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HIGH QUALITY THIN FILMS OF FULLERENE BY MEANS OF NUCLEATION-CONTROL ON THE SUBSTRATE SURFACE

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Abstract To fabricate ultrathin films of fullerene (C60) without any dislocation and stacking faults, nucleation and crystal growth during deposition should be precisely controlled. Slow evaporation of C60 onto the (001) planes of alkali halides, NaCl, KCl and KBr, and mica kept at higher temperature, leads the discrete nucleation, whose distances between the adjacent small crystals depended on the substrate temperature and the kinds of substrates. It was found that the island crystals on KCl tended to be especially created on the center of adjacent terraces and at the edge of surface step, and these distance between the neighboring islands depended on the width of terrace and substrate temperature. The nucleation mechanism of C60 was for the first time confirmed in the sense of crystal growth.

INTRODUCTION

There are huge number of investigations concerning with fullerene (C60) thin crystals, in which most of them were interested in physical properties of films, especially superconductivity of sample including alkali metals.[1,2] Thin solid films were fabricated on the surfaces of Si single crystal,[3,4] alkali halides,[5-7] CaF_2,[8] mica,[7,9,10] MoS_2,[11] and epitaxially grown films of Au.[12] It has been well-known that C60 molecules grew epitaxially to have face-centered-cubic (f.c.c.) structure

with a cell parameter of a=1.43 nm. The films tended to include lots of dislocations and stacking faults. These fine structure were characterized by using transmission electron microscopy (TEM), [5-7,9,10] and scanning tunneling microscopy (STM) and atomic force microscopy (AFM).[3,4,8,11,12]

To make single crystal films, the deposition condition should be precisely controlled to let the nucleation and the further crystal growth in good order. However, there have been no quantitative data to confirm how far can molecules migrate on the substrate surface and how can they adsorb on it.

In this paper we will describe the nucleation mechanism and surface migration of C60 molecules on the substrates of alkali halide and mica.

EXPERIMENTAL

Highly purified C60 powder was deposited onto the air-cleaved (001) planes of alkali halides, NaCl, KCl and KBr, and mica in a pressure of 1×10^{-4} Pa. The temperatures of K-cell type crucible and substrates were precisely controlled to be kept at 550°C and 0 - 300°C, respectively. The substrates with a size of 8 x 8 mm^2 were baked above 300°C for 1 h before sample evaporation. The deposition rate and final film thickness were 0.3 nm/min and 1 nm, respectively. The as-prepared thin films were observed by an atomic force microscope (AFM), Digital Instruments NanoScope-II, in air in the force imaging mode. Other films were reinforced by vacuum-deposited carbon film with a thickness of 3 nm by using another vacuum system. The films covered with amorphous carbon film were stripped from the substrate on the water surface and scooped up by Cu meshes. A transmission electron microscope (TEM) used here was Hitachi H-9000.

RESULTS AND DISCUSSION

Figure 1 shows AFM images of thin films formed on the substrates of alkali halides, NaCl (a), KCl (b) and KBr (c), and mica (d) kept at 200°C. There are few island crystals (8 - 21) with a diameter of 200 nm on the surfaces of alkali halides, while 900 islands with a diameter of 100 nm on mica. The density per unit area are 0.1, 0.04, 0.1 and 40 islands/μm^2 on NaCl, KCl, KBr and mica, respectively. It suggests that the condensation coefficient would depend on the kind of substrates, even if in the series of alkali halides. The electron diffraction patterns obtained from

these island crystals represented the net pattern indicating the epitaxial growth with the <111> axis normal to the film surface.

When the same amount of molecules was sublimed onto the substrates kept at higher temperature, 300°C, or less molecules were deposited on them kept at lower temperature, 100°C, the number of islands per unit area tended to decrease monotonously, except for in the case on KCl. The crystals on KCl could be found only at the edge of step with a height of 20 nm.

