Investigation of C_{60} Epitaxial Growth Mechanism on GaAs Substrates

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Intensity oscillations of reflection high-energy electron diffraction are observed during epitaxial growth of a C_{60} layer on GaAs (111)B, (111)A, and (001) substrates. The frequencies of the oscillations coincide well with the growth rates of C_{60} layers, suggesting that C_{60} layers grow by repeating nucleation and step-flow growth mode, as is the case with GaAs and other semiconductor materials. Anomalous oscillations are observed in the initial stage of C_{60} layer growth on a GaAs (111)B surface with (2x2) structure. These oscillations indicate that the growth of the first C_{60} layer is completed at the point of approximately 0.5 monolayer coverage by C_{60} molecules. This phenomenon is explained by a model in which C_{60} adsorption sites are limited by As trimers adsorbed on the GaAs (111)B surface. A similar relationship between C_{60} adsorption and surface reconstruction is observed on (001) GaAs substrates, i.e., the first C_{60} layer on the (2x4) surface is terminated at approximately 0.5 monolayer coverage, while full coverage is needed of the c(4x4) surface. These observed results

are strongly supported by the reported results of scanning tunnel microscopy.

1. Introduction

Extensive investigations have been carried out on the physical and chemical properties of C_{60} and have revealed its potential for use in superconductivity and photoconductivity.1) C_{60} molecules are highly symmetric and crystallize into a face-centered cubic structure on crystalline substrates such as Si and GaAs, despite of the large lattice mismatch between C_{60} and the substrates.2-7) Reflection high-energy electron diffraction (RHEED) is used to observe the growth and surface conditions of semiconductor films, and RHEED intensity oscillation enables dynamic effects to be investigated.8) RHEED intensity oscillation during C_{60} layer growth on mica (001) was observed using a specially designed system.9) In this work, to investigate the growth mechanism of C_{60} layers, we observe RHEED intensity oscillations during C_{60} epitaxial growth on GaAs substrates by conventional molecular beam epitaxy (MBE) using a RHEED system.10) Clear RHEED intensity oscillations have been successfully observed. The frequencies of the oscillations increase proportionally with the C_{60} flux and coincide well with the growth rates of C_{60} layers. This suggests that C_{60} layers grow by repeating nucleation and step-flow growth mode, as has been observed with growth of GaAs and other semiconductor materials.

2. Experimental Procedure

C_{60} layers are grown on GaAs (111)B, (111)A, and (001) substrates by using solid source MBE with a background pressure of 10^{-9} Torr. GaAs substrates are first etched in an alkaline etchant and loaded in the growth chamber. Native oxide layers on GaAs surfaces are removed by a thermal flash annealing at 580 °C in an As_4 atmosphere. After growing a GaAs buffer layer at 500 °C, the substrate temperature is lowered to between 70 and 200 °C. Then, C_{60} layer growth is carried out. High purity (99.5%) C_{60} powder is used for the C_{60} source. The C_{60} beam equivalent pressure (BEP) is varied between 4.0×10^{-7} and 2.4×10^{-6} Torr, which correspond to a C_{60} flux of 0.1 monolayer/s (ML/s) and 0.6 ML/s, respectively. RHEED measurements are performed with an electron beam along the <011> azimuth of the GaAs substrates. The intensities of the RHEED specular reflection are detected by a conventional video camera system, and the intensity oscillations are analyzed using a personal computer. After C_{60} layer growth, the crystalline quality of the films is investigated by X-ray diffraction (XRD) with Cu Kα radiation. Both $2\theta/\omega$ scan and XRD pole figure measurements are performed and compared with the results of the RHEED intensity oscillations.

3. Results and Discussion

3.1 C_{60} layer growth on GaAs (111)B surface with (2x2) structure

The RHEED patterns of C_{60} layers grown on GaAs (111)B, (111)A, and (001) substrates exhibit a 6-fold symmetry and indicate that the C_{60} epitaxial orientation is in the [111] direction.6) The streak intervals observed in the patterns indicate that the lattice constant of epitaxial cubic C_{60} films coincides well with that of bulk cubic C_{60} crystals.

