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Growth and phase transition of C_{60} monolayer film and $[(C_{60})_5(Cu)_5]_{52}$ multilayer film

Yasuhiro Yoneda, Kiyoshi Sakaue and Hikaru Terauchi

Department of Physics, Kwansei-Gakuin University, Nishinomiya 662, Japan

Artificial thin films of C_{60} $[(C_{60})_5(Cu)_5]_{52}$ multilayer were successfully grown on GaAs (111) surface by molecular beam epitaxy. The monolayer and multilayer films were investigated by *in situ* monitoring of reflected high energy electron diffraction and *ex situ* observation of X-ray diffraction. From these measurements, it was confirmed that C_{60} molecules grew into a monolayer film with the close-packing face-centered-cubic (fcc) configuration and that the C_{60} film was high-quality (111) oriented crystal. The transition temperature of C_{60} layers of the multilayer film was 260 K, but that of the C_{60} film is 240 K. The phase transition of the C_{60} film was somewhat different from that in the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film.

1. INTRODUCTION

The availability of single-crystalline films is important for investigating in detail the solid-state properties of fullerenes. The growth of epitaxial C_{60} thin films on metals [1-3], semiconductors [4,5] and alkali halides [6,7] under the well-defined conditions of molecular beam deposition has attracted much interest. The thin film crystals would show different behavior from the bulk crystal. Furthermore, in C_{60} film, novel properties were observed when the phase transition occurred [8, 9]; these properties are not observed in the bulk crystal.

In this paper, we report the growth of fullerene monolayer and copper/fullerene multilayer films by MBE method. The intermolecular distance of C_{60} is 10.02 Å and the nearest neighbor distance of Cu is 2.56 Å. The adsorbed C_{60} on Cu (111) occurred because of the formation of a commensurate interface with a 1:4 coincident site lattice (the mismatch is 2.5 % for a 1:4 lattice coincidence).

2. EXPERIMENTAL

Fullerene, C_{60} monolayer film and $[(C_{60})_5(Cu)_5]_{52}$ multilayer film were grown by the MBE method. Gallium arsenide (111) wafers were etched in H_2SO_4:H_2O_2:H_2O = 5:1:5 solution for 1 min to remove damaged layers induced during lapping. Then the substrates were introduced into a chamber. The surface oxide layer was removed by a thermal flash at 450 °C. The base pressure of the chamber was 1×10^{-8} Torr. Elemental C_{60} (purity 99.9%) was evaporated from Knudsen effusion cells, and the flux intensities were monitored by a nude-type ionization gauge equipped on the manipulator. The growth rate was 0.45 Å/s under typical growth conditions. A RHEED system was used for the real-time observation of the surface structure.

The X-ray diffraction measurements of the C_{60} film were carried out using double axis diffractometer. As an X-ray source, Cu-Kα radiation (40 kV, 240 mA) monochromatized by a pyrolytic graphite crystal was used and a scintillation counter was used as a detector. The C_{60} film was cooled from 300 K to 14 K by a closed-cycle He-gas refrigerator. The specimen temperature was controlled within ± 0.5 K.

3. RESULTS

3.1. Growth of monolayer and multilayer films

The substrate temperature was kept at 80 °C during the growth of C_{60} monolayer and $[(C_{60})_5(Cu)_5]_{52}$ multilayer film. Figure 1(a) shows streaky RHEED patterns of the GaAs (111) clean surface, suggesting that the substrate is flat. The direction of the incident electron beam was parallel to the $[11\bar{2}]$ crystal axis of the GaAs substrate in Fig. 1(a). The C_{60} monolayer with a thickness of 800 Å was used for buffer layer of the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film. Figure 1(b) shows RHEED patterns after the growth of C_{60} buffer layer. Directions of the incident electron beam of Fig. 1(b) was the same as that of Fig. 1(a). The arrangement of diffraction streaks and diffraction spots proves that the surface of the C_{60} buffer layer is smooth on the atomic scale. The RHEED pattern changed during the growth of $[(C_{60})_5(Cu)_5]_{52}$ multilayer film. Just after the start of the $[(C_{60})_5(Cu)_5]_{52}$ growth, the weak ring pattern co-existed on the streaky one. Figure 1(c) shows RHEED pattern of the multilayer film after 26-

