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Phase transitions of C_{60} thin films grown by molecular beam epitaxy

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Abstract. Epitaxial C_{60} monolayer and C_{60}/Cu multilayer thin films were successfully grown on GaAs(111) surfaces by molecular beam epitaxy. It was confirmed that these films grew in a close-packed fcc configuration. The lattice parameters of these films were investigated at temperatures from 300 K to 14 K to study the phase transitions of the C_{60} layers. Anomalies of the lattice parameters were observed in both types of film at the transition temperature T_C. Although the T_C of the C_{60} monolayer film was 20 K lower than that of bulk crystals, the T_C of the C_{60}/Cu multilayer film was the same as that of bulk crystals. The bulk C_{60} single crystal under hydrostatic pressure was also observed, to compare the epitaxial strains of the C_{60} films. The T_C of C_{60} molecules was shifted lower by epitaxial strain, but was shifted higher by the application of hydrostatic pressure.

1. Introduction

The structural and electric properties of the fullerene molecule, C_{60}, have been studied extensively. Recently, many attempts to obtain good epitaxial C_{60} films were carried out and there have been many investigations of the surfaces and interfaces of these materials [1–4]. The availability of single-crystalline films is important for investigating in detail the solid-state properties of fullerenes.

Previously, we investigated the growth of single-crystal C_{60} films on GaAs(111) substrate [5, 6]. Gallium arsenide is one of the most commonly used substrate materials for epitaxial growth of semiconductor films. The top layer of the GaAs(111) surface is covered with only one kind of atom (As atoms). Moreover, the apparent mismatch of C_{60} and GaAs can be adjusted by the formation of a commensurate interface, like for the MgO and GaAs system [7]. Despite the large lattice mismatch between MgO and GaAs (25.5%), an epitaxial cube-on-cube structure could be prepared because of the formation of a commensurate interface with a 4:3 coincident-site lattice (the mismatch is 0.65% for a 4:3 lattice coincidence). In the case of C_{60} on GaAs (note that the lattice parameters of C_{60} and GaAs are 14.16 Å and 5.635 Å, respectively), the possibility of formation of a commensurate interface can be assumed, with a 2:5 coincident-site lattice at the GaAs(111)$\|C_{60}$(111) interface (the mismatch is 0.27% for a 2:5 lattice coincidence at room temperature). We have also investigated the growth of C_{60} and Cu multilayer films [8]. The intermolecular distance of C_{60} is 10.02 Å and the nearest-neighbour distance of Cu is 2.56 Å. Adsorption of C_{60} on the Cu(111) surface also 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 this paper, we have investigated the phase transitions of C_{60} films. We have also characterized the phase transition of bulk C_{60} crystals under high pressure. We have clarified

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the difference between the epitaxial strain of the C_{60} films and the strain generated by hydrostatic pressure.

2. Experimental details

A fullerene, C_{60}, monolayer film and a $[(C_{60})_5(Cu)_5]_{52}$ multilayer film were grown by the molecular beam epitaxy (MBE) method. The detail is given in references [5] and [8]. When the substrate temperature was below 10 °C, C_{60} molecules did not form a single-crystal film, but formed a textured film. On the other hand, when the substrate temperature was over 120 °C, C_{60} molecules re-evaporated from the GaAs(111) surface, because of the weak interaction between the GaAs substrate and the C_{60} epi-layers. Therefore, the substrate temperature was kept at 80 °C during the growth of the C_{60} films.

X-ray diffraction measurements of the C_{60} films were carried out using a 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} films were cooled from 300 K to 14 K by a closed-cycle He-gas refrigerator. The specimen temperature was controlled within $\pm$0.5 K.

We used a diamond-anvil cell (DAC) specially designed for x-ray diffraction studies. Single crystals of C_{60} were prepared by the sublimation method. The size of the C_{60} single crystal was $1.0 \times 1.0 \times 0.4$ mm^3. It was trimmed to $0.2 \times 0.2 \times 0.3$ mm^3 to introduce the DAC. The C_{60} single crystal was mounted in a sample chamber that was a hole drilled in a metal gasket sandwiched between two opposed diamond anvils. Hydrostatic pressure was maintained up to 100 kbar by the use of an alcohol mixture (methanol:ethanol = 4:1 in volume) as the pressure-transmitting fluid. A large χ-cradle automatic four-circle diffractometer, of the Rigaku AFC off-centre type, was used for collecting the x-ray scattering data under high pressure with Mo Kα radiation obtained from a 50 kV, 240 mA source.