Figure 1 shows the intensity of the specular beam in the RHEED pattern of C_{60} layer growth at 200 °C with C_{60} BEP at $1.4\text{x}10^{-6}$ Torr on a GaAs (111)B surface with (2x2) structure. The lateral axis denotes the deposition thickness in monolayers. After a few monolayer depositions, a regular RHEED intensity oscillation is observed. Figure 2 shows frequencies of the oscillation as a function of C_{60} BEP. The lateral axis denotes C_{60} BEP, and the vertical axis is the frequency of RHEED intensity oscillations. The frequencies increase proportionally with the C_{60} BEP and are confirmed to coincide with the growth rates of C_{60} layers obtained from the film thickness. Therefore, the RHEED intensity oscillation during C_{60} layer growth is caused by the same mechanism as that for GaAs and other semiconductor growth. C_{60} layers grow by repeating nucleation and step-flow growth mode.

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 growth, as marked by an arrow in Fig. 1. The succeeding intensity peaks appear at 1.5 ML, 2.5 ML, and so on. This anomalous oscillation suggests a peculiar configuration of the C_{60} molecules in the first layer on the (111)B surface with (2x2) structure. In addition to these peaks, a clear RHEED intensity peak appears near 2 ML, as shown in Fig. 1. Although the origin of this peak is not clarified yet, small domains with regular one-monolayer by one-monolayer growth may be occurring, because a very small structure can be recognized in the bottom of the valley at 1 ML of the RHEED intensity trace in Fig. 1.

Figure 3 shows RHEED intensity oscillations of C_{60} growth for C_{60} BEP at 4.0×10^{-7} Torr on the (2x2) structure for different growth temperatures. The RHEED intensity oscillations are less pronounced at high growth temperatures. This is probably because a step-flow growth mode becomes dominant for higher growth temperatures as in the case of GaAs growth. In the initial stage of C_{60} layer growth, all the oscillations have the same features of a shoulder at 0.5 ML and intensity peaks at 1.5 ML.

Figure 4 shows adsorption models of the C_{60} first layer on a GaAs (111)B surface with (2x2) structure. Since the surface of the (2x2) structure has a periodic lattice structure by adsorbed As trimers,11) C_{60} adsorption sites should, therefore, be limited due to a three-dimensional 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. 4(a)] or 50% [Fig. 4(b)] of the full coverage. Therefore, the first layer growth should be completed at around 0.5 ML C_{60} deposition. The shoulder on the plot of 0.5 ML deposition probably indicates this event. The first peak appears at 1.5 ML deposition, indicating that C_{60} regular layer growth takes place after first layer deposition. The existence of small domains with regular one-monolayer by one-monolayer growth may be caused by the incomplete structure of (2x2) reconstruction.

3.2 C_{60} layer growth on GaAs (111)B surface with (√19x√19) structure

To verify the C_{60} first layer configuration model on the (111)B with (2x2) structure proposed, RHEED intensity oscillation is also investigated during the growth of C_{60} layers on the (111)B surface with (√19x√19) structure. Under As rich conditions, the surface reconstruction of GaAs (111)B substrates shows the (2x2) structure. On the other hand, under Ga rich conditions, the surface structure is converted to (√19x√19) structure with hexagonal rings. This (√19x√19) structure is prepared by annealing the (2x2) structure at 500 °C in ultra high vacuum (UHV), and is confirmed by RHEED observation. Figure 5 shows RHEED intensity oscillations during C_{60} layer growth with C_{60} BEP at 4.0×10^{-7} Torr on the (√19x√19) structure. After a few monolayer depositions, regular RHEED intensity oscillations are observed as in the case of the C_{60} layer growth on the (2x2) structure. In the initial stage of the growth, intensity peaks appear at 1.7 ML, 2.7 ML, and so on. These results imply that the C_{60} first layer configuration on the (√19x√19) structure is different from that on the (2x2) structure. Figure 6 shows adsorption models of the C_{60} first layer on a GaAs (111)B surface with (√19x√19) structure. The (√19x√19) structure has periodic hexagonal rings with ±6.6° rotation with respect to the [2-1-1] direction,11) and the density of C_{60} molecules shown in Fig. 6 is estimated to be 66% of the full coverage. The first RHEED intensity peak appears at 1.7 ML deposition. Therefore, the first layer growth may be completed at approximately 0.7 ML C_{60} deposition, and the C_{60} regular growth takes place after the first layer deposition. Indeed, a very faint shoulder appears at 0.7-0.8 ML on the plot of RHEED intensity for the C_{60} grown at 70 °C (see the arrow).