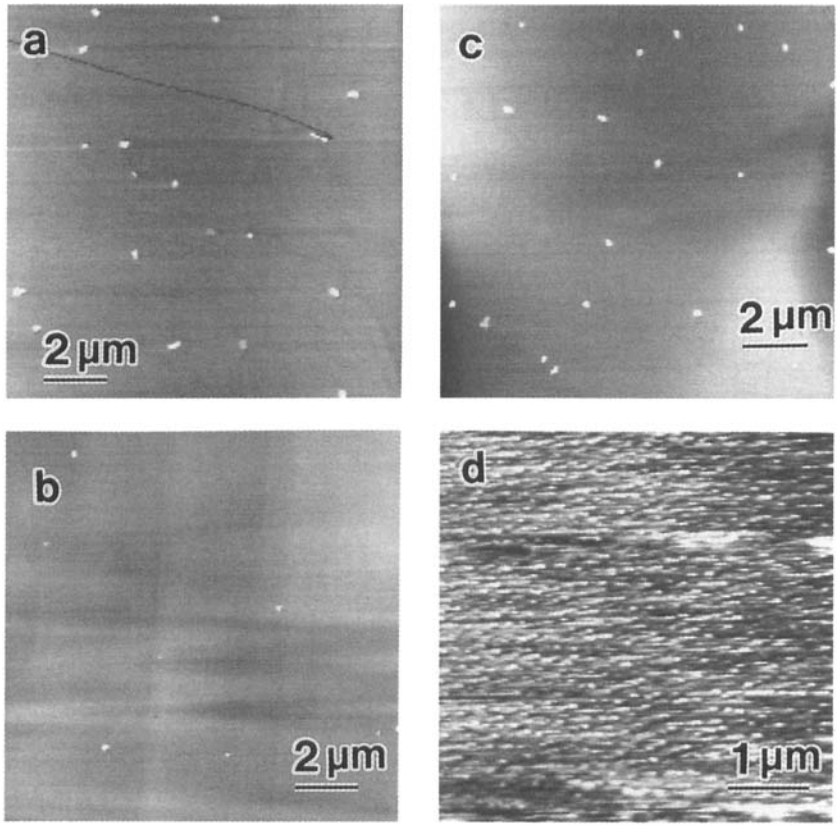

FIGURE 1 Atomic force micrographs of thin films of fullerene formed on the substrates of NaCl (a), KCl (b), KBr (c) and mica (d). The substrate temperature during evaporation was 200°C. The length of side is 13.4 μm in (a) to (c), and 5.0 μm in (d).

To evaluate the effect of such nucleation at the edge of step, the films formed on the KCl surfaces with much steps were performed. Figure 2 shows the surface morphology of films formed on KCl substrate kept at 100°C. With increasing the distance between the adjacent steps, the size of island crystals tends to increase from 200 nm to 500 nm. In addition to existing many nuclei at the edge of steps with a distance less than 100 nm, there are few arrays of islands parallel to the edge of steps. The number of arrays is also proportional to the width of terraces. These width should correspond to how far can molecules migrate along the direction normal to the edge of step, because they could not move to on another terrace beyond the step. From Figs. 2(a) and 2(b), these distances are evaluated as 400 nm to 1.8 μm. The distance between the neighboring island crystals on the same terrace was independent. It results that deposited molecules can diffuse in a range of 200 - 900 nm in the direction normal to the edge of step and at least 100 nm along the direction parallel to the edge on the KCl surface kept at 100°C.

The surface migration of deposited molecules would be enhanced by increasing substrate temperature. At the higher temperature of substrate, nuclei could be created only at the edge of steps. With increasing the temperature of KCl substrate from 100°C to 300°C, the distance between adjacent islands locating at the same edge of step also increase

