# Selective growth of $C_{60}$ layers on GaAs and their crystalline characteristics

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## Abstract

$C_{60}$ 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 $C_{60}$ 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 $C_{60}$ on GaAs (111)B substrates is successfully achieved by using $SiO_2$ 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 $C_{60}$.

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**Keywords**: $C_{60}$ films, GaAs, MBE, RHEED, X-ray diffraction, Area selective epitaxy

## 1. Introduction

The discovery of $C_{60}$ [1] and synthesis on a microscopic scale [2] of solid $C_{60}$

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 $C_{60}$ in semiconductors [6] and $C_{60}$/semiconductor heterostructures.

Sakurai et al. investigated the adsorption and film growth of $C_{60}$ on the various GaAs (001) surface phases by scanning tunneling microscopy [7]. 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 $C_{60}$ films grown on GaAs (111)A substrates by reflection high energy electron diffraction (RHEED) and X-ray diffraction (XRD) [8]. They grew $C_{60}$ films by molecular beam epitaxy (MBE), and obtained epitaxial relationships between $C_{60}$ and GaAs (111)A. Yao et al. prepared 180nm-thick $C_{60}$ films on GaAs (001) substrates by the vacuum vapor deposition technique and studied the crystalline properties by XRD [9]. However, their XRD evaluation was restricted to the $2\theta/\omega$ scan measurement. Therefore, no precise epitaxial relationship between thick $C_{60}$ films and GaAs substrates is established.

In this paper, we demonstrate the growth of 250nm-thick $C_{60}$ 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 $C_{60}$ 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 $2\theta/\omega$ scan measurement.

The area selective epitaxial growth of $C_{60}$ layers on GaAs substrates is successfully performed by using $SiO_2$ mask.

## 2. Experimental procedure

$C_{60}$ 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 flash at 580°C. After growing a 20-nm-thick GaAs buffer layer at 500°C, $C_{60}$ film growth is performed at substrate temperatures of 100°C, 150°C, and 200°C. $C_{60}$ (purity 99.5%) powder is used for the $C_{60}$ source. The beam equivalent pressure of $C_{60}$ is fixed at $1.0\text{x}10^{-7}$ Torr. Approximately 250nm-thick $C_{60}$ films are grown in the growth time of 3 hours. The surface structures of the substrates and grown films are investigated by RHEED with incident electron energy of 13 keV. After growth, $C_{60}$ films are characterized by XRD with Cu-K$\alpha$ radiation ($\lambda$= 1.54056Å) 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 $C_{60}$ 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 $C_{60}$ film growth has been performed at substrate temperatures of 100°C, 150°C, and 200°C, because no substantial growth occurs above 250°C. For all these substrate temperatures, we observe no essential change in the RHEED pattern. Fig. 1 shows the RHEED patterns of $C_{60}$ layer surface after 1-hour growth at 200°C on GaAs (111)B. The RHEED pattern of Fig. 1(a) is observed when the incident electron beam azimuth is parallel to the $[11\bar{2}]$ crystal axis of the GaAs substrate, while the pattern shown in Fig. 1(b) is obtained when the sample is rotated by 30° from the above direction. In the latter, the azimuth is parallel to the $[1\bar{1}0]$ axis. The streak intervals in Fig. 1(a) are approximately $\sqrt{3}$ times larger than those in Fig. 1(b), and the diffraction patterns also show a 6-fold symmetry, indicating that the epitaxial orientation is (111). The observed epitaxial relationships are $[11\bar{2}]_{GaAs} // [11\bar{2}]_{C60}$ and $[1\bar{1}0]_{GaAs} // [1\bar{1}0]_{C60}$. Fig. 2 shows the RHEED pattern of $C_{60}$ layer grown on a GaAs (001) substrate with an incident beam azimuth parallel to the $[1\bar{1}0]$ direction of the GaAs substrate. The RHEED pattern of Fig. 2 shows a 6-fold symmetry. Therefore, the $C_{60}$ 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 $C_{60}$, indicating that $[1\bar{1}0]_{GaAs} // [1\bar{1}0]_{C60}$.