3. Results and discussion

The conventional 2θ–θ profiles from the C_{60} monolayer film and the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film are shown in figure 1. The (*hhh*) reflections from C_{60} layers and Cu layers are seen, implying that the C_{60} monolayer film and the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film are (111)-oriented structures in the growth direction (along the [111] direction of the GaAs substrate). The cubic lattice parameters of the C_{60} monolayer film and the C_{60} layers of the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film are found to be 14.14 Å and 14.16 Å, respectively. The lattice parameters of the C_{60} layers were modified to allow the formation of the commensurate site lattice. In the C_{60} monolayer film the lattice parameter was shortened by strong epitaxial effects, but in the C_{60}/Cu multilayer film the lattice parameter took the bulk value.

A phase transition of bulk C_{60} crystals has been reported in several papers [9–11]. At room temperature, single-crystal x-ray diffraction shows that bulk C_{60} crystal has an fcc structure with a high degree of rotational disorder. With decreasing temperature, this rotation is reduced. Bulk C_{60} crystal undergoes a weak first-order phase transition at T_C = 260 K, where the crystal is transformed from the randomly oriented state of C_{60} molecules (fcc structure) to the orientationally disordered state (sc structure).

In order to clarify the details of the phase transition of the C_{60} films, an x-ray scattering experiment was conducted at temperatures from 300 K to 14 K. The temperature dependences of the lattice parameters of the C_{60} monolayer film (open circles) and the

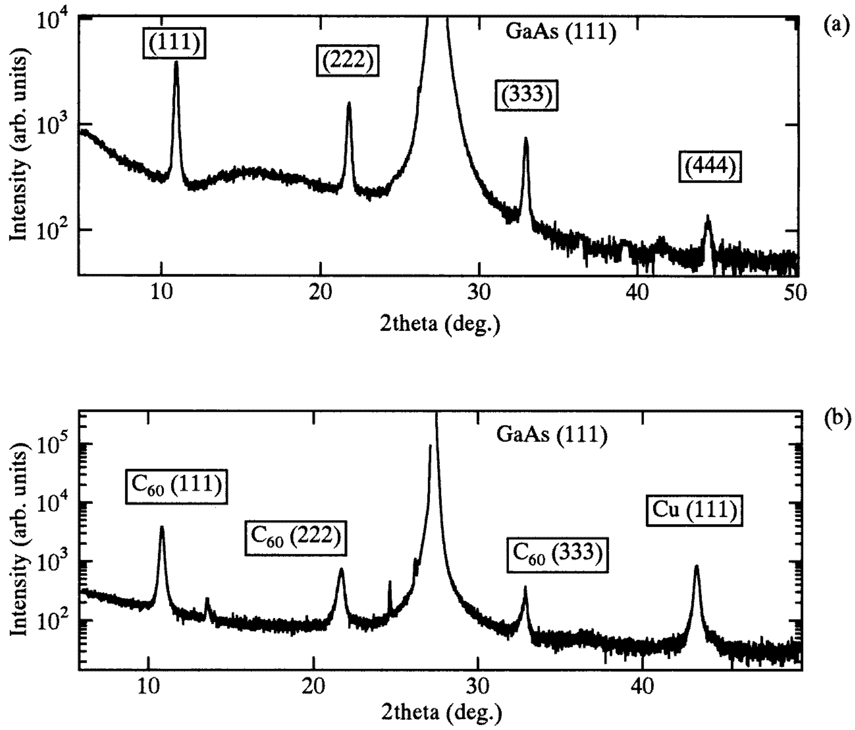

Figure 1. Conventional 2θ–θ profiles of C_{60} monolayer film on a GaAs(111) substrate (a) and $[(C_{60})_5(Cu)_5]_{52}$ multilayer film on a GaAs(111) substrate (b) with a C_{60} (800 Å) buffer. The Miller indices of the peaks are given. Those enclosed by squares refer to peaks due to C_{60} and Cu, while the rest refer to the GaAs substrate.

