

Selective growth of C₆₀ layers on GaAs and their crystalline characteristics

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Abstract

C₆₀ films are grown uniformly and area selectively on GaAs substrates by molecular beam epitaxy. Their crystalline and optical properties are investigated by reflection high energy electron diffraction, X-ray diffraction, and photoluminescence measurements. The C₆₀ films are found to be grown epitaxially on the substrates. The epitaxial relationships are [001]_{GaAs}//[111]_{C60}, [1 $\bar{1}$ 0]_{GaAs}//[1 $\bar{1}$ 0]_{C60} for GaAs (001) substrates and [111]_{GaAs}//[111]_{C60}, [1 $\bar{1}$ 0]_{GaAs}//[1 $\bar{1}$ 0]_{C60} for GaAs (111)B substrates. Area selective epitaxy of C₆₀ on GaAs (111)B substrates is successfully achieved by using SiO₂ mask. Efficient photoluminescence is observed in both uniformly and area selectively grown layers. The observed spectrum appears in the same spectral region as that observed in bulk cubic C₆₀.

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1. Introduction

The discovery of C₆₀ [1] and synthesis on a microscopic scale [2] of solid C₆₀ have stimulated intensive research efforts. The extensive investigation of physical and chemical properties has revealed its application to the fields of superconductivity [3], magnetism [4], and photoconductivity [5]. However, there are few reports investigating the characteristics of C₆₀ in semiconductors [6] and C₆₀/semiconductor heterostructures.

Sakurai et al. [7] investigated the adsorption and film growth of C₆₀ on the various GaAs (001) surface phases by scanning tunneling microscopy. Although they obtained clear epitaxial characteristics, the thicknesses they used are too thin to evaluate the crystal quality. Yoneda et al. investigated crystalline properties of C₆₀ films grown on GaAs (111)A substrates by reflection high energy electron diffraction (RHEED) and X-ray diffraction (XRD) [8]. They grew C₆₀ films by molecular beam epitaxy (MBE) and

obtained epitaxial relationships between C₆₀ and GaAs (111)A. Yao et al. [9] prepared 180-nm-thick C₆₀ films on GaAs (001) substrates by the vacuum vapor deposition technique and studied the crystalline properties by XRD. However, their XRD evaluation was restricted to the 2 θ / ω scan measurement. Therefore, no precise epitaxial relationship between thick C₆₀ films and GaAs substrates is established.

In this paper, we demonstrate the growth of 250-nm-thick C₆₀ films on GaAs (111)B and GaAs (001) substrates by MBE. The growth is performed uniformly and also area selectively. To establish the epitaxial relationships between C₆₀ films and GaAs substrates, the grown samples are investigated by using the grazing incidence X-ray diffraction (XRD-in-plane scan) measurement together with the 2 θ / ω scan measurement. The area selective epitaxial growth of C₆₀ layers on GaAs substrates is successfully performed by using SiO₂ mask.

2. Experimental procedure

C₆₀ films are grown on the GaAs (111)B and (001) substrates by the MBE methods. GaAs substrates are first etched in an alkaline etchant and loaded in the growth chamber. The surface oxide layer is removed by a thermal

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flash at 580 °C. After growing a 20-nm-thick GaAs buffer layer at 500 °C, C₆₀ film growth is performed at substrate temperatures of 100, 150 and 200 °C. C₆₀ (purity 99.5%) powder is used for the C₆₀ source. The beam equivalent pressure of C₆₀ is fixed at 1.0×10^{-7} Torr. Approximately 250-nm-thick C₆₀ films are grown in the growth time of 3 h. The surface structures of the substrates and grown films are investigated by RHEED with incident electron energy of 13 keV. After growth, C₆₀ films are characterized by XRD with Cu-K α radiation ($\lambda = 1.54056$ Å) at room temperature. Both the $2\theta/\omega$ scan and XRD-in-plane scan measurements are performed and compared with each other. The optical characteristics of C₆₀ films are studied by the photoluminescence (PL) measurement performed at 4.2 K using the 488 nm line of Ar ion laser as an excitation source.