From the observed streak intervals in both $C_{60}$ layers, the lattice constant of cubic $C_{60}$ is calculated to be approximately 14 Å that coincides well with the lattice constant of bulk cubic $C_{60}$ crystal [10]. Since the RHEED patterns are very sharp and clear, the crystal quality of grown $C_{60}$ layers is fairly good.

To investigate the crystalline quality more precisely, XRD measurements are performed. Fig. 3 shows the 2θ/ω diffraction patterns observed on the $C_{60}$ layers grown on (111)B and (001) GaAs substrates. In both samples, only the (111) diffraction is observed from the $C_{60}$ 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 14.1Å. In order to confirm the epitaxial relationships between $C_{60}$ films and GaAs substrates, the XRD-in-plane scan measurements are carried out. The XRD-in-plane scan pattern along the $\left[1\bar{1}0\right]$ direction of a GaAs (111)B substrate is demonstrated in Fig. 4(a), and that of a GaAs (001) substrate in Fig. 4(b). Fig. 4(a) exhibits the (220) and (440) diffraction, suggesting that the $\left[1\bar{1}0\right]$ directions of the $C_{60}$ and GaAs are parallel. The weak (422) diffraction peak may indicate a small amount of rotating domain. In Fig. 4(b), only the (422) diffraction peak is observed, indicating that the $\left[11\bar{2}\right]$ directions of the $C_{60}$ are parallel to the $\left[1\bar{1}0\right]$ 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 $\left[1\bar{1}0\right]$ directions of the $C_{60}$ 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 $C_{60}$ 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 $C_{60}$. A 30-nm-thick $SiO_2$ film is deposited on the GaAs (111)B substrate by a conventional sputtering technique.

By using photolithography and wet chemical etching methods, $SiO_2$ masks with 2μm diameter hole array (anti-dot structures) with 1μm spacing are fabricated. After the similar process as used in the uniform layer growth, 200-300 nm thick $C_{60}$ layers are grown at 100°C, 150°C, 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 $SiO_2$ masked substrate at 200°C. Although the $C_{60}$ layers are grown even on the $SiO_2$ mask at 100°C and 150°C, the $C_{60}$ growth occurs only on the GaAs open areas at 200°C. In addition, the $C_{60}$ layer growth on $SiO_2$ mask at temperatures of 100°C and 150°C exhibits no good crystal quality. Thus, the area selective growth of $C_{60}$/GaAs is successfully achieved at 200°C.

PL measurement is performed for both uniformly and area selectively grown $C_{60}$ layers. Both layers show a similar spectrum (Fig. 6). The 817 nm 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 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°C 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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## Figure Captions

Fig. 1 RHEED patterns of $C_{60}$ layer surface after 1-hour growth at 200°C on GaAs (111)B: Electron beam along the $[11\bar{2}]$ azimuth (a) and the $[1\bar{1}0]$ azimuth (b) of the GaAs substrate.

Fig. 2 RHEED pattern of $C_{60}$ layer surface after 1-hour growth at 200°C on GaAs (001) with the electron beam along the $[1\bar{1}0]$ azimuth of the GaAs substrate.

Fig. 3 X-ray $2\theta/\omega$ diffraction patterns of the $C_{60}$ films on GaAs (111)B (a) and GaAs (001) (b).

Fig. 4 XRD-in-plane scanning patterns along the $[1\bar{1}0]$ direction of the $C_{60}$ films on GaAs (111)B (a), and GaAs (001) (b).

Fig.5 SEM image of the $C_{60}$ hole array structure on $SiO_2$ masked substrate grown at 200°C.

Fig. 6 PL spectrum of a $C_{60}$ film measured at 4.2K. The sample is excited by the line 488nm of an Ar laser.

