modulations in the molecular layers which typically appear as regular occurrence of fullerenes displaying different contrast, bright and dim, in scanning tunneling microscopy (STM) images [6–14]. Incommensurate surfaces constitute an interesting class of reconstructed surfaces [15]. Such surfaces are typically characterized by a quasi-periodic domain structure associated with strain-relief pattern. Starting from the seminal work on the growth of Ag and Cu layers on Pt(111) [16], self-assembly of atoms [17] and molecules, in particular C_{60} fullerenes [3,18], on the incommensurate surfaces has become an advanced topic in surface science.

Cu/Si(111)'pseudo-5 × 5' reconstruction presents a vivid example of the incommensurate surface. The surface shows up as a honeycomb-like array formed by domain-boundary network with domains having a shape of non-regular hexagons. The hexagon sizes are close (but not identical), being ~$5.5a_0$ in average. The latter coins the 'pseudo-5 × 5' notation of the reconstruction to underline its quasi-periodic arrangement. [$a_0 = 3.84$ Å, the lattice constant of the non-reconstructed Si(111)1 × 1 surface.] The $5.5a_0 = 21.12$ Å, that is close to the doubled C_{60}–C_{60} distance (~20 Å) in the bulk fullerite and monomolecular close-packed C_{60} arrays on the surfaces. Thus, the surface seems to be a promising template for growing ordered C_{60} layers. As shown in Ref. [17], upon room temperature (RT) adsorption of ~0.1 ML (1 monolayer (ML) $= 7.8 \times 10^{14}$ cm^{-2}) of Ge, the Cu/Si(111)'pseudo-5 × 5' reconstruction is preserved, while Ge atoms form an ordered array of atomic clusters. Thus, Ge-modified Cu/Si(111)'pseudo-5 × 5' surface can be thought as a template having the same periodicity as the parent surface but different chemical and topographic properties.

In the present work, using scanning tunneling microscopy (STM) observations we have explored self-assembly of C_{60} layers on the pristine and Ge-modified incommensurate Cu/Si(111)'pseudo-5 × 5' surfaces.

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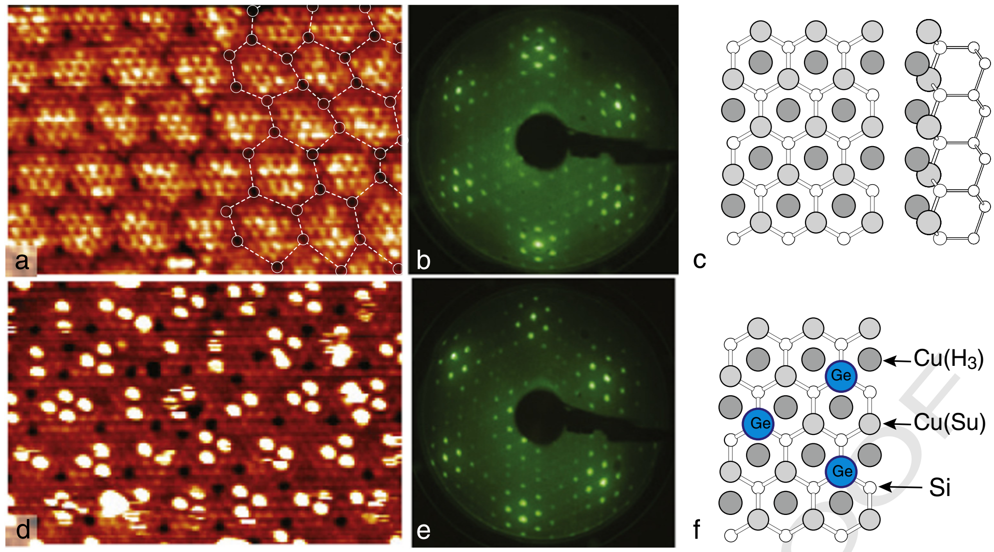

Fig. 1. STM images (scale: 150 × 100 Å^2) and LEED patterns (E_p = 40eV) of (a, b) pristine Si(111)'pseudo-5 × 5'-Cu surface and (d, e) Si(111)'pseudo-5 × 5'-Cu surface with adsorbed 0.1 ML Ge. In the right half of (a), boundaries of the hexagonal domains are outlined by dashed lines and crater defects are marked by open circles. Schematic diagrams illustrating atomic structure of the (c) pristine Si(111)'pseudo-5 × 5'-Cu surface and (f) Si(111)'pseudo-5 × 5'-Cu surface with adsorbed Ge atoms. Cu(Su) and Cu(H_3) atoms are shown by light gray and dark gray circles, respectively, Si atoms by white circles and Ge atoms by blue circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental details

