Molecular beam epitaxy of C_{60} onto the CaF_2(111) surface

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Heteroepitaxial film growth of C_{60} on CaF_2(111) has been studied *in situ* by reflection high-energy electron diffraction (RHEED) at growth temperatures of 30-300 °C and average thicknesses of 1-50 nm. Over the entire temperature range, C_{60} forms an incommensurate overgrowth of fcc-stacked close-packed layers with a characteristic intermolecular spacing of 0.99 nm. The in-plane orientation of the C_{60} overgrowth depends strongly on the growth temperature. Deposition below 150 °C leads to unidirectional growth in accordance with the crystallographic directions of the substrate. Higher deposition temperatures result in two equivalent, rotated domain orientations characterized by a significantly lower degree of lattice mismatch (3% vs. 16% for the unidirectional structure).

1. INTRODUCTION

Increasing interest is being focused on the thin film growth of C_{60} since this novel material exhibits various significant electrical and optical properties. For instance, C_{60} shows ultrafast nonlinear optical response due to its delocalized π-electron system [1] and high-temperature superconductivity caused by doping with alkali metals [2].

In order to explore the growth mechanisms of molecular-beam-deposited C_{60} films, their structural properties have been studied on various surfaces ranging from metal [3] and semiconductor substrates [4-6] to the surfaces of insulators [7,8]. The resulting growth structure is determined by the balance between adsorbate-substrate interaction and the van der Waals-type adsorbate-adsorbate interaction. For example, a considerable adsorbate-substrate interaction causes the formation of commensurate rotated domains on Au(111) [3], whereas unidirectional growth occurs despite a large lattice mismatch on van der Waals-interacting layered compound surfaces (i.e., GaSe(0001) [5] and MoS_2(0001) [8]).

We recently reported [9,10], that C_{60} films heteroepitaxially grown on the ionic CaF_2(111) surface represent an interesting intermediate

case in which lattice matching conditions, as well as the growth temperature, determine the occurrence of particular domain orientations. Both unidirectional and rotated in-plane orientations can be obtained.

2. EXPERIMENTAL

The investigations were performed in a UHV system providing a base pressure of 2×10^{-8} Pa. Polished CaF_2(111) wafer substrates (*Furuuchi Chemical Corp.*) were cleaned by argon ion sputtering and subsequent heating to 1000 °C. After degassing at 350 °C for 5 h, C_{60} powder (*Texas Fullerenes Corp.*, purity >99.9%) was evaporated out of a SiO_2 crucible at 300-340 °C with deposition rates of 0.2 nm/min. The residual gas pressure during deposition was about 1×10^{-7} Pa.

The long-range order properties of the substrate and grown C_{60} films were investigated *in situ* by reflection high-energy electron diffraction (RHEED) at an electron energy of 20 keV and a beam current of 1 nA. No beam-induced changes were detected in the observed patterns either for the substrate or for the C_{60} overgrowth.

3. RESULTS AND DISCUSSION

C_{60} growth was performed at substrate temperatures of 30-300 °C. Figures 1(a) and 1(b) illustrate the resulting RHEED patterns after deposition of a 15 nm thick overlayer at a growth temperature of 35 °C, followed by subsequent annealing to 200 °C for 45 min. The azimuthal angles are the [$\bar{1}\bar{1}2$] and [$\bar{1}01$] directions of the substrate.
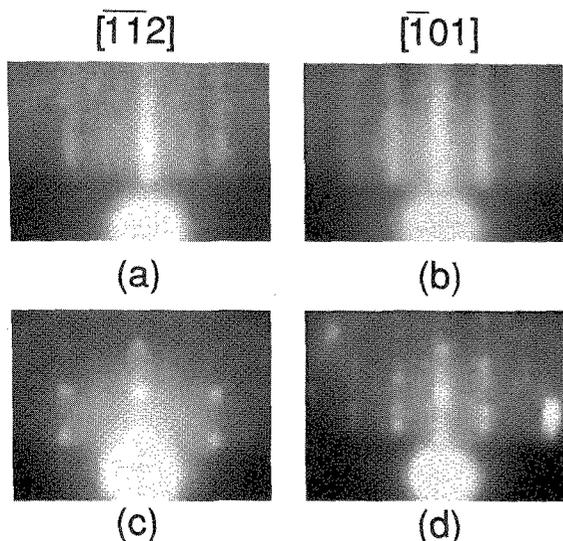

$$[\bar{1}\bar{1}2] \qquad [\bar{1}01]$$

(a) (b)

(c) (d)

Figure 1. RHEED patterns along the [$\bar{1}\bar{1}2$] and [$\bar{1}01$] azimuth after C_{60} deposition at 35 °C and subsequent annealing at 200 °C (a,b) and after heating to 290 °C (c,d).