C_{60}/Cu multilayer film (closed circles) are shown in figure 2. Anomalies were observed at T_C = 240 K (C_{60} monolayer film) and T_C = 260 K (C_{60}/Cu multilayer film). The lattice parameters changed when the phase transition of the C_{60} films occurred. To estimate the anomalous parts of the lattice parameter, we calculated the lattice parameter on the basis of the Debye approximation using the data on the fcc phase. The results extrapolated to 0 K are represented by the solid lines. The lattice parameter of the C_{60} films in the growth direction was equal to that in the growth plane [5]. Thus, the structure of the films remains fcc in the high-temperature phase. When the phase transition occurred, the C_{60} films transformed from fcc structure to sc structure, like bulk C_{60} crystals.

We also examined the lattice parameter of a bulk C_{60} single crystal under hydrostatic pressure. Open triangles in figure 2 show the temperature dependence of the bulk C_{60} crystal under 10 kbar. Bulk C_{60} crystals under atmospheric pressure show a first-order phase transition, as mentioned before. The observed temperature dependence of the bulk C_{60} crystal under 10 kbar also jumped at T_C. However, the lattice parameter of the C_{60} films did not jump drastically at T_C. It appears that the phase transition of the C_{60} films is of second order rather than of first order. This implies that the substrate has a strong influence on the transition in our opinion. In the bulk state, C_{60} molecules exist in the dynamically disordered state and reorient rapidly and isotropically in the temperature range of the fcc state. In the film state, C_{60} molecules are inert, but the interaction between C_{60}

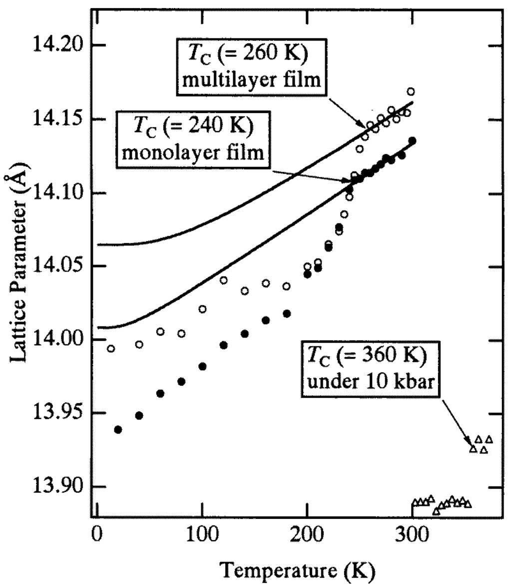

Figure 2. The temperature dependence of the lattice parameter in C_{60} monolayer film (closed circles), $[(C_{60})_5(Cu)_5]_{52}$ multilayer film (open circles), and bulk C_{60} crystal under 10 kbar (open triangles). The solid lines extrapolated to 0 K are the results calculated by the Debye approximation using the data on the high-temperature phase.

molecules and the GaAs substrate (or Cu layers) is strong enough to hold individual C_{60} molecules immobile even in the high-temperature phase. Alternatively, the phase transition of the bulk C_{60} crystal under high pressure can be explained as follows. Increased pressure will hinder the reorientational motion of the C_{60} molecules, thus frustrating the disordering process and raising the order–disorder phase transition temperature. Our results for the bulk C_{60} single crystal under 10 kbar agree with previous work [12].

The transition temperature of the bulk crystal under 10 kbar was 100 K higher, but the transition temperature of the C_{60} monolayer film is 20 K lower than that of the bulk state. On the other hand, an anomaly of the lattice parameter of the C_{60} layers in the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film was observed at T_C = 260 K. The transition temperature of the C_{60}/Cu multilayer film is exactly same as that of bulk crystals. The mismatch between C_{60} layers and Cu layers with a 1:4 coincident-site lattice is much larger than the mismatch between C_{60} layers and a GaAs substrate with a 2:5 coincident-site lattice. In the case of molecular crystals, a large-mismatch system would not be influenced strongly by epitaxial effects. The epitaxial strain is generated in the slight-mismatch system. The orientational disordering of C_{60} layers in the C_{60}/Cu multilayer film was influenced by the interaction between C_{60} and Cu, but the mismatch is too large for the interaction to generate the mismatch strain.