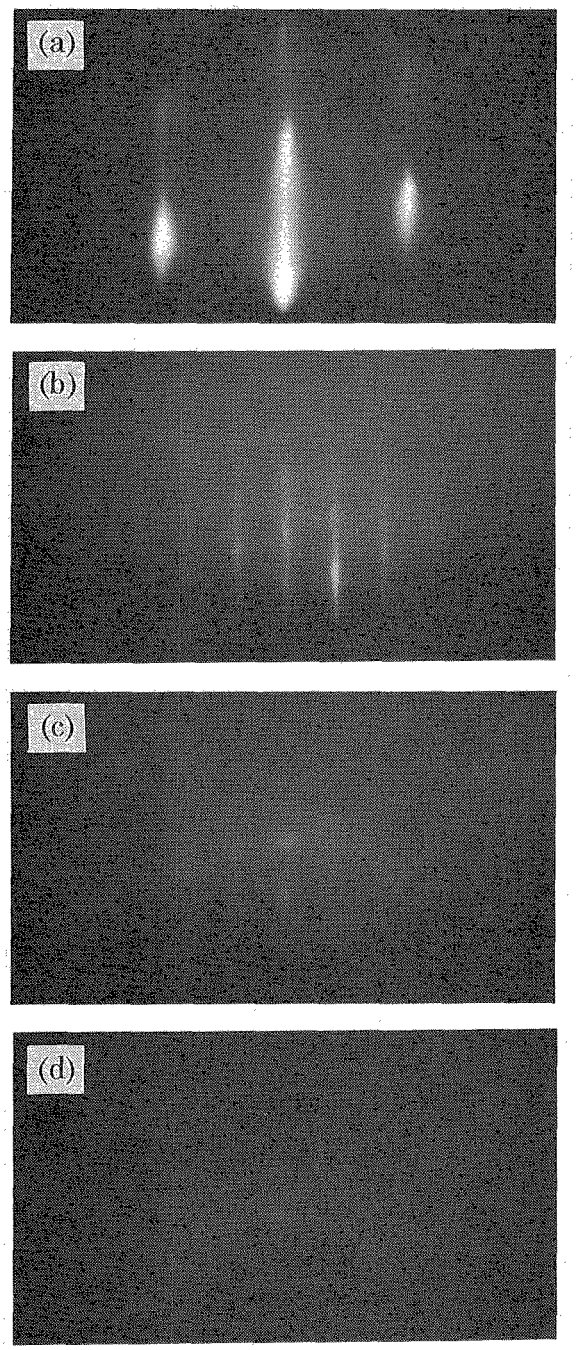

Figure 1. RHEED patterns of GaAs substrate (a), C_{60} (800 Å) buffer (b), after 26-periods-growth of $(C_{60})_5(Cu)_5$ multilayer film (c), and after 52-periods-growth of $(C_{60})_5(Cu)_5$ multilayer film (d). The incident electron beam is parallel to the $[11\bar{2}]$ axis of the GaAs substrate.

periods-growth. The thickness of the film after 26-periods-growth was more than 1000 Å. Thus, the grow layers of $[(C_{60})_5(Cu)_5]_{52}$ multilayer film covered the entire buffer surface. Above 26-period-growth, the stacking orientation of the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film was still arranged and in-plane structure of the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film was observed. As continuing the film growth, the streaky RHEED pattern turned to the ring pattern. This indicates that the stacking orientations get in disorder as film thickness increasing. Figure 1(d) shows RHEED pattern of the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film after the end of growth. The total thickness of the multilayer film was 2000 Å. The ring patterns suggest that the in-plane structure of the top layer of the multilayer film grew into a texture film.

3.2. X-ray diffraction

The conventional 2θ-θ profile from the C_{60} monolayer film and the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film is shown in Fig. 2. The *hhh* reflections from C_{60} layers and Cu layers are observed, implying that the C_{60} monolayer film and the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film are (111) oriented structure in the growth direction (along the [111] direction of the GaAs substrate). The cubic lattice parameters of the C_{60} monolayers and C_{60} layers of the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film are found to be 14.14 Å and 14.17 Å (the lattice parameter of the solid state C_{60} crystal is 14.16 Å), respectively. It made a great difference to the lattice parameter which layer C_{60} was grown, on Cu layer, or on GaAs layer. The mosaic spread of the multilayer film was determined from the transverse scan through the C_{60} 111 to be 0.25 ° and through the Cu 111 to be 0.32 ° [compared to the full width at half maximum (FWHM) of 0.23 ° for the C_{60} buffer layer and 0.15 ° for the GaAs substrate].