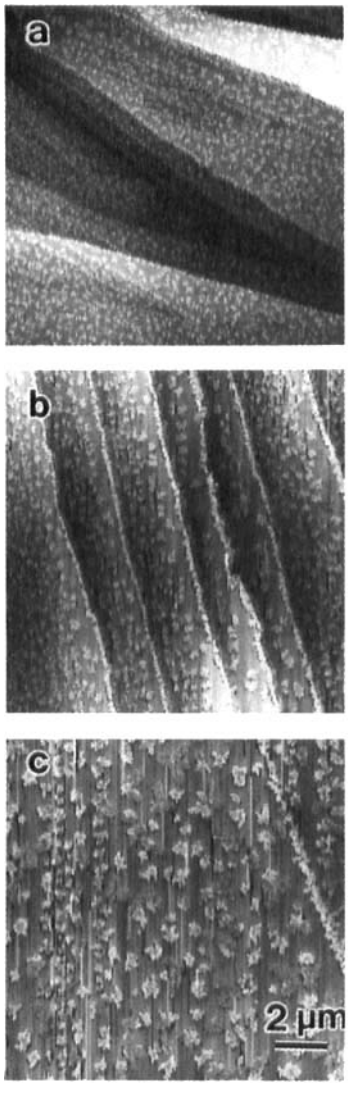

FIGURE 2 Surface morphologies of thin films formed on the KCl substrate kept at 100°C. With increasing the width of terraces in (a) to (c), the size of island crystals locating on the terrace and at the edge of step tends to increase. And the number of arrays of islands aligning along the edge of step also increases. The length of side is 13.4 μm.

from 100 nm to more than 10 μm. It means that molecules can migrate along the edge of step by hundred times at 300°C than can do at 100°C.

In order to fabricate high quality thin crystals of C60, it is important to control the nucleation and further crystal growth. When the sample was kept at higher temperature after deposition, the coalescing of island crystals and crystal growth should be promoted. Figure 3 shows a high resolution electron micrograph of thin film formed on the KCl substrate. The film was maintained at 100°C for 1 h after deposition on the KCl substrate had been kept at the same temperature. The single crystal region without any stacking faults could be imaged in the mode of high resolution TEM observation. However it extended only to 200 nm in a diameter.

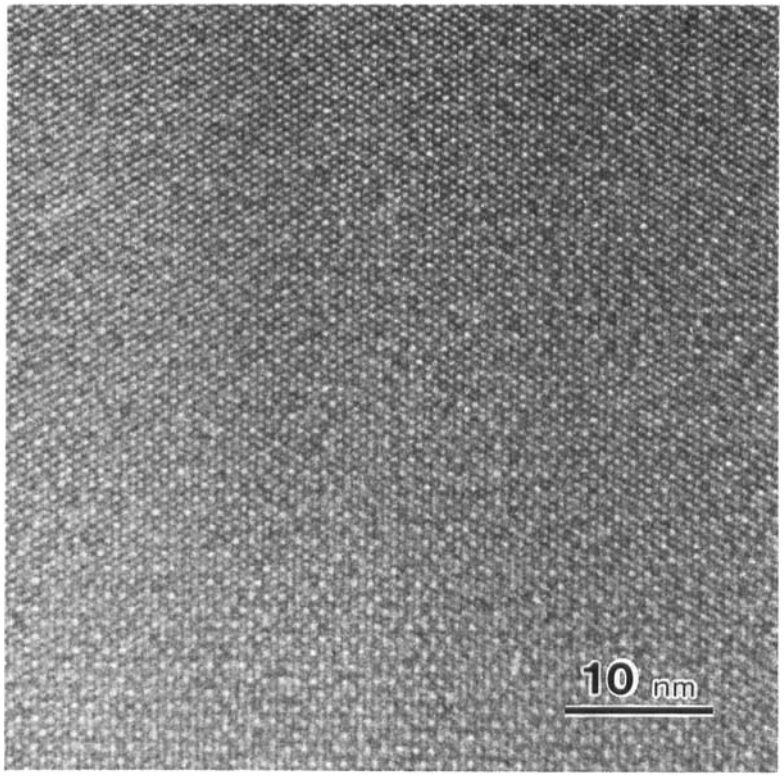

FIGURE 3 High resolution electron micrograph of thin crystal film obtained on the surface of KCl substrate. Whole the region in this picture is single crystal.

Now we are progressing on further experiment to fabricate the single crystal films with a size larger than μm^2 for the characterization of physical properties of them.

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