Moreover, another anomaly was observed in the temperature dependence of the lattice parameter of the C_{60}/Cu multilayer film at 120 K. This behaviour is characteristic of a disordered substance undergoing a glass transition of C_{60} [13, 14]. The experiment shows that the lattice parameter increases with a smaller slope above T_g (=120 K) than below. The temperature dependence of the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film suggests a glass transition remarkably like that of bulk crystals. However, the glassy phase was not observed in the C_{60} monolayer film. The glassy phase was absent in the C_{60} monolayer film because

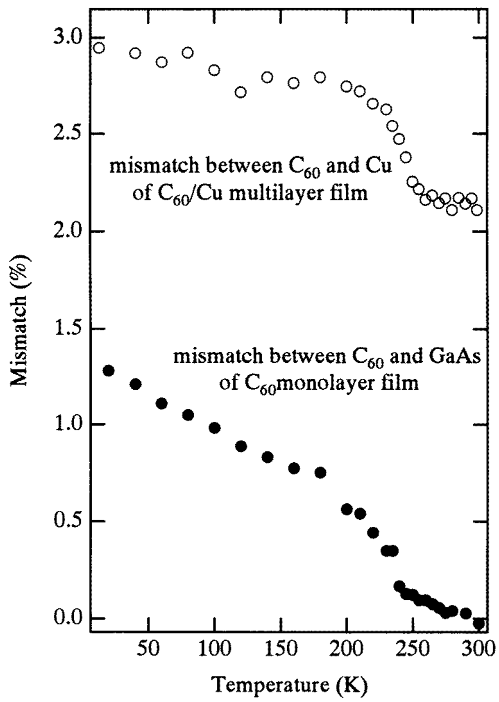

Figure 3. The temperature dependence of the lattice mismatch between grown C_{60} layers and the GaAs substrate with a 2:5 coincident-site lattice, and that of the lattice mismatch between C_{60} layers and Cu layers with a 1:4 coincident-site lattice.

of the strong epitaxial effect. Figure 3 shows the lattice mismatches between the C_{60} monolayer film and: (i) the GaAs(111) substrate based on the assumption of the formation of a commensurate interface with a 2:5 coincident-site lattice; and (ii) the $[(C_{60})_5(Cu)_5]_{52}$ multilayer film for a 1:4 coincident-site lattice, as functions of temperature. The lattice mismatch of the C_{60}/Cu multilayer film was much larger than that of the C_{60} monolayer film at room temperature. The mismatch between C_{60} and Cu increased strikingly below T_C, and it was positive throughout the whole temperature range. The lattice parameter of the GaAs substrate decreased slightly down to 14 K, but the lattice parameter of the C_{60} monolayer film changed remarkably at T_C. Therefore, the mismatch between the C_{60} monolayer film and the GaAs substrate crossed zero and increased strikingly below T_C. The internal strain of the C_{60} monolayer film has a great influence on the crystallographic quality. In the fcc phase (above 240 K), the lattice parameter of the C_{60} monolayer film and that of the C_{60}/Cu multilayer film decreased with the same thermal expansion rate. Below T_C (=240 K), the thermal expansion rate in the C_{60} monolayer film was larger than that in the C_{60}/Cu multilayer film because of the epitaxial effect. Although the lattice parameter of the C_{60} monolayer film decreases with decreasing temperature, the thermal expansion of the C_{60} molecules was limited in the growth plane. Therefore, the thermal expansion was evident only in the lattice parameter of the growth direction. The thermal expansion rate of the film in the temperature range of the C_{60} monolayer film on the GaAs substrate was more than twice that of the C_{60}/Cu multilayer film. However, the lattice coincidence between C_{60} epi-layers and the GaAs substrate was broken gradually in the sc phase. In

