RHEED intensity oscillation of C₆₀ layer epitaxial growth

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Abstract

Intensity oscillations of reflection high-energy electron diffraction are observed during a C₆₀ layer epitaxial growth on GaAs (111)B, (114)A and (114)B substrates. Frequencies of the oscillations coincide well with growth rates of C₆₀ layers, suggesting that C₆₀ layers grow by layer-by-layer growth mode as with GaAs and other semiconductor materials. Anomalous oscillations are observed in the initial stage of a C₆₀ layer growth on GaAs (111)B surface with (2x2) reconstruction. These oscillations indicate that the C₆₀ first-layer growth is completed at approximately half monolayer coverage. This phenomenon is explained by a model that C₆₀ adsorption sites are limited due to As-trimers adsorbed on GaAs surface. Clear oscillations are observed during a C₆₀ layer growth on GaAs (114)A substrate, and X-ray diffraction peaks of the layer are sharp. In contrast, no oscillation is detected during the growth on the (114)B substrate, and these layers exhibit poor X-ray diffraction characteristics. Thus, the C₆₀ epitaxial layer growth on GaAs substrates is strongly affected

by the GaAs surface reconstruction and polarity.

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1. Introduction

Extensive investigations have been done for the physical and chemical properties of C_{60} crystals, and unique potentialities of C_{60} such as superconductivity [1] and photoconductivity have been revealed. C_{60} molecules are highly symmetric and crystallize into a face-centered cubic structure on crystalline substrates such as Si and GaAs, in spite of the large lattice mismatch between C_{60} and the substrates [2-7]. Reflection high-energy electron diffraction (RHEED) is used to observe growth and surface conditions of semiconductor films, and its specular beam intensity oscillation enables the dynamic process of epitaxial growths to be investigated [8]. Organic materials tend to be decomposed by electron beam irradiations [9]. But C_{60} molecules have a stable structure, and the C_{60} crystal growth may not be influenced by RHEED measurement. In the present work, to investigate the growth mechanism of C_{60} layers, we observe RHEED intensity oscillations during C_{60} epitaxial growth on GaAs (111)B substrates. Frequencies of the oscillations proportionally increase with the C_{60} flux, and coincide well with the growth rates of C_{60} layers obtained from the film thickness. This suggests that C_{60} layers grow with

layer-by-layer growth mode as with growths of GaAs and other semiconductor materials. In order to investigate C_{60} nucleation process more precisely, C_{60} layer growth on GaAs (114)A and (114)B is performed because the surface symmetry of the (114) substrates is different from that of the (111) substrates. The RHEED intensity oscillations are observed during the C_{60} layer growth on GaAs (114)A. In contrast, no periodic variation of RHEED intensity is detected during the growth on GaAs (114)B. In addition, the resulting layers on the (114)B substrate show poor crystal quality. This suggests that the nucleation of C_{60} layer growth occurs much more easily on the A surface than on the B surface.

2. Experimental Procedure

C_{60} layers are grown on GaAs (111)B, (114)A and (114)B substrates by using solid source molecular beam epitaxy (MBE). GaAs substrates are first etched in an alkaline etchant, and loaded in the growth chamber. Native oxide layers of GaAs surfaces are removed by a thermal flash at 580 °C in As_4 atmosphere. After growing a GaAs buffer layer at 500 °C, the substrate temperature is lowered to between 70 °C and 200 °C. Then, C_{60} layer growth is performed. High purity (99.5%) C_{60} powder is used for the C_{60} source. C_{60} beam equivalent pressure (BEP) is varied between 4.0×10^{-7} Torr and 1.4×10^{-6} Torr which correspond to the C_{60} flux of 0.1 monolayer/s (ML/s) and 0.35 ML/s. RHEED measurements are performed with an electron beam along the $\langle 011 \rangle$ azimuth of the GaAs substrates, and the incident electron beam angle is fixed at 1°. Intensities of the RHEED specular reflection

are detected by a conventional video camera system, and the intensity oscillations are analyzed by a personal computer. After a C₆₀ layer growth, the crystalline quality of the films is investigated by X-ray diffraction (XRD) with Cu-K α radiation. Both the 2 θ/ω scan and XRD pole-figure measurements are performed and compared with the results of the RHEED intensity oscillations.

