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Preparation of Continuous C60 Thin Films with Flat Surfaces by Vacuum Evaporation

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We have prepared C60 thin films on Si and mica substrates by a vacuum evaporation technique. As a thin film growth mode a Volmer-Weber and a Frank-van der Merwe type of growth was observed in the substrate temperature range of 200 ～ 230 ℃ and 240 ～ 260 ℃, respectively. As a result almost continuous and flat C60 ultrathin films about 10 nm thick were obtained on mica substrates at 250℃.
Key words : C60, crystalline C60 film, mica Substrate, vacuum evaporation, ultrathin film

1. INTRODUCTION

The structure of C60 constituted of only carbon shows the regular truncated icosahedron, that is soccer-ball configuration, which has been namely known as the third allotrope next to graphite and diamond. The C60 was found at 1985 by Kroto, Smally, and Curl.[1] Since the method of synthesis with a large quantity for C60 were established, the studies in various fields have been done, and it is expected that C60 will be a novel functional material.[2]

When we consider the application for electronic devices of C60, we have to establish the growth method of C60 thin films. There are a lot of reports concerning about growth of C60 thin films.[3] Especially, epitaxial growth had been studied on van der Waals substrates for C60 crystallized with weak intermolecular forces. However, no studies was reported in continuous films, while many studies were reported in initial growth stage of C60 thin films.

The aim of this study is to growth of continuous C60 ultrathin films on mica substrate for application of electronic devices. Predominantly, an optimum substrate temperature (T_S) was investigated for the ultrathin films. As a result, the C60 ultrathin film was successfully grown on the mica substrate.

2.EXPERIMENTAL PROCEDURES

We grew C60 thin films in a general vacuum chamber composed of growth chamber with a background pressure of 6×10^{-8} Torr evacuated by a 2000 l/s oil-diffusion-pump and pre-chamber evacuated by a 180 l/s turbo molecular pump. The growth chamber and the pre-chamber are separated by a gate-valve in order to change and transfer the substrate to growth-chamber without exposure to the air in it.

C60 powder with 99.9 % pure in pylolytic born nitride (PBN) was evaporated by a Knudsen-cell on the mica substrates and Si substrates. The substrates were cleaned by rinsing in ethanol, by which the air entering between layers was removed in the case of mica substrates. They were clamped to the substrate holder, which was radiatively heated from the backside. The carbon ribbon heater coated with SiC was used. Between the heater and the substrate holder, temperature of the substrate was measured. Total pressure while growing was less than 6×10^{-7} Torr.

Grown films were evaluated by an atomic force microscopy (AFM) and an X-ray photoelectron spectroscopy (XPS).

3.RESULTS and DISCUSSION

In Fig.1, the depth profile of C1s core level XPS spectra for the C60 thin film by a 0.01 minutes etching are shown. Films were grown on mica substrates without heating. At 285 eV, the dotted line is described. Around the surface the peak at 285 eV was found, expected from adatom of carbon or oxidized C60. As the film was etched more than 0.02 minutes, typical spectra of C60, a little lower energy level from 285 eV, were appeared, which signify that C60 evaporated from K-cell arrived at the substrate and grew without thermal decomposition.

Figure 2 shows the AFM images of the films grown on Si and mica substrates at T_S of 100 ℃ and 200 ℃ for 30 min. At T_S of 100 ℃ as shown in Fig.2(a), the grain size of square like shape for C60 was 0.2 μm on Si substrate and 0.05 μm on mica substrate, while at T_S of 200 ℃ as shown in Fig. 2(b), the size was almost same on Si substrate and 0.15 μm on mica substrate. Compared with T_S of 100 ℃, on Si substrate the amount of grains decreased, and on mica substrate the surface morphology became smooth by connecting partially between grains at T_S of 200 ℃. Namely on Si substrate at T_S of 200 ℃, it is difficult to get the smooth surface by a thermal migration due to a re-evaporation of C60.