3. Results and discussion

The C₆₀ film growth has been performed at substrate temperatures of 100, 150, and 200 °C, because no substantial growth occurs above 250 °C. For all these substrate

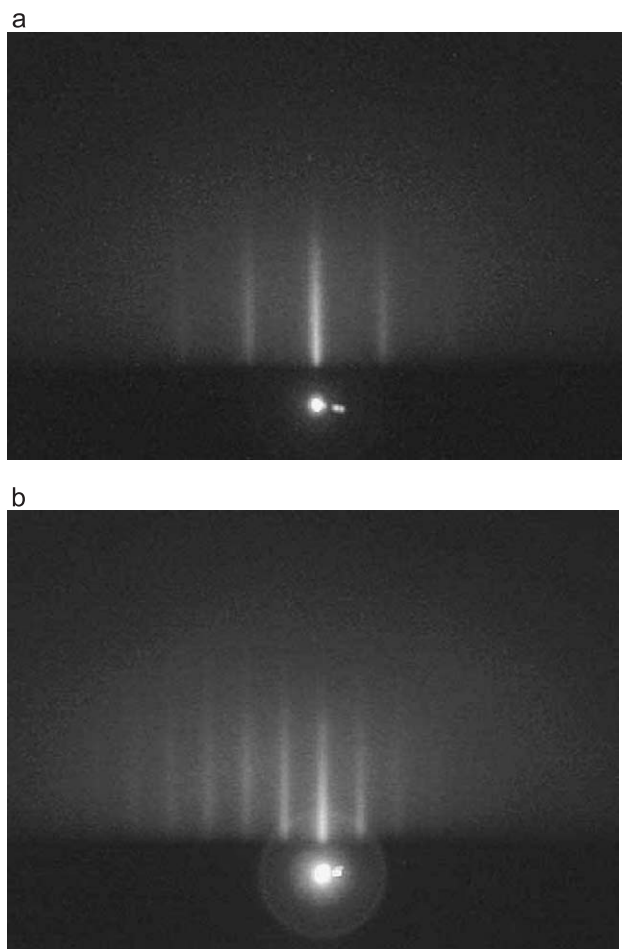


Fig. 1. RHEED patterns of C₆₀ layer surface after 1-h growth at 200 °C on GaAs (111)B: Electron beam along the [112] azimuth (a) and the [110] azimuth (b) of the GaAs substrate.

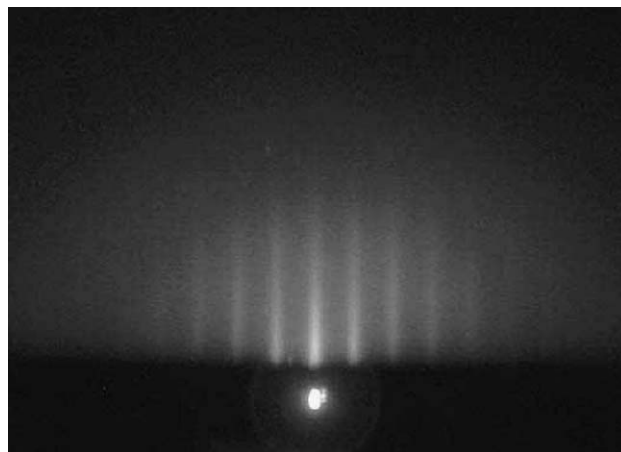


Fig. 2. RHEED pattern of C₆₀ layer surface after 1-h growth at 200 °C on GaAs (001) with the electron beam along the [110] azimuth of the GaAs substrate.

temperatures, we observe no essential change in the RHEED pattern. Fig. 1 shows the RHEED patterns of C₆₀ layer surface after 1-hour growth at 200 °C on GaAs (111)B. The RHEED pattern of Fig. 1a is observed when the incident electron beam azimuth is parallel to the [112] crystal axis of the GaAs substrate, while the pattern shown in Fig. 1b is obtained when the sample is rotated by 30° from the above direction. In the latter, the azimuth is parallel to the [110] axis. The streak intervals in Fig. 1a are approximately $\sqrt{3}$ times larger than those in Fig. 1b, and the diffraction patterns also show a 6-fold symmetry, indicating that the epitaxial orientation is (111). The observed epitaxial relationships are $[11\bar{2}]_{\text{GaAs}}//[11\bar{2}]_{\text{C}_{60}}$ and $[1\bar{1}0]_{\text{GaAs}}//[1\bar{1}0]_{\text{C}_{60}}$. Fig. 2 shows the RHEED pattern of C₆₀ layer grown on a GaAs (001) substrate with an incident beam azimuth parallel to the [110] direction of the GaAs substrate. The RHEED pattern of Fig. 2 shows a 6-fold symmetry. Therefore, the C₆₀ epitaxial layer is oriented the [111] direction as with the films grown on (111)B surface. The observed streak intervals coincide well with the (110) plane spacing of cubic C₆₀, indicating that $[1\bar{1}0]_{\text{GaAs}}//[1\bar{1}0]_{\text{C}_{60}}$.

