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Morphological study of C60 thin films prepared by physical vapor deposition

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Highly purified C60 (fullerene) molecules were deposited onto solid substrates and observed by electron microscope and atomic force microscope. The morphological characterization revealed that the thin films consisted of fine island crystals with many stacking faults and the formation mechanism depending on the kind of substrates

1. Introduction

After isolated pure C60 (fullerene) molecules and confirmed the molecular structure, it has been investigated the physical properties of single crystal and thin solid films [1-4]. Thin solid films were mainly fabricated on the surface of silicone single crystal or deposited films of metal by physical vapor deposition (PVD) technique and characterized their electronic properties, especially superconductivity by co-evaporated with alkali metals.

On the other hand, thin films formed on the air-cleaved surfaces of alkali halides, mica, CaF_2 and MoS_2, have been investigated in the sense of crystal growth to make single crystal film. When the deposited molecules grew epitaxially with an axial relationship between molecules and the substrate surface, they tended to form many grains, in which each of them aligned along one in the equivalent axes of substrate. In the case of epitaxial growth, even if adsorption and nucleation of deposited molecules occurred at random, the growing directions should be limited by two or three directions according to the symmetry of substrate surface. So that monotonous crystal growth would be taken place within the regions, in which molecules could freely diffuse or migrate. It is called surface diffusion length. If the frequency or density per unit area and unit period was controlled, one could truly fabricate giant single crystal film.

In this paper we will discuss morphology of thin crystals, fine structure in them and growth mechanism, especially nucleation depending on the kinds of substrates.

2. Experiments

Highly purified C60 was evaporated on air-cleaved (001) planes of alkali halides, NaCl, KCl and KBr, and mica maintained at 100 °C in a pressure of 5×10^{-7} Torr. The deposition rate and averaged film thickness were 0.3 nm/min, and 1 and 5 nm, respectively. For electron microscopic observation, the thin solid films were reinforced by vacuum-deposited carbon film with a thickness of 3 nm, stripped from the substrates on the water surface, and then scooped up onto Cu meshes.

The morphology and crystallinity of thin films were characterized by using transmis-sion electron microscope (TEM), Hitachi H-9000, scanning electron micro-scope (SEM) and scanning transmission electron microscope (STEM), TOPCON ABT-150F, and atomic force microscope (AFM), Digital Instruments NanoScope-II.

In the case of TEM and STEM observation, the peculiar reflections of thin crystals, (2,-2,0) spots, were employed in imaging in addition to being recorded by normal mode (bright-field (BF) imaging). Such dark field (DF) imaging without transmitting electrons through the specimen is available not only to enhance the contrast of images but also to make clear dislocations and stacking faults in crystals [5].

3. Results and discussion

Figures 1(a) to (c) and (d) to (f) are TEM images, BF and DF, and selected area electron diffraction patterns obtained from thin films on KCl and mica substrates, respectively. Averaged film thickness was 1 nm. BF images reveal the presence of growth hillocks with faint contrast and DF ones are visualized not only the morphology of island crystals but also the fine structure in them. The growth hillocks on KCl are dendric with a size of 100 - 200 nm and those on mica are small cap-shaped with a size less than 100 nm. Such features of growth hillocks was also confirmed by SEM and STEM observation, especially SEM image revealed the overgrown hillocks on the terrace of the first growth hillock.

In spite of the difference in these morphology, the electron diffraction patterns are the same and represent the (2,-2,0) spacings of 0.49 nm with hexagonal symmetry indicating f.c.c. structure (a=1.4 nm). In the pattern of thin crystals on KCl, weak reflections appear inside (2,-2,0) and (0,-2,2) reflections. These forbidden reflections can be indexed as 1/3(4,-2,-2) or 1/3(2,-4,2) and occasionally accompanied with streaks running normal to the directions of (2,-2,0) and (0,-2,2) reflections. They represent the existence of stacking faults normal to the direction. Such stacking faults were recorded in DF images as fine lines and in high resolution images as arrays of dot corresponding to each molecules. The results were in good agreement with those obtained from thin crystals formed on alkali halides and mica substrate [6-8].

In order to estimate the dependence of growth mechanism on the kinds of substrate, thin films were prepared on several alkali halides. Figure 2 shows AFM images of the films formed on KCl (a), KBr (b), NaCl (c) and mica (d). The feature of thin films on KCl and mica are as same as those by TEM. The morphology of island crystals on KBr and NaCl is different from others: small crystals on NaCl gathered and make chain-like structure, while those on KBr grew normal to the substrate surface to be higher compared with them on different substrates.