Fig. 1a

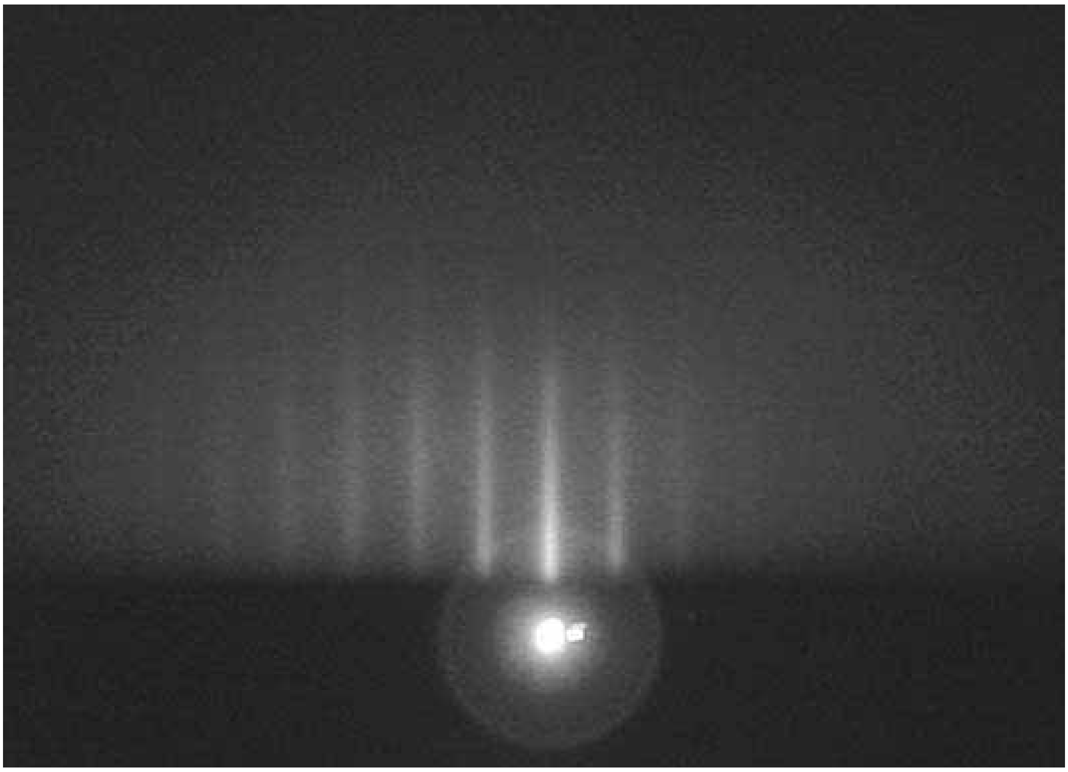

Fig. 1b

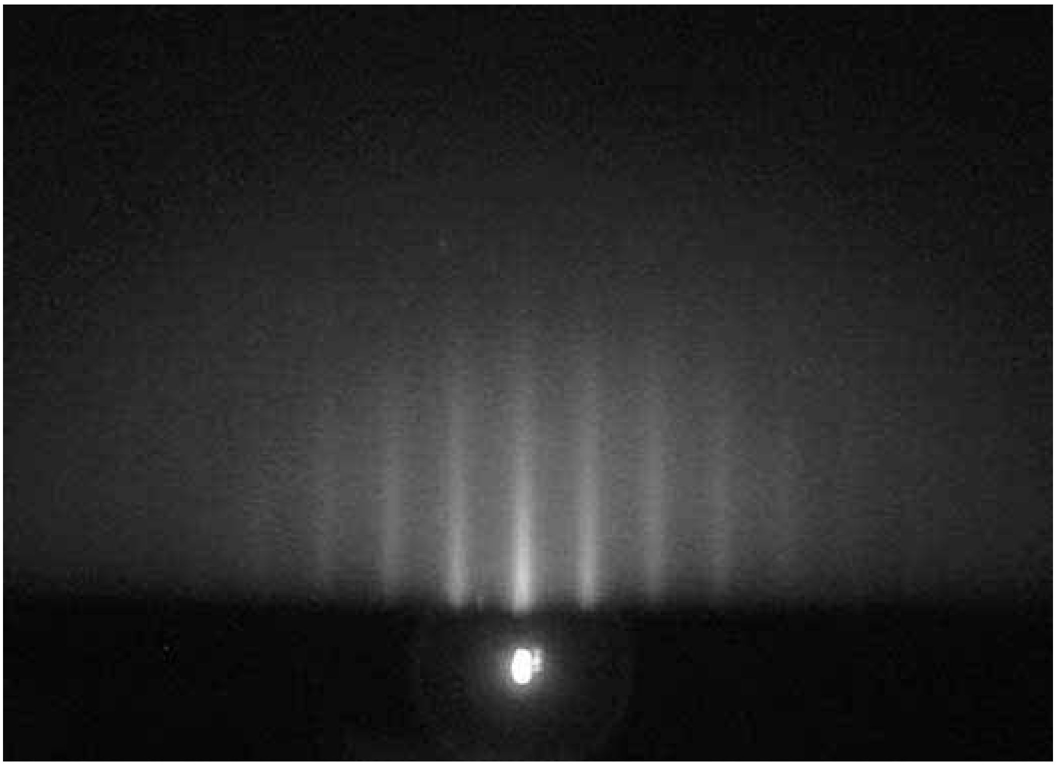

Fig. 2