3. Results and Discussion

RHEED patterns of C₆₀ layers grown on GaAs (111)B with (2x2) structure show clear streak, and indicate that the C₆₀ epitaxial orientation is [111] direction [6]. The observed streak intervals of the patterns indicate that the lattice constant of epitaxial cubic C₆₀ films coincides well with the value of bulk cubic C₆₀ crystals.

Fig. 1 shows the intensity of the specular beam in the RHEED pattern of a C₆₀ layer growth at 200 °C with C₆₀ BEP of 1.4x10⁻⁶ Torr on GaAs (111)B surface with (2x2) structure. The lateral axis denotes a deposition thickness in monolayers. After a few monolayer depositions, a regular RHEED intensity oscillation is observed. Frequencies of the RHEED intensity oscillations are confirmed to proportionally increase with the C₆₀ BEP, and coincide well with growth rates of C₆₀ layers obtained from the film thickness. Therefore, the RHEED intensity oscillation during a C₆₀ layer growth may be caused by repeating surface roughening and smoothening during the formation of a single complete layer, i.e., C₆₀ layers grow with layer-by-layer growth mode [8].

In the initial stage of the C_{60} layer growth on the (2x2) surface of GaAs (111)B substrate, anomalous behavior appears in the RHEED intensity variation. A clear shoulder is observed after 0.5 ML deposition as marked by an arrow. The succeeding intensity peaks appear at 1.5 ML, 2.5 ML and so on. This anomalous oscillation suggests a peculiar configuration of the first-layer C_{60} molecules on the (111)B surface with (2x2) structure. Fig. 2 shows adsorption models of the C_{60} first-layer on GaAs (111)B surface with (2x2) reconstruction. Since the surface of the (2x2) structure has a periodic lattice structure by adsorbed As-trimers [10], C_{60} adsorption sites should, therefore, be limited due to a steric structure between C_{60} molecules and As-trimers. In this case, the density of C_{60} adsorption sites is estimated to be approximately 40% (Fig. 2a) or 50% (Fig. 2b) of the full coverage. Therefore, the first-layer growth should be completed at around 0.5 ML C_{60} deposition. The shoulder of 0.5 ML deposition probably corresponds to this event. The first peak appears at 1.5 ML deposition, indicating that a C_{60} regular layer growth takes place after first-layer deposition.

In order to verify the C_{60} first-layer configuration model on the (111)B with (2x2) surface, RHEED intensity oscillation is also investigated during the growth of C_{60} layers on the (111)B surface with $(\sqrt{19} \times \sqrt{19})$ structure. Under As-rich conditions, the surface reconstruction of GaAs (111)B substrates shows (2x2) structure. On the other hand, under Ga-rich conditions, the surface structure is converted to $(\sqrt{19} \times \sqrt{19})$ structure with hexagonal rings. This $(\sqrt{19} \times \sqrt{19})$ structure is prepared by annealing the (2x2) structure at 500 °C in