Symmetrical streak patterns were observed with streak spacing $\sqrt{3}$ times larger for the [$\bar{1}\bar{1}2$] direction than that of the [$\bar{1}01$] direction. Identical patterns appeared for azimuthal angle separations of 60°. Hence, the long-range ordered overgrowth exhibits hexagonal surface symmetry, and its orientation is unidirectional with respect to the $CaF_2(111)$ substrate. An intermolecular distance of 0.99 nm within the hexagonal plane is derived from the streak separations, in close agreement with the nearest-neighbor spacing in solid C_{60} [11]. Accordingly, the overgrowth consists of

stacked hexagonal layers. The stacking sequence corresponds to a face-centered-cubic structure. This is evident from the resulting transmission patterns in Figures 1(c) and 1(d), which were observed after heating the film to 290 °C for 5 min. Three-dimensional C_{60} islands were formed, maintaining their crystallographic orientation relative to the substrate.

Figure 2 shows representations of the reciprocal fcc-lattice planes, which correspond to the observed transmission patterns in Figures 1(c) and 1(d). In particular, the pattern in Fig. 1(d) corresponds to a reciprocal ($\bar{1}01$) plane superimposed on its mirrored equivalent, a ($10\bar{1}$) plane. Consequently, twinned domains are present. The derived film orientation is summarized by the following crystallographic relations:
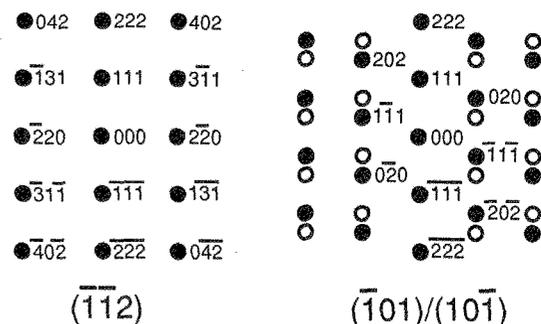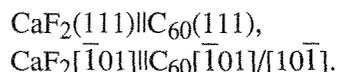
$$CaF_2(111) \| C_{60}(111),$$
$$CaF_2[\bar{1}01] \| C_{60}[\bar{1}01]/[10\bar{1}].$$

$$(\bar{1}\bar{1}2) \qquad (\bar{1}01)/(10\bar{1})$$

Figure 2. Representation of reciprocal fcc-lattice planes, left: a ($\bar{1}\bar{1}2$) plane, right: a super-position of a ($\bar{1}01$) plane (full circles) with its mirrored equivalent, a ($10\bar{1}$) plane.

A considerable change in the overlayer orientation occurs when the growth temperature is increased. Unidirectional growth occurs up to about 150 °C, however, for higher substrate temperatures additional rotated domain orientations begin to appear. At growth temperatures above 200 °C, the formation of two equivalent rotated domains replaces the unidirectional orientation completely. These domains also consist of stacked hexagonal layers with a

characteristic nearest-neighbor distance of 0.99 nm. Related RHEED patterns are shown in Figures 3(a) and 3(b), which are observed after C_{60} deposition at 250 °C for azimuthal angles of 19° ±3.5° respectively (relative to the $[\bar{1}01]$ direction of the substrate).

(a)

(b)
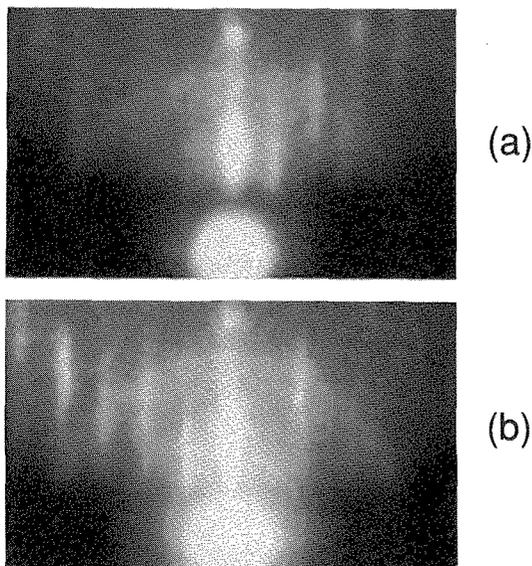
Figure 3. RHEED patterns after C_{60} deposition at 250 °C, observed at azimuthal angles of 22.5° (a) and 15.5° (b), with respect to the $CaF_2[\bar{1}01]$ direction.

Both patterns display the characteristic lattice-rod spacing which corresponds to the $C_{60}[\bar{1}01]$ direction (compare with Fig. 1(b)). In particular, an intermediate azimuthal angle of 19° would correspond to an azimuthal orientation in which the incident electron beam (i.e., the initial wave vector k_0) is parallel to the $C_{60}[\bar{1}01]$ direction. Furthermore, Fig. 3(b) shows both the lattice-rod spacings of the $C_{60}[\bar{1}01]$ and $C_{60}[\bar{1}\bar{1}2]$ directions together, thus demonstrating the presence of individual rotated domains. A detailed evaluation of the streak positions relative to the azimuthal angle yields the reciprocal surface periodicity, which corresponds to the superposition of two hexagonal lattice planes rotated by about ±19° with respect to the $CaF_2[\bar{1}01]$ direction [9].