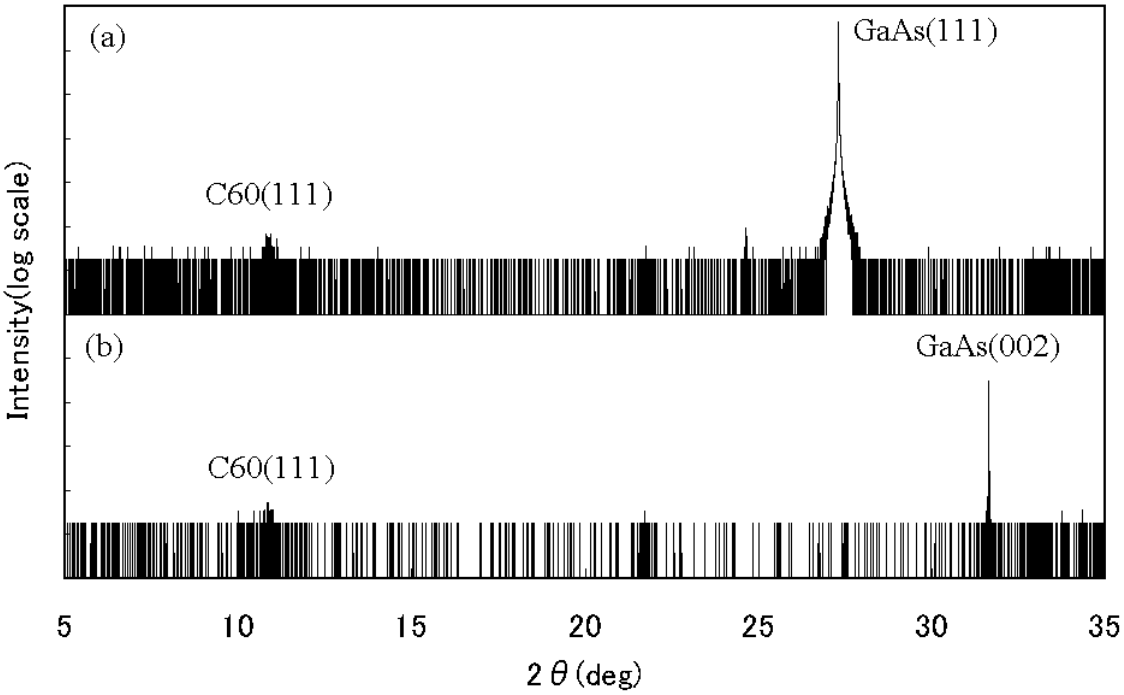
(a)
GaAs(111)
C60(111)
(b)
GaAs(002)
C60(111)
Intensity(log scale)
5
10
15
20
25
30
35
2 θ (deg)