In this case, the first layer arrangement should have two domains with 13° rotation between them, as shown in Fig. 6. To investigate the crystalline properties of C_{60} layers, XRD measurements are performed. The XRD $2\theta/\omega$ scan shows that only (*hhh*) diffractions are observed from a C_{60} layer on the (√19x√19) structure. Figure 7 shows an XRD pole figure of a 400 nm-thick C_{60} film on the GaAs (111)B surface with (√19x√19) structure where 2θ is set at 10.83° [C_{60}(111) diffraction]. Figure 8 compares the XRD ϕ-scan pattern of C_{60} diffraction (2θ=10.83°) with that of GaAs(111) diffraction (2θ=27.31°). The C_{60} layer on the (√19x√19) structure has two domains with 13° rotation between them, strongly supporting the adsorption models shown in Fig. 6.

In summary, a C_{60} first layer configuration is determined by a three-dimensional structure between C_{60} molecules and reconstruction of the surface, and the flexibility of the first layer arrangements makes strain due to a lattice mismatch between C_{60} and substrates relieved. Therefore, C_{60} regular layer growth with high-crystalline quality is formed after a C_{60} first layer deposition.

3.3 C_{60} layer growth on GaAs (111)A surface with (2x2) structure

Figure 9 shows the intensity variations of the specular beam in the RHEED patterns of the C_{60} layer deposition for C_{60} BEP at 4.0×10^{-7} Torr on the (2x2) surface of a GaAs (111)A substrate. After a few monolayer depositions, regular RHEED intensity oscillations are confirmed, just as in the results on GaAs (111)B substrates. In the initial stage of C_{60} layer growth, the first peak appears at 0.5 ML, and the succeeding peaks appear at 1.5 ML, 2.5 ML, and so on. Figure 10 shows adsorption models of first layer C_{60} molecules on a GaAs (111)A surface with (2x2) structure. The (2x2) structure is gallium terminated with one out of four surface gallium atoms missing.12) Since the binding energy between C_{60} molecules and Ga atoms is expected to be higher than that between C_{60} molecules and As atoms,13) C_{60} adsorption tends to occur at the Ga-enriched sites, as shown in Fig. 10. In this case, the density of the adsorption sites is estimated to be 40% [Fig. 10(a)] or 50% [Fig. 10(b)] of the full coverage. Thus, the first

C_{60} layer growth is completed at approximately 0.5 ML coverage, resulting in the first RHEED intensity peak at 0.5 ML. The regular C_{60} layer by layer growth takes place after first layer deposition, as with the growth on the (111)B substrates.

