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Formation of highly crystalline C_{60} molecular films on Bi(0001)/Si(111) surface

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We report the results of scanning tunneling microscopy (STM) investigation of a controllable growth of C_{60} adsorption on the Bi(0001)/Si(111) surface. Using UHV STM it has been shown that the most favorable sites for initial stage of C_{60} adsorption are the double steps and domain boundaries. At ~ 1 monolayer of C_{60} coverage the modulation pattern caused by epitaxial relation between C_{60} and Bi unit cells has been observed. Increasing of C_{60} coverage up to several monolayers results in the formation of highly crystalline molecular film.

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During last decade organic materials have become very popular and important subject for investigation because of their exclusive and promising properties. Among them caged carbon structures [1] have attracted a significant scientific interest due to possible application in electron technology, particularly in fabrication of electro-active elements in solar cells and active layers in organic thin film transistors [2, 3]. Accordingly, for most technological applications the controllable epitaxial growth and formation of homogeneously ordered structures are the questions of primary importance because the density of defects is crucial for the devices functioning [4, 5]. This problem has stimulated the study of C_{60} growth on different semiconductor surfaces [6 – 8]. To obtain high ordered crystalline C_{60} molecular films it is necessary to estimate the balance between two interactions:an intermolecular interaction and the interaction between C_{60} molecule and a substrate. Usually the interaction between C_{60} and substrate is the strongest one due to influence of surface dangling bonds. This influence can drastically change the surface morphology during epitaxial film growth. Therefore several works were aimed to decrease the number of semiconductor surface dangling bonds before C_{60} growth [9 – 11]. Authors of these works used hydrogenated silicon surface as substrate for C_{60} deposition. In work [9] high-resolution electron-energy-loss spectroscopy have been used to characterize C_{60} films up to 4.0 monolayers grown at room temperature on hydrogen-terminated Si(100). Compared with C_{60} films on clean Si(100) surfaces a considerably higher degree of order in the as-deposited films has been achieved. Results of experiment indicate a wan der Waals-type interaction between C_{60} and H/Si(100)$-(2 \times 1)$. Results of work [10], based on vibrational study of C_{60} overlayers on H/Si(111)$-(1 \times 1)$, point to van der Waals-type bonding. No evidence for chemical interaction between C_{60} and H/Si(111)$-(1 \times 1)$ has been found. Adsorption of C_{60} monolayers on metal results in charge transfer and LUMO-metal state mixing that assures Fermi-level alignment and accounts for additional bonding beyond van der Waals bonding [12]. It has been shown that well-ordered Bi films on the Si(111)-7×7 surface are rather inert and have an electronic structure which is intermediate between the metallic and insulating substrates [13, 14].

We utilized this unique semi-metallic Bi(0001)/Si(111) template as a substrate for the deposition of C_{60} and preparation of C_{60} nanostructures with long-range order and uniform size. In this paper we present the results of our scanning tunneling microscopy (STM) investigations of the initial stages of nucleation, formation and growth of C_{60} films. All experiments have been carried out at room temperature using a home-built ultra high vacuum field ion - scanning tunneling microscope (base pressure $2 \cdot 10^{-11}$ Torr) equipped with standard surface preparation facilities [15]. Samples $(20 \times 4 \times 0.5)$ mm in size were cut from P-doped (111) orientated Si wafers with sheet resistance $1.6\,\Omega\cdot$cm, the nominal doping concentration was about $8 \cdot 10^{17}\,\mathrm{cm}^{-3}$. Samples were ultrasonically cleaned in acetone and distilled water. Using "Ni-free" tools they