From the observed streak intervals in both C₆₀ layers, the lattice constant of cubic C₆₀ is calculated to be approximately 14 Å that coincides well with the lattice constant of bulk cubic C₆₀ crystal [10]. Since the RHEED patterns are very sharp and clear, the crystal quality of grown C₆₀ layers is fairly good.

To investigate the crystalline quality more precisely, XRD measurements are performed. Fig. 3 shows the $2\theta/\omega$ diffraction patterns observed on the C₆₀ layers grown on (111)B and (001) GaAs substrates. In both samples, only the (111) diffraction is observed from the C₆₀ film, implying that the films are (111) oriented single crystals with a fcc structure. From 2θ value of 10.85° at the (111) peak, the cubic lattice constant of the film is calculated to be approximately 14.1 Å. In order to confirm the epitaxial relationships between C₆₀ films and GaAs substrates, the XRD-in-plane scan

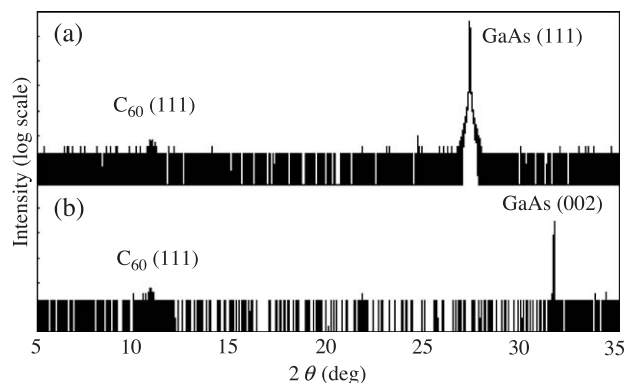


Fig. 3. X-ray $2\theta/\omega$ diffraction patterns of the C₆₀ films on GaAs (111)B (a) and GaAs (001) (b).

measurements are carried out. The XRD-in-plane scan pattern along the $[1\bar{1}0]$ direction of a GaAs (111)B substrate is demonstrated in Fig. 4a, and that of a GaAs (001) substrate in Fig. 4b. Fig. 4a exhibits the (220) and (440) diffraction, suggesting that the $[1\bar{1}0]$ directions of the C₆₀ and GaAs are parallel. The weak (422) diffraction peak may indicate a small amount of rotating domain. In Fig. 4b, only the (422) diffraction peak is observed, indicating that the $[11\bar{2}]$ directions of the C₆₀ are parallel to the $[1\bar{1}0]$ directions of GaAs. Since this peak has a 6-fold symmetry and the GaAs (220) peak has a 4-fold symmetry, this result again shows the $[1\bar{1}0]$ directions of the C₆₀ and GaAs are parallel. These results agree well with the results by RHEED measurements. Since no additional diffraction peaks are observed in the layers grown on (001) GaAs, the crystal quality of C₆₀ films grown on GaAs (001) substrates is probably better than those grown on GaAs (111)B substrates.

Next, we discuss the results of area selective epitaxy of C₆₀. A 30-nm-thick SiO₂ film is deposited on the GaAs (111)B substrate by a conventional sputtering technique. By using photolithography and wet chemical etching methods, SiO₂ masks with 2 μm diameter hole array (anti-dot structures) with 1 μm spacing are fabri-

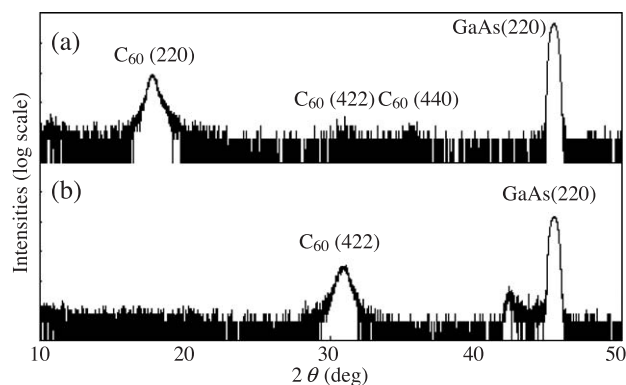


Fig. 4. XRD-in-plane scanning patterns along the $[1\bar{1}0]$ direction of the C₆₀ films on GaAs (111)B (a), and GaAs (001) (b).