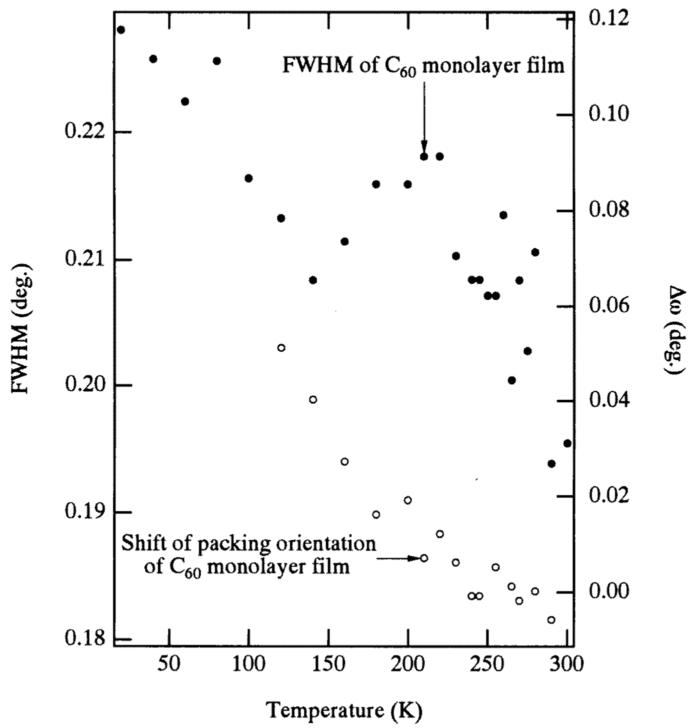

Figure 4. The temperature dependence of $\Delta\omega$ (open circles) and the FWHM (closed circles) in C_{60} monolayer film on a GaAs(111) substrate.

the sc phase, the positions of the observed Bragg peaks of the C_{60} monolayer film shifted from the reciprocal-lattice axis of the substrate. In other words, the [111] direction of the film (the packing azimuth of the C_{60} molecules) is shifted from the [111] direction of the GaAs substrate. Figure 4 shows the temperature dependence of $\Delta\omega$ of the C_{60} monolayer film, and the differences between the peak position of the C_{60}(111) reflection and that of the substrate, using ω-scanning (open circles). In the fcc phase, the $\Delta\omega$ was nearly equal to zero within the error bars. Below T_C, the $\Delta\omega$ increased with decreasing temperature. This behaviour affected the crystallographic quality of the C_{60} films.

Figure 4 also shows the FWHM of the C_{60}(222) reflection as a function of temperature (closed circles). First, the FWHM broadened from just above the temperature at which the phase transition occurred to 210 K. Next, the FWHM became narrower from 210 K to 120 K because the [111] packing orientation ($\Delta\omega$) shifted in order to relax the misfit strain. Finally, the thermal expansion rate of the C_{60} is much larger than that of the GaAs substrate at low temperature. The misfit strain increased and the FWHM was increased again. These behaviours were observed only in the C_{60} monolayer film. Thus, the shifting of the packing orientation worked like a strain relaxation.

4. Summary and conclusions

The existence of a 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 the C_{60}/Cu multilayer film was the same as that of bulk crystals. We also confirmed that the transition temperature shifted to higher temperature under hydrostatic pressure, but the transition temperature of the C_{60} monolayer film under epitaxial strain shifted to lower temperature. The phase transition of the C_{60} monolayer film was somewhat different from that of the C_{60}/Cu multilayer film and that of bulk crystals.

It is rare for C_{60} films and the bulk state to have different phase transitions. In our C_{60}/Cu multilayer film, the phase transition occurred at 260 K (the 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. In the C_{60} film with a high lattice mismatch, the order–disorder phase transition was the same as in bulk crystals. The mismatch order parameter was not observed in the C_{60}/Cu multilayer film. The mismatch was too small to generate misfit dislocations, so the resulting strain had a strong effect on the phase transition in the C_{60} layers in the C_{60} monolayer film on a GaAs(111) substrate.

Acknowledgments

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