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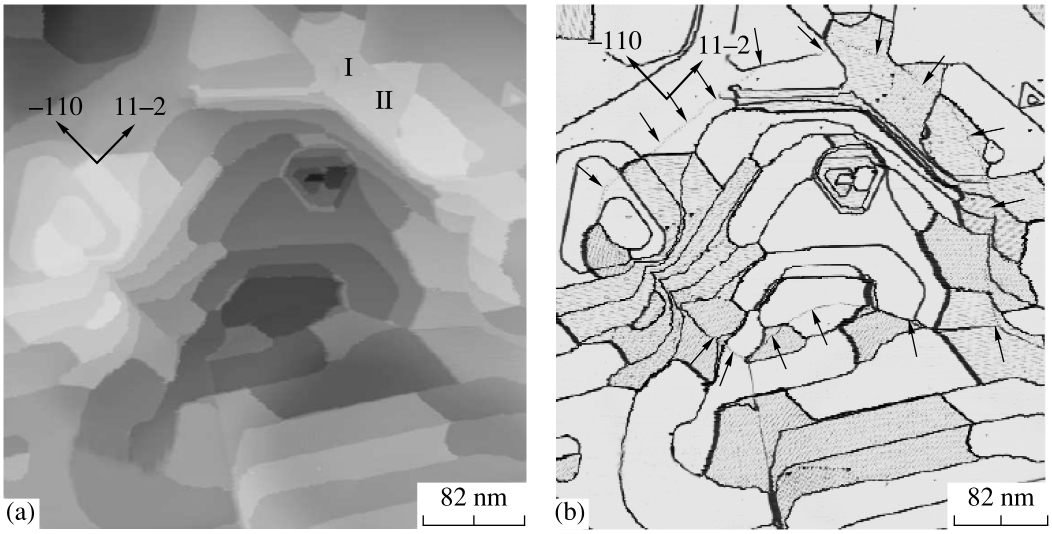

Fig.1. C_{60} islands on the Bi(0001)/Si(111)−(7 × 7) surface at submonolayer C_{60} coverage; heights of islands correspond to Bi steps: (a) STM image (bias voltage $V_s = +2.3$ V, tunneling current $I_t = 20$ pA) shows C_{60} molecules starting to grow on the twin boundary. (b) The same image as in Fig.(a), but indicates the distribution of surface normal directions; the twin boundaries are marked by arrows

were mounted on tantalum sample holder. Samples were degassed at 600 °C during 12 hours. In the final stage of surface preparation the samples were flashed at 1200 °C by a direct current followed by slow cooling. Bi was deposited from an alumina-coated tungsten basket on a clean Si(111)−7 × 7 surface kept at room temperature. More detailed information regarding parameters of Bi deposition is presented in [16]. The morphology of the resulting well-ordered Bi(0001) film was finally improved by moderate annealing at 120 °C. The C_{60} deposition rate was in the range of 0.05-0.1 monolayer (ML) per minute, where 1.0 ML corresponds to the molecular density of the C_{60} bulk crystal fcc(111) plane. The self-epitaxial nucleation and growth of C_{60} films have been performed at substrate temperature of 120 °C. Due to semimetallic and chemically inert character of Bi films fullerene molecules on the Bi(0001)/Si(111)−(7×7) surface interact with substrate by means of van der Waals forces only. This interaction is rather weak and C_{60} molecules can diffuse on this surface easily. In our STM measurements we observed highly ordered islands from fullerene molecules even at submonolayer coverage. But the initial nucleation of deposited molecules occurs preferentially in some regions. These preferred sites ("anchor sites") for C_{60} nucleations can be determined from Fig.1 and Fig.2. Fig.1a, b shows the STM images after deposition of 0.12 ML of C_{60} on Bi(0001)/Si(111)−(7 × 7). A careful analysis of this and similar images enabled us to single out at least six directions of C_{60} domains on