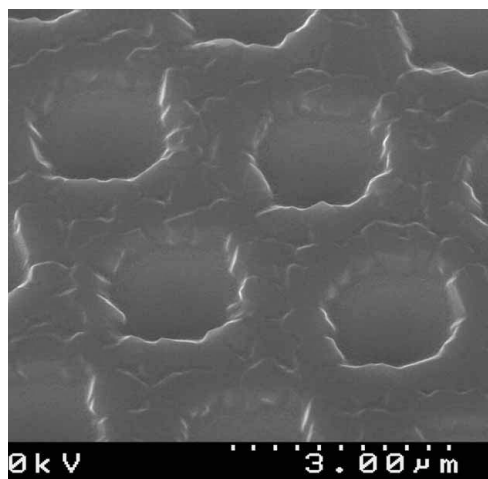


Fig. 5. SEM image of the C₆₀ hole array structure on SiO₂ masked substrate grown at 200 °C.

cated. After the similar process as used in the uniform layer growth, 200–300 nm thick C₆₀ layers are grown at 100, 150 and 200 °C. The grown structures are evaluated by scanning electron microscopy (SEM) and micro-photoluminescence (micro-PL) measurements. Fig. 5 shows a SEM micrograph of the grown structure on the SiO₂ masked substrate at 200 °C. Although the C₆₀ layers are grown even on the SiO₂ mask at 100 °C and 150 °C, the C₆₀ growth occurs only on the GaAs open areas at 200 °C. In addition, the C₆₀ layer growth on SiO₂ mask at temperatures of 100 and 150 °C exhibits no good crystal quality. Thus, the area selective growth of C₆₀/GaAs is successfully achieved at 200 °C.

PL measurement is performed for both uniformly and area selectively grown C₆₀ layers. Both layers show a similar spectrum (Fig. 6). The 817 and 830 nm peaks correspond to the edge emission and acceptor related emission both from the GaAs substrate, while the other peaks around 730 nm are

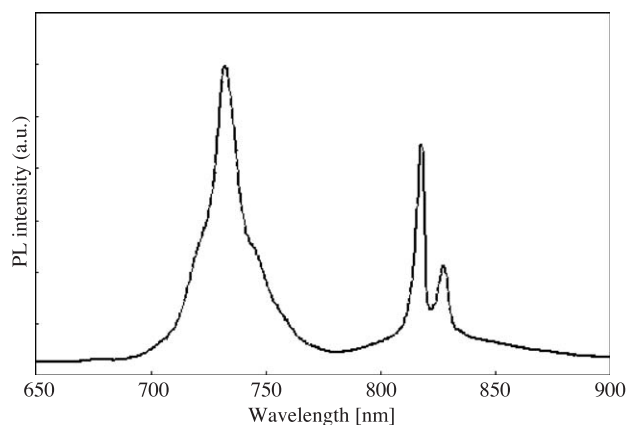


Fig. 6. PL spectrum of a C₆₀ film measured at 4.2 K. The sample is excited by the line 488 nm of an Ar laser.

caused by the C_{60} film. The latter peaks coincide well with those observed in bulk cubic C_{60} crystals, suggesting that the C_{60} films grown in this experiment are crystalline C_{60} . Micro-PL measurement is also performed for the area selectively grown hole array C_{60} samples. The observed PL pattern clearly exhibits that the bright PL region occurs only in the GaAs open areas where C_{60} layers are grown, indicating that the C_{60} layers grown area selectively have also high optical quality. The C_{60} layers grown SiO_2 mask, which occur when the substrate temperatures are 100 or 150 °C, exhibit very weak PL compared with those of open GaAs area.

4. Conclusions

High quality (111) oriented C_{60} single crystal films are grown on GaAs (111)B and GaAs (001) by solid source molecular beam epitaxy. The lattice constant of the grown C_{60} films calculated from RHEED and XRD results coincides well with that of bulk C_{60} crystal. The XRD-in-plane scan results indicate that the $[1\bar{1}0]$ directions of the C_{60} and GaAs are parallel. The XRD-in-plane scan measurement to C_{60} layers grown on GaAs (111)B shows an additional diffraction peak (422) implying an existence of rotating domains. However, no such peaks are observed in the layers grown on GaAs (001). Thus, the C_{60} films grown on GaAs (001) substrates may have higher epitaxial quality. Area selective epitaxy of

C_{60} on GaAs (111)B substrates masked by SiO_2 is successfully achieved at 200 °C.

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