3.4 C_{60} layer growth on a GaAs (001) surface with c(4x4) and (2x4) structures

Investigations of C_{60} first layer configurations on GaAs (001) substrates by scanning tunnel microscopy (STM) were reported by Sakurai et al.[5,14] In this section, to compare with results of the STM measurements, we investigate the RHEED intensity oscillations of C_{60} layer growth on the c(4x4) and (2x4) structures of GaAs (001) substrates. The c(4x4) structure is prepared by low temperature annealing under As atmosphere after the high-temperature buffer layer growth. This structure consists of over-adsorbed As atoms on the fully As-covered surface. The interactions between C_{60} molecules and the surface of the c(4x4) structure should be very weak. Thus, the impinging As atoms have no preferential sites, resulting in a C_{60} close-packed hexagonal configuration that is confirmed by STM observations.[5] Figure 11 shows the RHEED intensity oscillation of C_{60} layer growth of C_{60} BEP at 4.0×10^{-7} Torr on the c(4x4) structure at 70 °C. In the initial stage of C_{60} growth, intensity peaks appear at 2.0 and 3.0 ML, indicating that regular C_{60} layer growth takes place from the beginning. These results coincide well with the results observed by STM.[14] The c(4x4) surface is stable, and seems to provide no preferential sites for C_{60} adsorption. This may be the cause of the regular layer by layer growth in the initial stage. As the growth proceeds, however, the oscillation period becomes shorter. The origin of the period shortening has not yet been clarified. The STM study of C_{60} growth revealed that three-dimensional growth takes place easily on the c(4x4) surface.5) The observed period shortening is probably related to this growth characteristic.

Next, RHEED intensity oscillations are investigated during the growth of a C_{60} layer on the (2x4) structure. The (2x4) structure is prepared from the c(4x4) structure by a thermal annealing in UHV. Figure 12 shows an adsorption site model of C_{60} molecules on the (2x4)β structure on GaAs (001) substrates suggested by STM observations.5,14) The missing As dimer rows align straight along the [-110] direction separated by 16.0 Å and produce deep and wide troughs between the As-dimer rows on the surface. C_{60} molecules are adsorbed in the troughs, and they form C_{60}-C_{60} pairs whose intermolecular distance is 10.54 Å, and each chain is separated by 24.0 Å. In this case, the density of the C_{60} first layer is estimated to be 50% of the full coverage of the hexagonal configuration. Figure 13 shows the RHEED intensity oscillation during C_{60} growth at 70ºC for C_{60} BEP at 4.0×10^{-7} Torr on a GaAs (001) surface with the (2x4) structure. In the initial stage of C_{60} growth, there is a shoulder at 0.5 ML, and intensity peaks appear at 1.5 and 2.5 ML, indicating that the density of the adsorption sites on the structure is estimated to be 50% of the full coverage. This density of adsorption sites coincides well with the density determined by STM measurements. The small peak near 1 ML deposition is probably caused by the small regular growth domains, as discussed in connection with Fig. 1.

4. Conclusions

Clear RHEED intensity oscillation is successfully observed during epitaxial growth of C_{60} layers on GaAs (111)B, (111)A, and (001) substrates. The frequencies of the oscillation increase proportionally with C_{60} BEP and coincide well with the growth rates of C_{60} layers. Therefore, C_{60} layers grow by repeating nucleation and step-flow growth mode as in the case of the growth of GaAs and other semiconductor materials. The initial C_{60} layer growth on GaAs substrates is affected strongly by the reconstruction of the substrate surface. For example, the first layer growth on the (111)B surface with (2x2) structure terminates with 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 the 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 at 0.5 ML deposition. Similar phenomena have been observed on different surface reconstructions. These results suggest that the C_{60} molecules can be incorporated in the GaAs crystal lattice even if the size of the molecules is much larger than that of the GaAs lattice.

Acknowledgements

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Figure Captions

Fig. 1. RHEED intensity oscillation during C_{60} growth at 200ºC with C_{60} BEP at $1.4x10^{-6}$ Torr on a GaAs (111)B surface with (2x2) structure as a function of C_{60} deposition thickness in monolayers.

Fig. 2. C_{60} BEP dependence of the RHEED intensity oscillation frequencies.

Fig. 3. RHEED intensity oscillations during C_{60} growth at different temperatures with C_{60} BEP at $4.0x10^{-7}$ Torr on a GaAs (111)B surface with (2x2) structure.

Fig. 4. Adsorption models of the C_{60} first layer on a GaAs (111)B surface with (2x2) structure. The density of C_{60} adsorption sites is (a) 40% and (b) 50% of the full coverage.

Fig. 5. RHEED intensity oscillations during C_{60} growth with C_{60} BEP at $4.0x10^{-7}$ Torr on a GaAs (111)B surface with ($\sqrt{19}$x$\sqrt{19}$) structure.