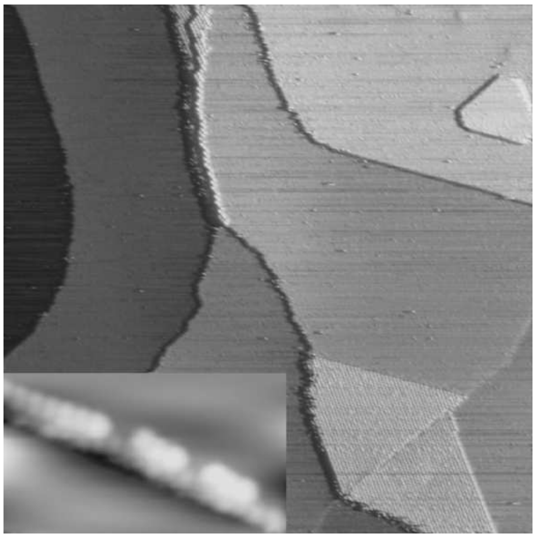

Fig.2. STM image ($V_s = +1.5$ V, $I_t = 20$ pA) of a Bi(0001)/Si(111)−(7 × 7) surface with submonolayer of C_{60} showing C_{60} molecules starting to grow on the double height step; inset - high resolution STM image ($V_s = +2.2$ V, $I_t = 20$ pA) showing the individual C_{60} molecules adsorbed on the double height step

the Bi(0001)/Si(111)−(7 × 7) surface with hexagonally close-packed structures which are formed the angles of +4, −4, +80, +58, +14, −18 with the Si[$\bar{1}$10] direction. These domains are partially shown in Fig.1a and denoted as I, II. Fig.1b shows the same area as Fig.1a but indicates the distribution of surface normal directions.

As can be seen from Fig.1a, b the nuclear sites of the C_{60} are located near of Bi twin boundary [17]. The Bi twin boundary is shown by arrows in Fig.1b. Another STM image in Fig.2 reveals that besides, the C_{60} islands also initiate a nucleation on the double steps of Bi(0001)/Si(111)$-(7 \times 7)$ surface while a Bi template is clearly seen. In the inset one can recognize the individual C_{60} molecules located along the double step. The second layer of C_{60} starts to form directly above the chain of C_{60} located along the step filling the intermediate sites between two neighbor molecules. After that the C_{60} growth above smooth terraces becomes possible. To further investigate the growth mode, we carried out a series of experiments with C_{60} coverage ranging from 0.1 ML to above full monolayer coverage and more. Figure 3 shows an STM image of 1 ML C_{60} coverage on the Bi(0001)/Si(111)$-(7 \times 7)$ surface. The

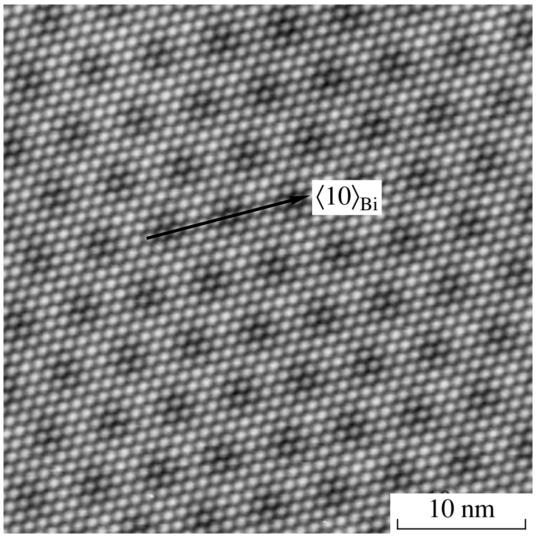

Fig.3. STM image of one monolayer C_{60} coverage on the Bi(0001)/Si(111)$-(7 \times 7)$ surface ($V_s = -2.3$ V, $I_t = 20$ pA)

modulation pattern observed in this image is caused by the epitaxial relation between Bi and C_{60} lattices. Five lattice parameters of C_{60} unit cell correspond to eleven parameters of Bi unit cell. The STM images of thick layers of C_{60} (4–5 monolayers) did not exhibit any manifestation of modulation (Fig.4). The C_{60} molecules completely cover Bi template forming a good quality film. The step height in this case was the same as for the Bi layer (0.39 nm) which indicates directly that the interaction between C_{60} film and the substrate is not so strong. To estimate the possible charge transfer between C_{60} layer and substrate we carried out the scanning tunneling spectroscopy (STS) measurements above thin C_{60} film (the coverage was 1 ML or less)