UHV, and is confirmed by RHEED observations [10]. Fig. 3 shows RHEED intensity oscillations during a C_{60} layer growth at 70 °C with C_{60} BEP of 4.0×10^{-7} Torr on the $(\sqrt{19} \times \sqrt{19})$ structure, and the inset shows the detail of the intensity oscillations at the C_{60} initial growth. After a few monolayer depositions, regular RHEED intensity oscillations are observed as with the C_{60} layer growth on the (2x2) structure. In the initial stage of the growth, intensity peaks are found to appear at 1.7 ML, 2.7 ML and so on. These results imply that the C_{60} first-layer configuration on the $(\sqrt{19} \times \sqrt{19})$ structure is different from those on the (2x2) structure. Fig. 4 shows adsorption models of the C_{60} first-layer on GaAs (111)B surface with $(\sqrt{19} \times \sqrt{19})$ structure. The $(\sqrt{19} \times \sqrt{19})$ reconstruction has periodic structures of hexagonal rings with $\pm 6.6^\circ$ rotation with respect to the [2-1-1] direction [10]. The size of the space around the hexagonal rings is the same as that of C_{60} molecules, and the C_{60} molecules may be adsorbed on the space shown in Fig.4. The density of C_{60} molecules shown in Fig. 4 is estimated to be 66% of the full coverage. If the first-layer growth is completed at around 0.7 ML C_{60} deposition based on the above discussion, the first prominent RHEED intensity peak at 1.7 ML deposition corresponds to the completing of the 2nd monolayer growth.

In this case, since the $(\sqrt{19} \times \sqrt{19})$ reconstruction has two type arrangements with 13° rotation between them, the C_{60} first-layer arrangement should have two domains with 13° rotation as shown in Fig. 4. To investigate crystalline properties of C_{60} layers, XRD pole-figure measurements are performed. Fig. 5 shows the XRD ϕ -scan patterns of C_{60} layers on GaAs (111)B with (2x2) reconstruction and $(\sqrt{19} \times \sqrt{19})$ reconstruction with C_{60} (111)

diffraction ($2\theta=10.83^\circ$). The C_{60} layer on the ($\sqrt{19}\times\sqrt{19}$) structure is confirmed to have two domains with 13° rotation between them, strongly supporting the adsorption models shown in Fig. 4.

As described above, a C_{60} first-layer configuration is decided by a steric structure between C_{60} molecules and surface reconstruction structures, and the flexibility of the first-layer arrangements may make a strain due to a lattice mismatch between C_{60} and substrates relieved. Therefore, a C_{60} regular layer growth with high-crystalline quality takes place after a C_{60} first-layer deposition.

Next, to investigate the effect of substrates polarity on the C_{60} epitaxial growth mechanism, we perform C_{60} layer growth on GaAs (114)A and (114)B substrates. GaAs (114) surface is inclined by 19.5° against the (001) surface in the $\langle 110 \rangle$ direction. The size of the rectangular (1x1) unit cell is $4\text{\AA}$ and $17\text{\AA}$ [11]. Then, the surface symmetry structure is complex compared with (111) and (001) surfaces. Fig. 6 shows the intensity variation of the specular beam during a C_{60} growth at 70°C with C_{60} BEP of 4.0×10^{-7} Torr on GaAs (114)A and (114)B substrates. Clear RHEED intensity oscillation is observed on the (114)A substrate. In the initial stage of the C_{60} layer growth on the (114)A substrate, intensity peak appears at 0.3ML deposition. During the C_{60} first-layer deposition, the RHEED patterns always show halo patterns. Therefore, the peak at 0.3ML deposition is caused by the halo patterns, and the peak doesn't mean a complete layer. After the first-layer deposition, the diffraction patterns of C_{60} layer appear clearly, and the intensity peak at 1.0ML indicates that

a close-packed C_{60} layer growth takes place from the first-layer. On the other hand, no oscillation is detected for the growth on GaAs (114)B substrate. This result implies that the C_{60} growth mode on GaAs (114)B substrate is different from that on GaAs (114)A substrate.

To compare the crystalline quality of C_{60} films on the (114)A and (114)B substrates, XRD measurements are performed. XRD $2\theta/\omega$ scan shows that only (hhh) diffractions are observed from the C_{60} layers on both substrates, indicating that the both films are [111] oriented crystals. Fig. 7 shows the XRD ϕ -scan patterns with $\psi = 70.5^\circ$ and C_{60} (111) diffraction ($2\theta=10.83^\circ$). The C_{60} layer on GaAs (114)A substrate have 12 diffraction peaks, but their diffraction peaks are relatively sharp. This indicates a clear in-plane epitaxial relationship between C_{60} layer and the (114)A substrates. In contrast, the diffraction peaks of C_{60} layer on GaAs (114)B substrates are very weak and broad. The growth orientation of the C_{60} layer on the (114)B substrate is confirmed to be [111], suggesting that C_{60} layers on (114)B substrate have many rotational domains.