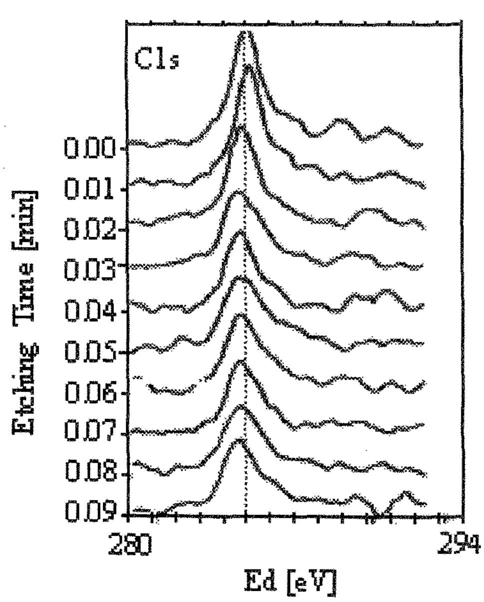

Figure 1 : C1s XPS spectra of C60 thin film

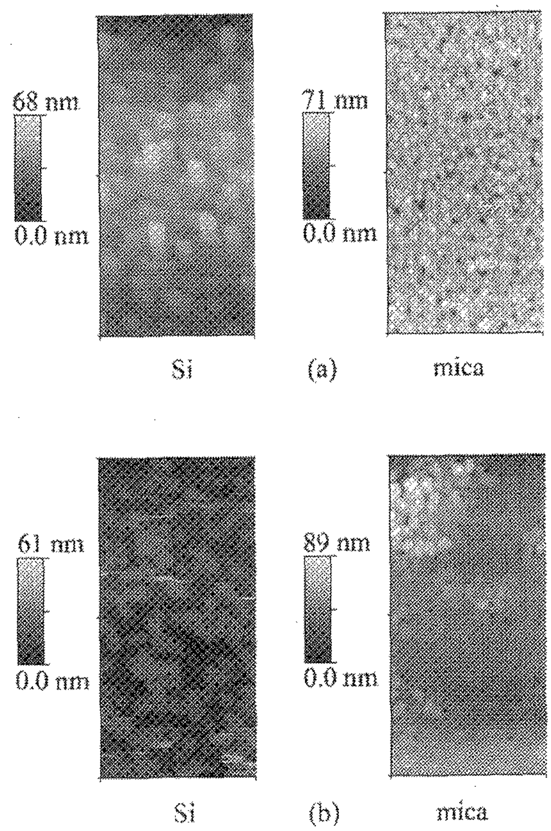

Figure 2 : AFM images on Si and mica substrates grown at (a) 100 ℃ and (b) 200 ℃ in T_S. The size of the photographs is 5× 2.5 μm. The height gauge is set at the left side of the each photograph.

In Fig.3 the AFM images are shown for C60 films grown on mica substrates. As growth conditions T_S were between 200 ℃ ~ 260 ℃ and growth time was 5 minutes. The surface morphology of each film was summarized in Table I.

With increasing T_S up to 230 ℃, the diameter and the height of grains with spherical shape showed an increasing tendency, where three-dimensional grain growth was clearly, that is the Vomer-Weber (VW) growth mode. However, a complicated surface morphology appeared at T_S of 240 ℃. There were two shapes in grains, that is a spherical shape with the diameter of 0.2 μm and the height of 35 nm, and plate shape with the diameter of 0.6 μm and the height of 13 nm as shown in Fig. 3(d) and Table I. The spherical grains also grew on the plate grains. Around T_S of

240 ℃ it was expected that the growth mode changed. Extremely flat and continuous film grew at T_S of 250 ℃ of which the surface morphology was quite different from that of films grown below T_S of 240 ℃. The continuous and flat surfaces indicated the Frank-van der Merwe (FM) mode for the film grown at T_S of 250 ℃. At T_S of 260 ℃, continuous surface was not observed.

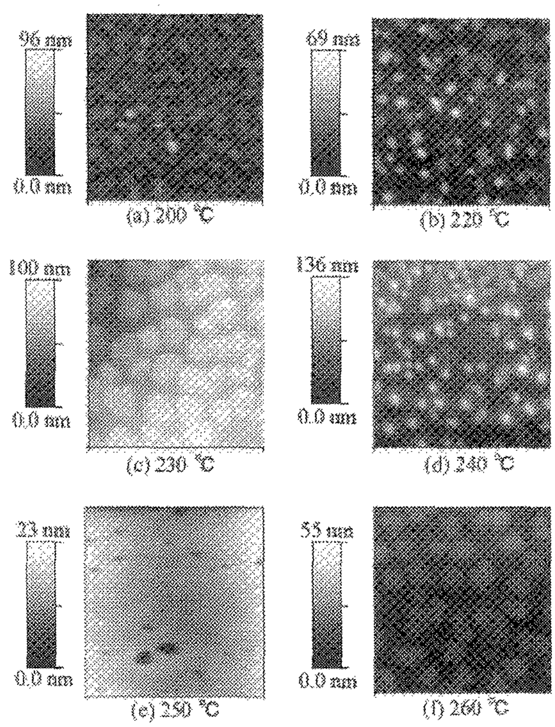

Figure 3 : AFM images of films with 2.5 μm square grown at various T_S with same evaporation rate in C60 flux.