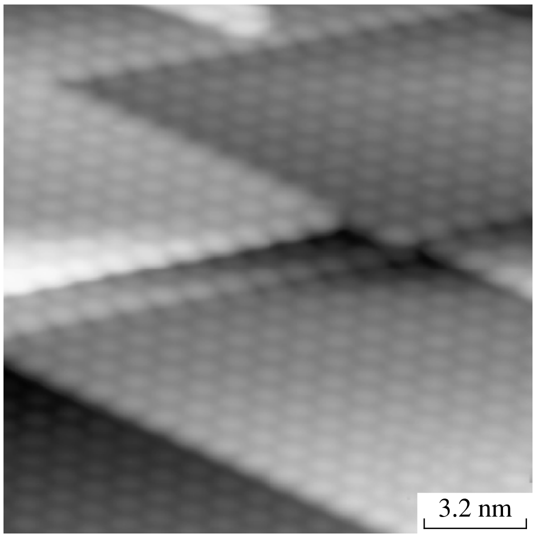

Fig.4. STM image of the thick C_{60} film on the Bi(0001)/Si(111)$-(7 \times 7)$ surface ($V_s = 2.3$ V, $I_t = 20$ pA)

and thick C_{60} film (the coverage was ≥ 5 ML). If charge transfer takes place, the position of peaks at LUMO states should be different for different C_{60} coverage due to the interaction of the first layer with substrate. Fig.5 shows the normalized tunneling conductivity spectra

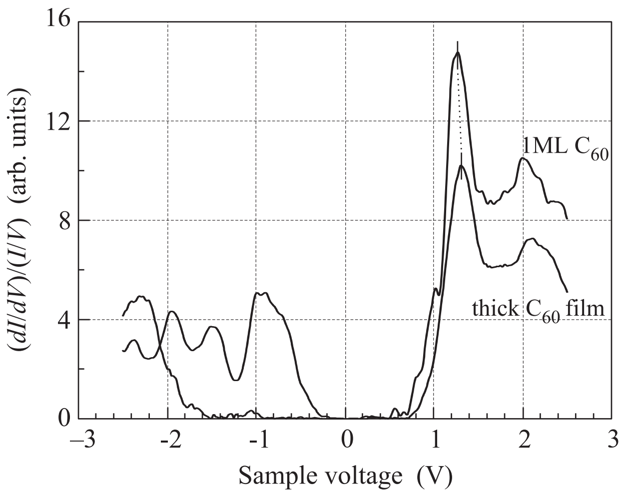

Fig.5. Normalized conductivity tunneling spectra measured above C_{60} submonolayer coverage (upper curve) and above C_{60} thick layer coverage (bottom curve)

for C_{60} adsorbed on a thick Bi layer. The bottom curve in Fig.5 has been measured above thick C_{60} layer. The main peak, located at -2.3 V bellow Fermi level (E_F), corresponds to the C_{60} HOMO level. It agrees well with results obtained from photoemission valence-band spectra for C_{60} condensed on a 12 nm-thick Bi layer [12]. The shake-up features superimposed on Bi conduction-band are clearly seen at 1.31 V and 2.06 V above E_F. The upper curve in Fig.5 has been measured above 1 ML C_{60} film. The contribution from C_{60} HOMO level is still visible but some additional peaks bellow Fermi level are presented. The position of peaks at LUMO states (at positive range of sample voltage) changes slightly compared with bottom curve (about 0.06 V) emphasizing the weak interaction of C_{60} film with substrate. Our results for C_{60} molecules adsorbed on the Bi(0001)/Si(111)$-(7 \times 7)$ surface indicate clearly that the amount of charge transfer is small. Therefore undisturbed growth of C_{60} thick film on the Bi(0001)/Si(111)$-(7 \times 7)$ surface becomes possible.

In summary, we have successfully prepared C_{60} epitaxial thin films with long-range order on a semi-metallic Bi(0001)/Si(111) template surface. It has been proved that most favorable sites for C_{60} nucleation are double steps and Bi twin domain boundaries. In spite of a weak interaction between C_{60} molecules and Bi(0001) surface, which is confirmed by a negligible charge transfer evidenced in STS data, the epitaxial structure of C_{60} has been realized. Our results may be the basis for further developing of fullerene-based thin film transistors.

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