Orientations of the overlayer with its $[\bar{1}01]$ direction parallel to the $CaF_2[\bar{3}12]$ and $CaF_2[\bar{2}13]$ directions are equivalent to rotations by ±19.11° respectively. Furthermore, it is evident from the unit cell arrangements represented in Fig. 4(a), that this domain rotation corresponds to a significantly smaller lattice mismatch (3%) than that of the unidirectional arrangement (16%), which is shown in Fig. 4(b).
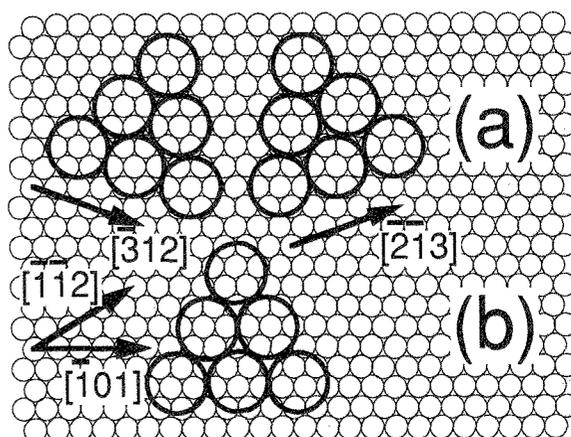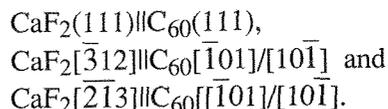

Figure 4. Relationships between unit cell periodicity of substrate and overlayer for equivalent rotated domains (a) and the unidirectional structure (b).

The domain rotation optimizes the lattice matching between the incommensurate overgrowth and the substrate surface. In this case, the crystallographic relations are:

$CaF_2(111)\|C_{60}(111)$,
$CaF_2[\bar{3}12]\|C_{60}[\bar{1}01]/[10\bar{1}]$ and
$CaF_2[\bar{2}\bar{1}3]\|C_{60}[[\bar{1}01]/[10\bar{1}]$.

Systematic variation of both coverage (corresponding to thicknesses of 1-50 nm) and the subsequent thermal treatment gave no evidence that domain orientation is dependent on these parameters. Thus, only the substrate temperature during the initial stage of growth determines the interfacial arrangement, and therefore the domain orientation.

4. CONCLUSIONS

The $CaF_2(111)$ surface is a suitable substrate on which to heteroepitaxially grow C_{60} films. Two different in-plane orientations of the incommensurate overgrowth were observed, unidirectional film orientation and the formation of rotation domains.

The occurrence of unidirectional orientation despite a large lattice mismatch corroborates the findings for layered compound substrates like GaSe [5], mica [7] or MoS_2 [8], which weakly interact with adsorbed C_{60} molecules by means of van der Waals forces. The observed film orientation on these substrates is exclusively unidirectional. This growth structure can be expected to be stabilized by substrate surface steps, which should preferably align along directions of high symmetry.

The film structure observed at higher growth temperatures, on the other hand, implies a significant influence of the substrate surface corrugation, which induces a rotated orientation of the incommensurate overlayer. Thus, it can be concluded that step alignment and domain rotation optimizing the lattice-matching act as two competing processes, which govern the initial growth stage on the $CaF_2(111)$ surface. The observed temperature dependence, however, represents peculiar behavior since it can not result from a simple effect of growth kinetics, which should favor step nucleation at higher temperatures by means of enhanced surface diffusion. To explain the significant influence of the surface corrugation at high temperatures we propose that a thermally activated change occurs in the adsorption state of C_{60} molecules. If the C_{60} adsorption is characterized by a physisorptive precursor state preferably occupied at low substrate temperature and a thermally activated chemisorptive state (a well-known feature of various adsorbate-substrate systems [12]) the adsorbate-substrate interaction, and therefore the substrate surface corrugation, plays the dominant role at high growth temperatures.

Interestingly, C_{60} growth on the Si(111) 7x7 surface [6] results in rotated domains with orientations identical to our present case. Si substrates are supposed to interact comparably strongly with adsorbed C_{60} molecules by means of dangling bonds. Furthermore, the bulk-lattice constant of Si is very close to that of CaF_2 (within 0.5%). Although the reconstructed Si(111) substrate causes specific growth mechanisms involving a coverage-dependent disorder-to-order transition [6], the significant adsorbate-substrate interaction and the similarity in the surface periodicity lead to identical rotated domain orientations.

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