Fig. 6. Adsorption models of the C_{60} first layer on a GaAs (111)B surface with ($\sqrt{19}$x$\sqrt{19}$) structure.

Fig. 7. XRD pole figure of a 400 nm-thick C_{60} film on a GaAs (111)B surface with ($\sqrt{19}$x$\sqrt{19}$) structure where 2θ is set to 10.83° [C_{60}(111) diffraction].

Fig. 8. XRD ϕ scan patterns of a C_{60} film on a GaAs (111)B surface with ($\sqrt{19}$x$\sqrt{19}$) structure with C_{60}(111) diffraction (2θ=10.83°) and GaAs(111) diffraction (2θ=27.31°).

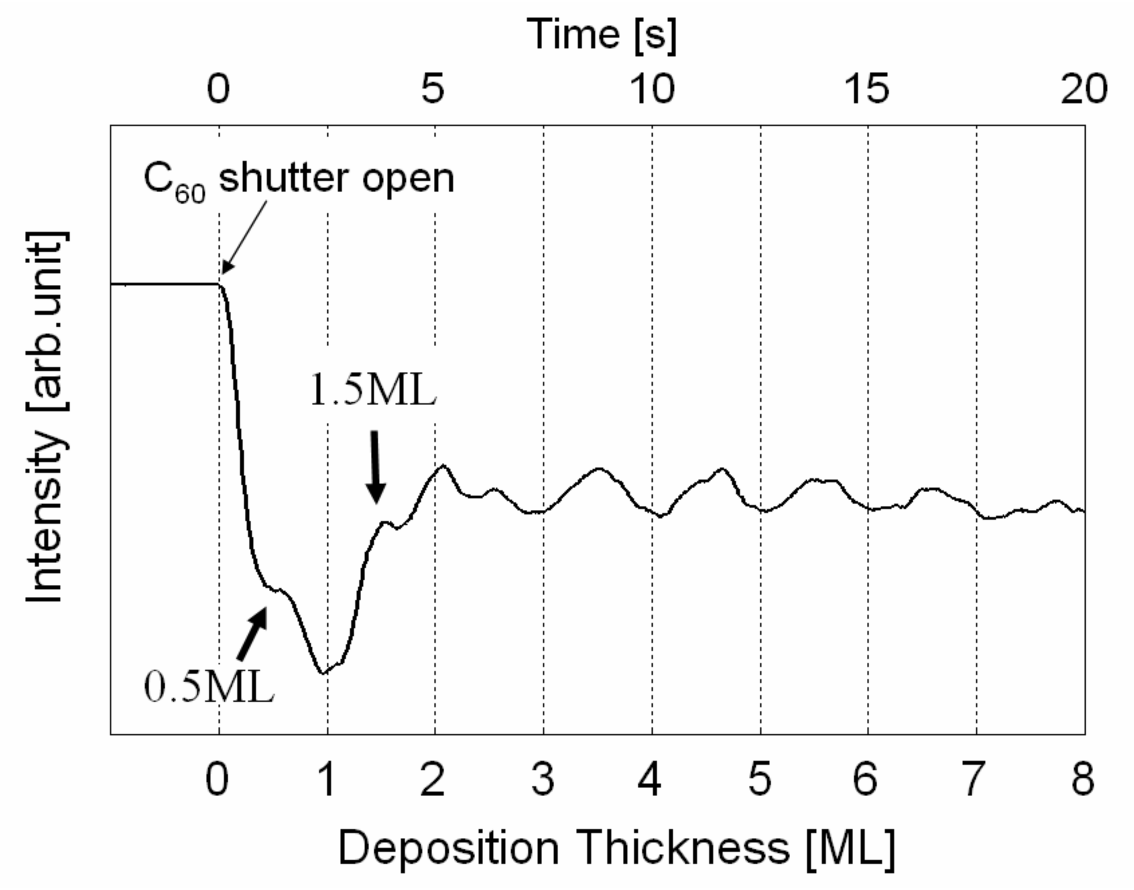
Fig. 9. RHEED intensity oscillations during C_{60} growth at different temperatures with C_{60} BEP at 4.0×10^{-7} Torr on a GaAs (111)A surface with (2x2) structure.