3.3. Phase transition

The temperature dependence of the lattice parameter of the C_{60} monolayer film is shown in Fig. 3 (open circles). The value of the lattice parameter was determined using 111 and 333 reflections (from 300K to 180K) and the 222 reflection (below 160K). The *hhh* reflections indicate the lattice parameter only in the growth direction. An anomaly was observed at T_C = 240 K. This behavior shows that the phase transition C_{60} monolayer film occurred. To estimate the anomalous

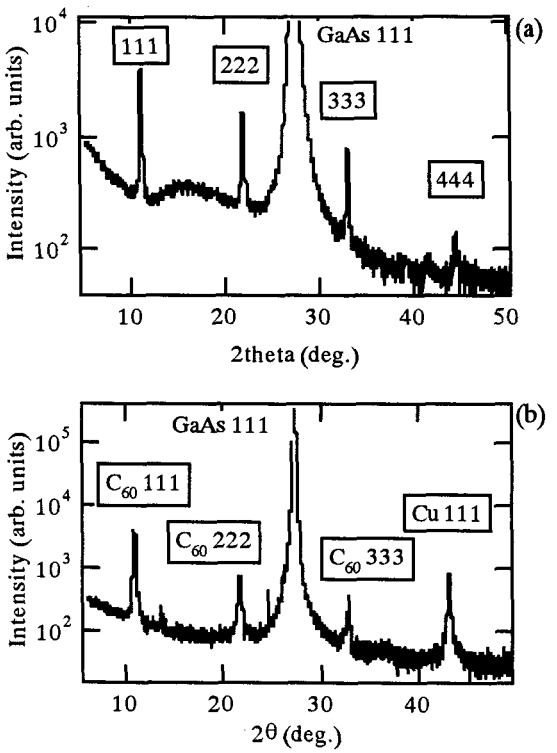

Figure 2. Conventional 2θ-θ profile of C_{60} monolayer film on GaAs (111) substrate (a) and $[(C_{60})_5(Cu)_5]_{52}$ multilayer film on GaAs (111) substrate (b) with C_{60} (800 Å) buffer. The Miller indices of the peaks are given. Those enclosed by a square refer to peaks due to C_{60} and Cu while the rest refer to the GaAs substrate.

parts of the lattice parameter, we calculated the lattice parameter based on the Debye approximation using the data above 240K. The results extrapolated to 0K are represented by the solid line. The lattice parameter of the C_{60} film in the growth direction was equal to that in the growth plane. Thus, the structure of the film will keep fcc in the high temperature phase. When the phase transition occurred, the C_{60} film transformed from fcc structure to sc structure like bulk C_{60} crystal. The observed lattice parameters of C_{60} layers and Cu layers of the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film are plotted in Fig. 3 as a function of temperature, where the estimated errors of the measurement are included in small circles. The values of the lattice parameters are determined by C_{60} 222 reflection and Cu 111 reflection. An anomaly of lattice parameter of C_{60} layers was observed at T_C = 260 K. This behavior shows that the phase transition of C_{60} layers of $[(C_{60})_5(Cu)_5]_{52}$ multilayer occurred. The transition temperature of $[(C_{60})_5(Cu)_5]_{52}$ multilayer is exactly same as that of the bulk C_{60} crystal. To estimate the anomalous parts of the Debye approximation, the calculation was carried out using the data above 260 K. The results extrapolated to 0K are represented by the solid line. Although the lattice parameter of C_{60} changed drastically, no anomaly was observed in the temperature dependence of lattice parameter of Cu. The lattice parameter of Cu layer decreased gradually with decreasing temperature down to 14 K.