Table I : The T_S dependence of grain size of the films

T_S (℃)	Diameter (μm)	Height (nm)
200	~0.1	~11
220	~0.25	~17
230	~0.3	~15
240	~0.2	~35
	~0.6	~13
250	not defined	not defined
260	~0.15	~10

In Fig. 4 Arrhenius plot of the number of grains per unit area, N_G, is shown. The N_G was determined from the AFM images. Below T_S of 230 ℃, in the Vomer-Weber (VW) area, the number of grains decreased exponentially with increasing T_S. From the result the activation energy E_G for a surface migration was estimated to be 0.33 eV, by fitting with the function of N_G = C exp (E_G / k_BT) (C is a factor). With increasing T_S more than 240 ℃, in the Frank-van der Merwe (FM) area, the N_G rapidly decreased and showed the minimum value (N_G = 1) at T_S of 250 ℃, meaning that the surface morphology was flat and continuous film grew, mentioned above in Fig.3(e). It was expected from the balance between the effects of a migration on the film surface and a re-evaporation. At T_S of 260 ℃, effect of the re-evaporation increased and the N_G raised again.

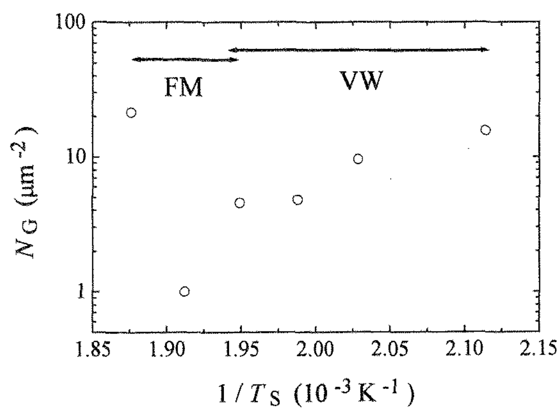

Figure 4 : Arrhenius plot of the number of grains per unit area, N_G.

The AFM image is shown for film grown on mica substrate at 240 ℃ in Fig.5. The grains of triangle were clearly seen, aligned the side of triangle with parallel. It was expected that crystalline C60 thin film, in other words epitaxial film, with fcc structure partially grew along the (111) direction normal to the plane. The epitaxial growth was the same to the results in Ref.[3], in which C60 molecules aligns parallel to the crystallographic axis of (001) mica substrate.

Figure 6 shows the difference between surface morphology of the as-grown film and the annealed film in the growth chamber without exposure to the air. For the film with 7 nm thick in a thickness gauge (not exact thickness), no annealing effect was detected, while for the film with thickness more than 8 nm in the gauge, annealing effect was observed as shown in Fig.6(b), demonstrating the more continuous film. It is expected that the film growth with an interval, during which no deposition takes place, are achieved with more continuous surfaces. Such the film is required for the C60 electronic devices.

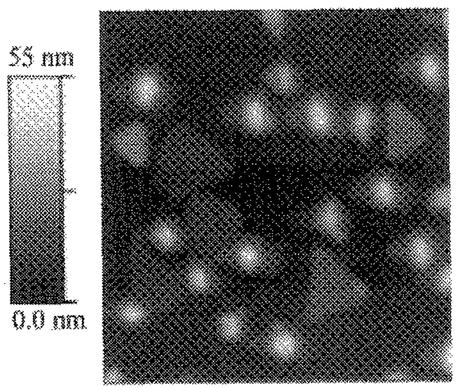

Figure 5 : AFM image of film grown at T_S of 240 ℃.

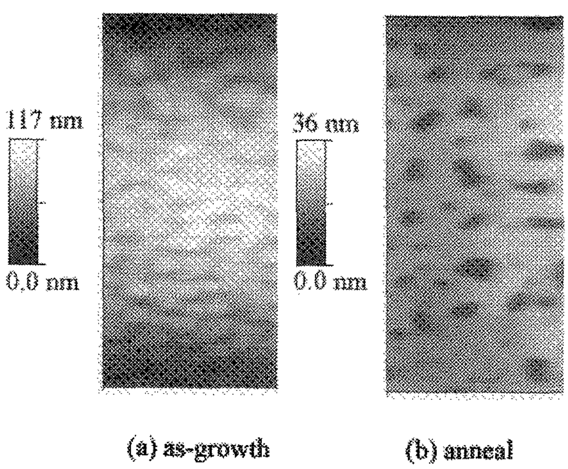

Figure 6 : AFM images with the size of 2.5× 1.25 μm. The T_S was 240 ℃.

4.SUMMARIES

We grew C60 ultrathin films on Si and mica substrates by a normal vacuum evaporation method. Results were summarized as follows :

- The C60 evaporated from K-cell arrived at the substrate and grew without thermal decomposition.
- Only on the mica substrate, flat surfaces and continuous films were obtained at T_S of 250 ℃ and after annealing of films grown at 240 ℃.
- Films grew with the Vomer-Weber mode below 240 ℃ and with the Frank-van der Merwe above 240 ℃ on mica substrate.
- Crystalline C60 film partially grew on mica substrate at 240 ℃.

Such the flat and continuous film is expected to apply for the C60 electronic devices.

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