Fig. 3

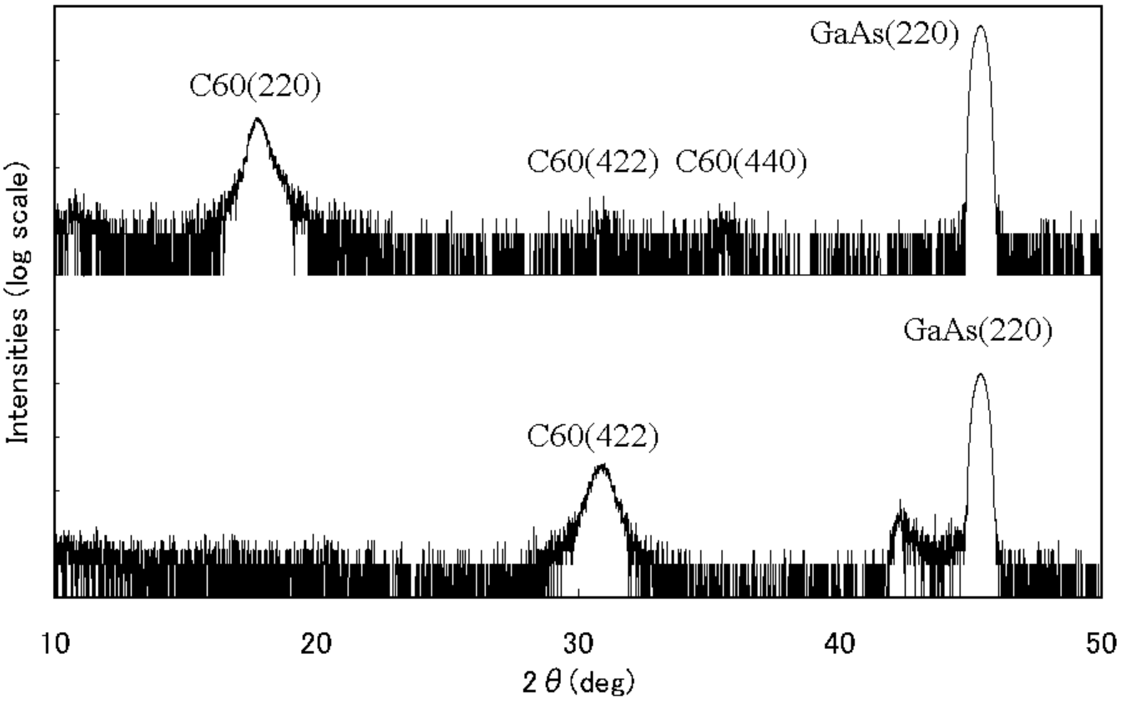
GaAs(220)
C60(220)
C60(422)
C60(440)
Intensities (log scale)
GaAs(220)
C60(422)
10
20
30
40
50
2θ(deg)