With increasing the amount of molecules deposited onto such substrates, the density of island crystals tended to increase monotonously except for those on KCl. In the ultrathin film with an averaged thickness less than 1 nm, small crystals could be found only on the surface steps on KCl substrate. It was also confirmed by several images of the dependence of the crystal size on the distance between the adjacent steps. With increasing the distance, dendric crystals tended to grow larger.

In conclusion, although adsorption on the surface steps of KCl substrate occurred at the first stage in the nucleation, surface migration of molecules should promote further crystal growth. On the other hand, the nucleation might be the rate-limiting step on NaCl, KBr and mica and no

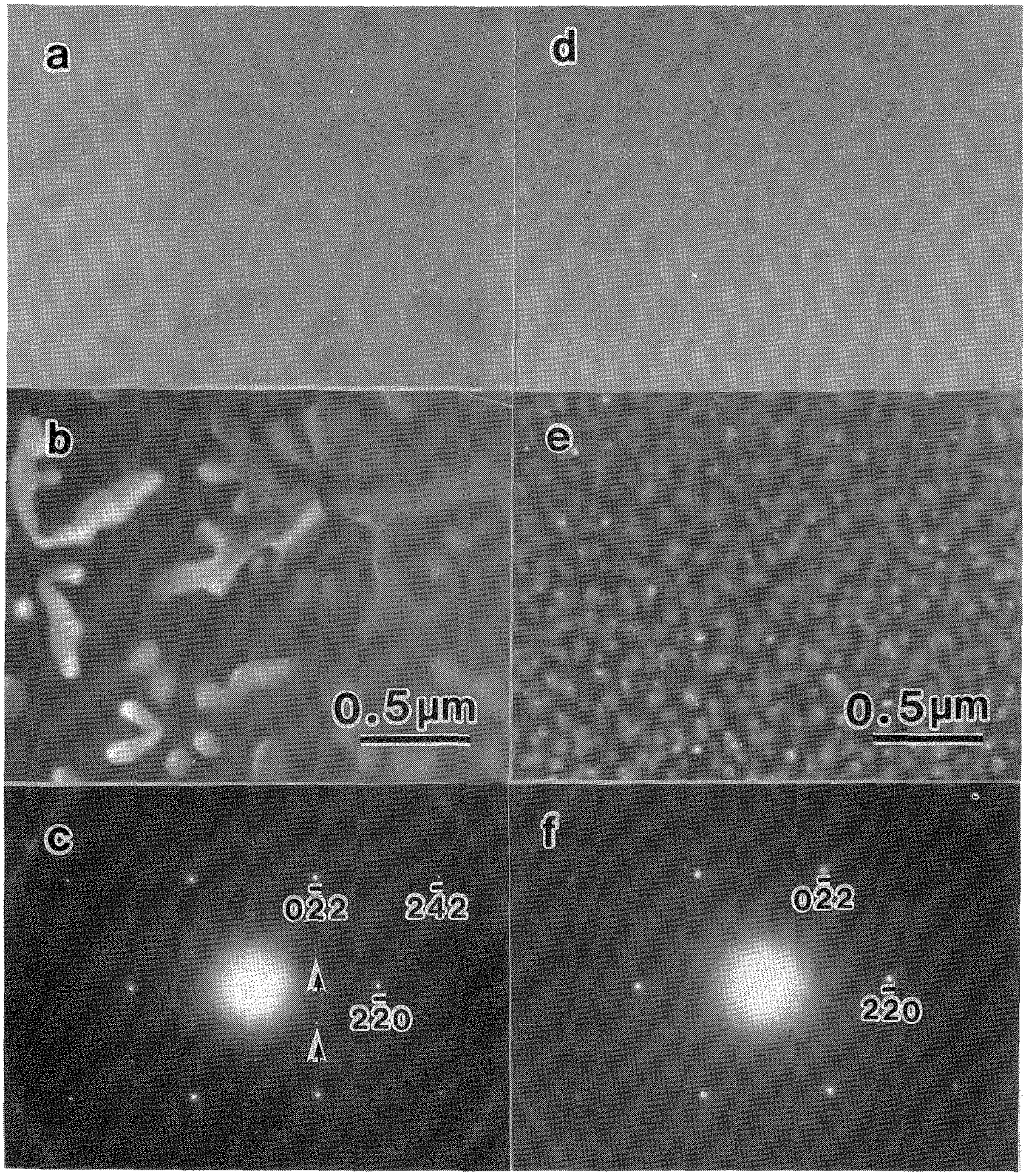

Figure 1. Transmission electron micrographs, BF and DF imaging, and electron diffraction patterns of thin films formed on KCl (a) to (c), and mica (d) to (f), respectively.

further crystal growth of each island could be observed in this deposition conditions.