4. DISCUSSION

From the RHEED patterns shown in Fig. 1, it is evident that at least two distinct types of surface morphologies, and accordingly the growth mechanism of $[(C_{60})_5(Cu)_5]_{52}$ multilayer film is different from that of C_{60} buffer layer. These differences are a reflection of the fact that the terrace edge of semiconductor surface is rather stable, while the step of metal surface is very reactive. During the growth of C_{60} buffer layer on GaAs (111) surface, streaky RHEED patterns were observed, indicating

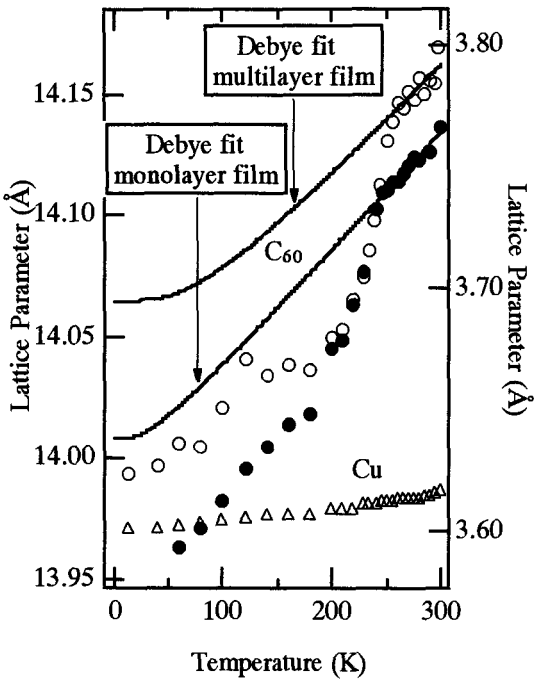

Figure 3. Temperature dependence of lattice parameter in C_{60} monolayer film (closed circle) and $[(C_{60})_5(Cu)_5]_{52}$ multilayer film (open circle and triangle). The solid lines extrapolated to 0 K are the results calculated by the Debye approximation.

that C_{60} buffer layer was smooth on the atomic scale, and surface morphology improved with increasing buffer layer thickness. When starting $[(C_{60})_5(Cu)_5]_{52}$ multilayer deposition, the C_{60} molecules adsorb rather randomly along the terrace edge without forming linear chains, because the interaction between the C_{60} molecules and Cu atoms is stronger than that between neighboring C_{60} molecules along the terrace edge. These observations are markedly different from that of the growth of C_{60} buffer layer on GaAs (111) surface. The crystallographic property of C_{60} in the $[(C_{60})_5(Cu)_5]_{52}$ multilayer is different from that of C_{60} in the buffer layer.

It is rare for C_{60} films to occur different phase transition from bulk state. In C_{60}/Cu multilayer film, the phase transition occurred at 260 K (just same as the bulk T_C). The epitaxial growth of the C_{60}/Cu multilayer film occurred because of the formation of a commensurate interface with a 1:4 coincident site lattice (the mismatch is 2.5 % for a 1:4 lattice coincidence). In the high lattice mismatch system, C_{60} films occurred the usual phase transition and the lattice parameter of C_{60} epi-layers was also same as bulk C_{60} crystals. Since the high lattice mismatch will generate misfit dislocations at interface, the C_{60} layers are free from the strain of the epitaxial effect. However, in the C_{60} monolayer film on GaAs (111) substrate, the mismatch was so small that misfit dislocations can not be generated and the strain of epitaxial effect influenced the C_{60} layers, strongly.

We also observed another anomaly was observed in the temperature dependence of lattice parameter of C_{60} layers at 120 K. But no anomaly was observed in that of Cu layers. This behavior is characteristic of a disordered substance undergoing a glass transition of C_{60} [10, 11]. The experiment shows that the lattice parameter increases with a smaller slope above T_g (= 120 K) than below. The temperature dependence of $[(C_{60})_5(Cu)_5]_{52}$ multilayer film suggests the glass transition remarkably. On the other hand, no anomaly was observed around 120 K in the C_{60} monolayer film. The glassy phase of the C_{60} monolayer film was absent because of the strong epitaxial effect of small mismatch system.

4. CONCLUSIONS

The phase transition was confirmed from the temperature dependence of the lattice parameter of the C_{60} films. The transition temperature T_C of the C_{60} monolayer film was 20 K lower than that of bulk crystals. However, the T_C of C_{60}/Cu multilayer film was the same as that of bulk crystals. The phase transition of the C_{60} monolayer film was somewhat different from that of the C_{60}/Cu multilayer film.

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