Fig. 4

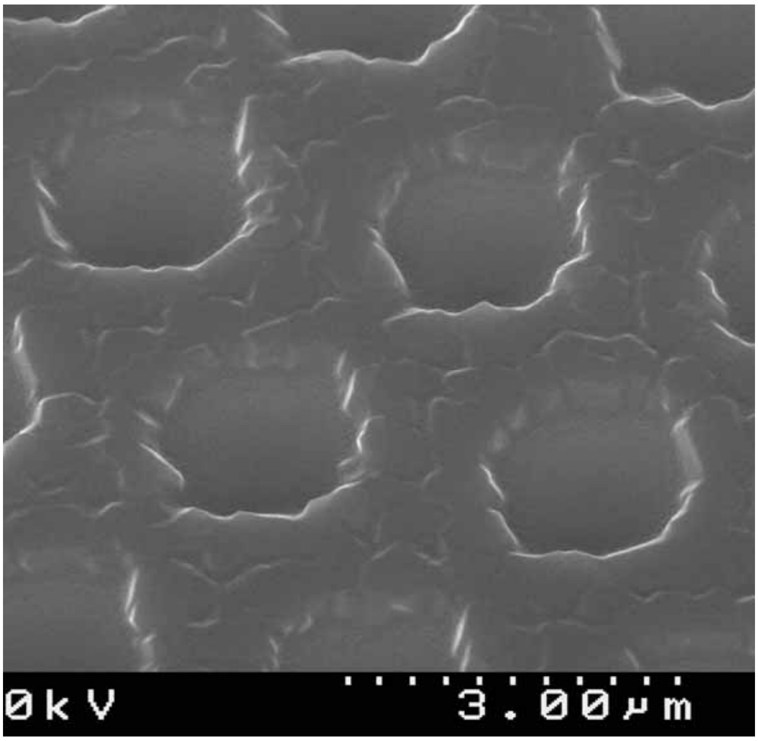
0kV
3.00μm

Fig. 5

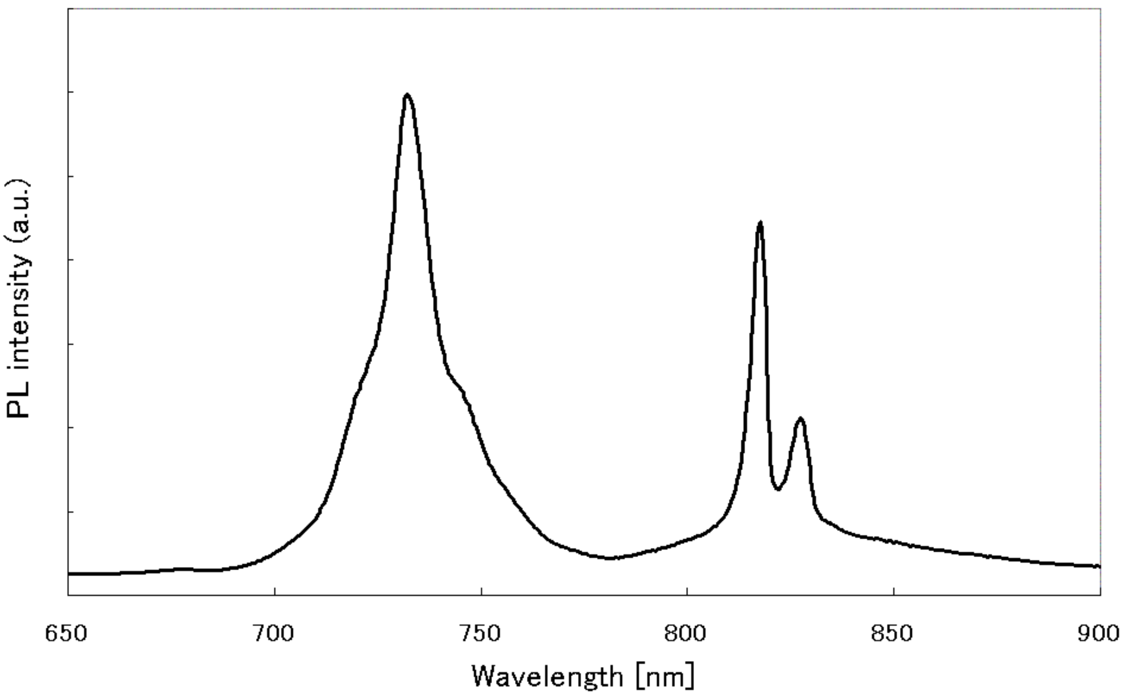

Fig. 6