REFERENCES

1. H.W.Kroto, *Angew.Chem.Int.Ed. Engl.*, **31** (1992) 111.
2. R.S.Averback et al. (eds.), *Cluster and Cluster-Assembled Materials* (MRS Symposia Proceedings, No.206), Material Research Society, Pittsburgh, 1991.
3. H.W.Kroto, et al. (eds.), *The Fullerenes*, Pergamon, 1993.
4. D.Koruga, et al.(eds.), *Fullerene C60: History, Physics, Nanobiology, Nanotechnology*, Elsevier, 1993.
5. K.Yase, S.Kazaoui, N.Minami and T. Suzuki, submitted to *Thin Solid Films*.
6. T.Ichihashi, K.Tanigaki, T.Ebbesen, S.Kuroshima and S.Iijima, *Chem.Phys. Lett.*, **190** (1992) 179.
7. W.Krakow, N.M.Rivera, R.A.Roy, R.S.Ruoff and J.J.Cuomo, *J.Mater.Res.*, **7** (1992) 784.
8. H.-G.Busmann, R.Hiss, H.Gaber and I.V.Hertel, *Surface Sci.*, **289** (1993) 381.

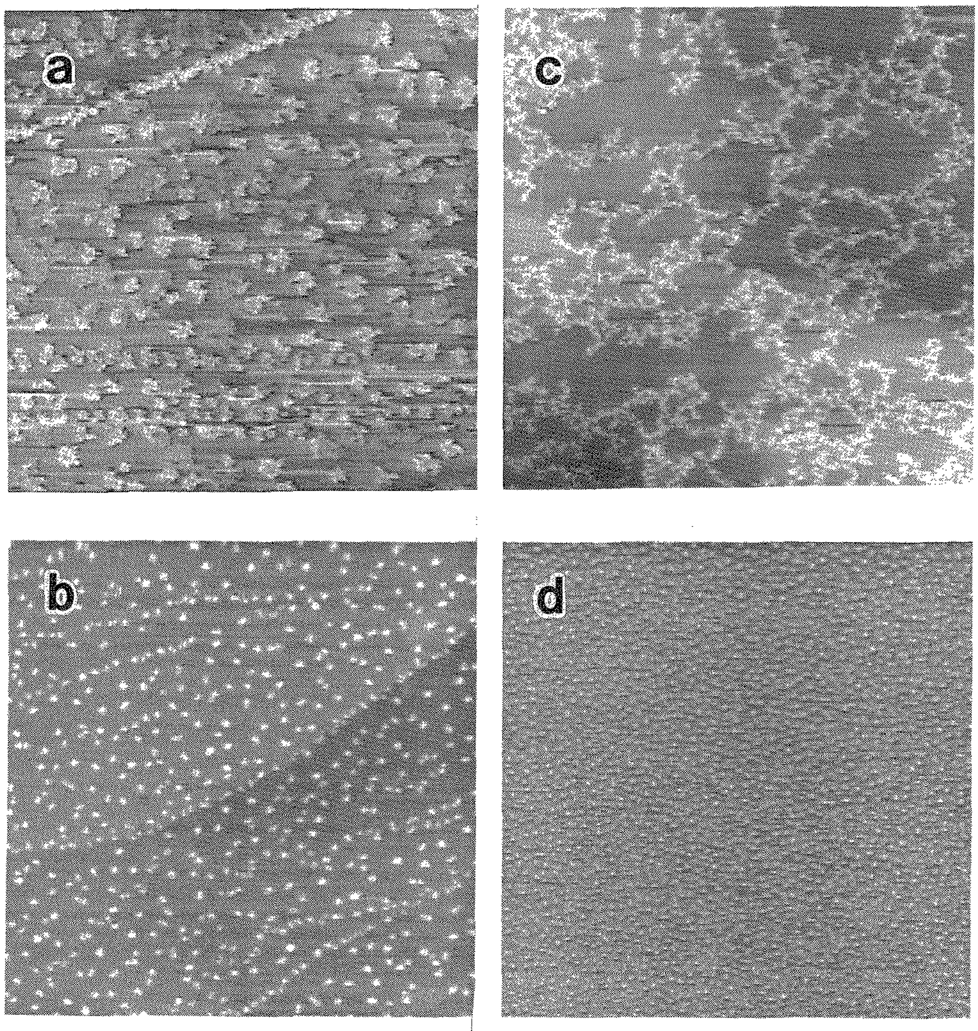

Figure 2. AFM images of thin films formed on KCl (a), KBr (b) and NaCl (c) and mica (d). The length of side is 13 μm in (a) to (c), and 5 μm in (d).