Our experiments were performed with an Omicron VT-STM operating in an ultrahigh vacuum (~2.0 × 10^{-10}Torr). Atomically-clean Si(111)7 × 7 surfaces were prepared *in situ* by flashing to 1280 °C after the samples were first outgassed at 600 °C for several hours. Copper and germanium were deposited from W filaments and C_{60} fullerenes from a Ta boat. In order to form the Si(111)'pseudo-5 × 5'-Cu surface, 2.0 ML of Cu was deposited onto the Si(111)7 × 7 surface held at RT followed by brief (~15 s) annealing with DC current at 600 °C. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed.

3. Results and discussion

Fig. 1a and b show STM images of the pristine and Ge-adsorbed Si(111)'pseudo-5 × 5'-Cu surfaces, respectively. In agreement with the reported STM observations [19–22], at a large scale the Si(111)'pseudo-

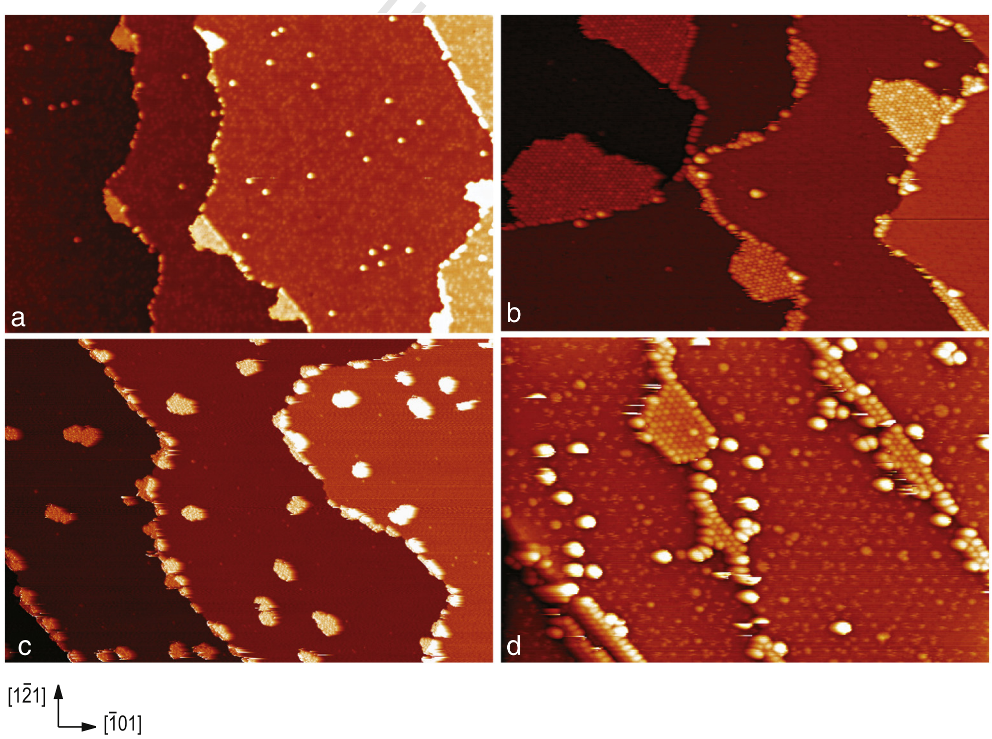

Fig. 2. STM images illustrating early stages of C_{60} layer growth. Si(111)'pseudo-5 × 5'-Cu surface after RT adsorption of (a) ~5% and (b) ~10% of C_{60} monomolecular layer. (c) Si(111)'pseudo-5 × 5'-Cu surface after adsorption of ~10% of C_{60} monomolecular layer at 110 K. (d) Ge-adsorbed Si(111)'pseudo-5 × 5'-Cu surface after RT adsorption of ~10% C_{60} monomolecular layer. Scale: (a) 1900 × 1300 Å^2; (b) and (c) 1000 × 670 Å^2; (d) 750 × 500 Å^2.

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