Now, we discuss the difference of C_{60} nucleation on the substrate surface polarity, i.e., the A surface and B surface. The binding energy between C_{60} molecules and Ga atoms is expected to be higher than that between C_{60} molecules and As atoms [12]. For C_{60} layer growth on GaAs (114)A substrates, C_{60} nucleation occurs on the dangling bonds of Ga, and the epitaxial orientation between C_{60} crystal nuclei and GaAs (114)A substrate is defined clearly due to the strong bonding between C_{60} molecules and Ga atoms. In contrast, since the binding energy between C_{60} molecules and As atoms is weak, the epitaxial orientation

relationship between C_{60} crystal nuclei and the (114)B substrate may be less pronounced. Therefore, many rotational domains occur in the C_{60} layer growth on the B surface, and the surface flatness may be inferior from the initial stage.

4. Conclusions

Clear RHEED intensity oscillation is successfully observed during epitaxial growths of C_{60} layers on GaAs substrates. Frequencies of the oscillation proportionally increase with C_{60} BEP, and coincide well with the growth rates of C_{60} layers. Therefore, C_{60} layers grow with layer-by-layer growth mode as with the growths of GaAs and other semiconductor materials. The initial C_{60} layer growth on GaAs substrates is found to be affected strongly by the reconstruction of the substrate surface. For example, the first-layer growth on the (111)B surface with (2x2) reconstruction terminates at the deposition of approximately 0.5 ML of C_{60} . This result is understood by considering the surface structure of the (2x2) reconstruction; The As-trimers on GaAs (111)B surface provide useful sites for C_{60} adsorption. The density of the sites in this case is approximately 50% of the full coverage, and therefore, the first-layer growth is completed with 0.5 ML deposition. Clear oscillations are observed during a C_{60} layer growth on GaAs (114)A substrate, and X-ray diffraction peaks of the layer are relatively sharp. Although the X-ray diffraction measurements indicate the existence of rotational domains, the epitaxial orientations between C_{60} crystal nuclei and the (114)A substrates are defined clearly due to the strong bonding between C_{60} molecules and Ga

atoms. In contrast, no oscillation is detected for the growth on the (114)B substrate. The X-ray diffraction peaks of the resulting layers are very weak and broad, indicating poor crystal quality of C₆₀ layers grown on the (114)B substrate.

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Figure captions

Fig. 1. RHEED intensity oscillation during a C₆₀ growth at 200 °C with C₆₀ BEP of 1.4x10⁻⁶ Torr on GaAs (111)B surface with (2x2) structure as a function of C₆₀ deposition thickness in monolayers.

Fig. 2. Adsorption models of the C₆₀ first-layer on GaAs (111)B surface with (2x2) structure.

Fig. 3. RHEED intensity oscillation during a C₆₀ growth at 70 °C with C₆₀ BEP of 4.0x10⁻⁷ Torr on GaAs (111)B surface with (√19x√19) structure. The inset shows the detail of the intensity oscillations at the C₆₀ initial growth.

Fig. 4. Adsorption models of the C₆₀ first-layer on GaAs (111)B surface with (√19x√19) structure.

Fig. 5. XRD ϕ scan patterns of C_{60} films on GaAs (111)B surface with (2x2) structure and ($\sqrt{19}\times\sqrt{19}$) structure with C_{60} (111) diffraction ($2\theta=10.83^\circ$).

Fig. 6. RHEED intensity oscillation during a C_{60} growth at 70 °C with C_{60} BEP of 4.0×10^{-7} Torr on GaAs (114)A and (114)B substrates.

Fig. 7. XRD ϕ scan patterns of C_{60} films on GaAs (114)A and (114)B substrates with C_{60} (111) diffraction ($2\theta=10.83^\circ$).

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