Fig. 10. Adsorption models for C_{60} first layer on a GaAs (111)A surface with (2x2) structure. The density of the adsorption sites is (a) 40% and (b) 50% of the full coverage.

Fig. 11. RHEED intensity oscillation during C_{60} growth of C_{60} BEP at 4.0×10^{-7} Torr on a GaAs (001) surface with c(4x4) structure grown at 70 °C.

Fig. 12. Adsorption configuration of C_{60} molecules on a GaAs (001) surface with (2x4)β phase structure suggested by STM measurements.[5,14)]

Fig. 13. RHEED intensity oscillation during C_{60} growth of C_{60} BEP at 4.0×10^{-7} Torr on GaAs (001) surface with (2x4) structure grown at 70 °C.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5
10
15
20
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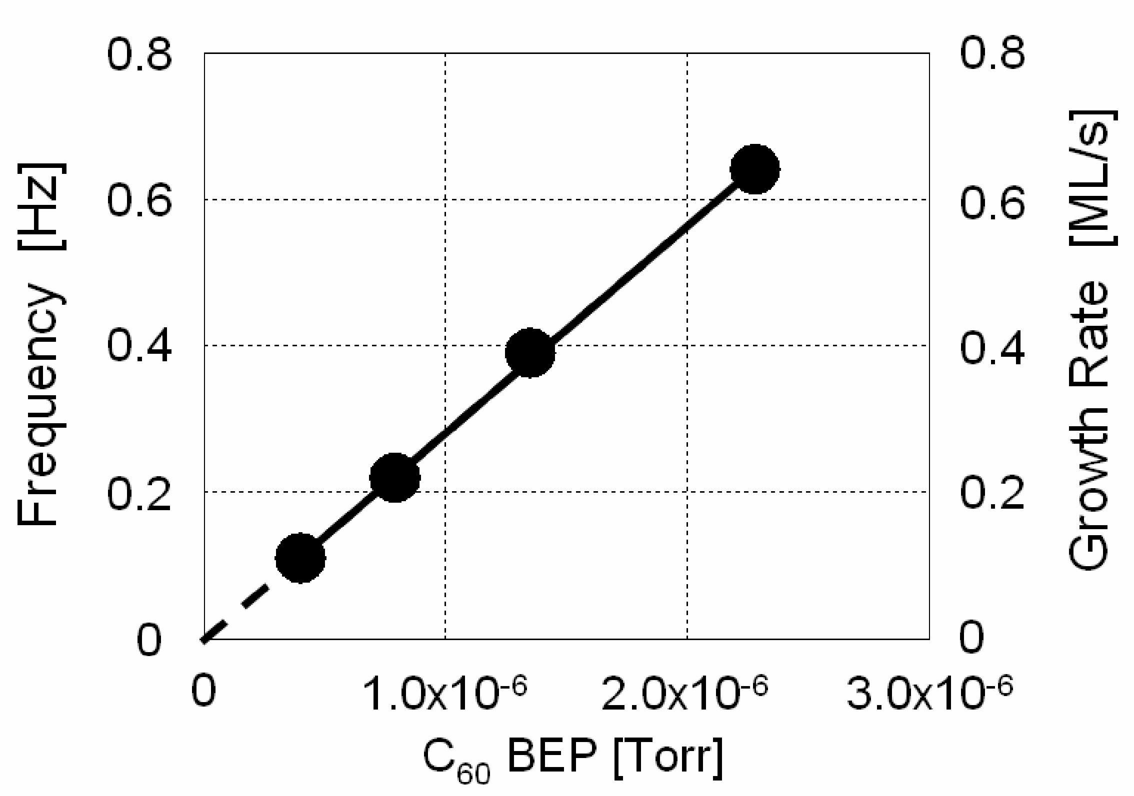
2
3
4
5
6
7
8
Deposition Thickness [ML]

Fig. 1.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0.6
0.4
0.2
0
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Growth Rate [ML/s]
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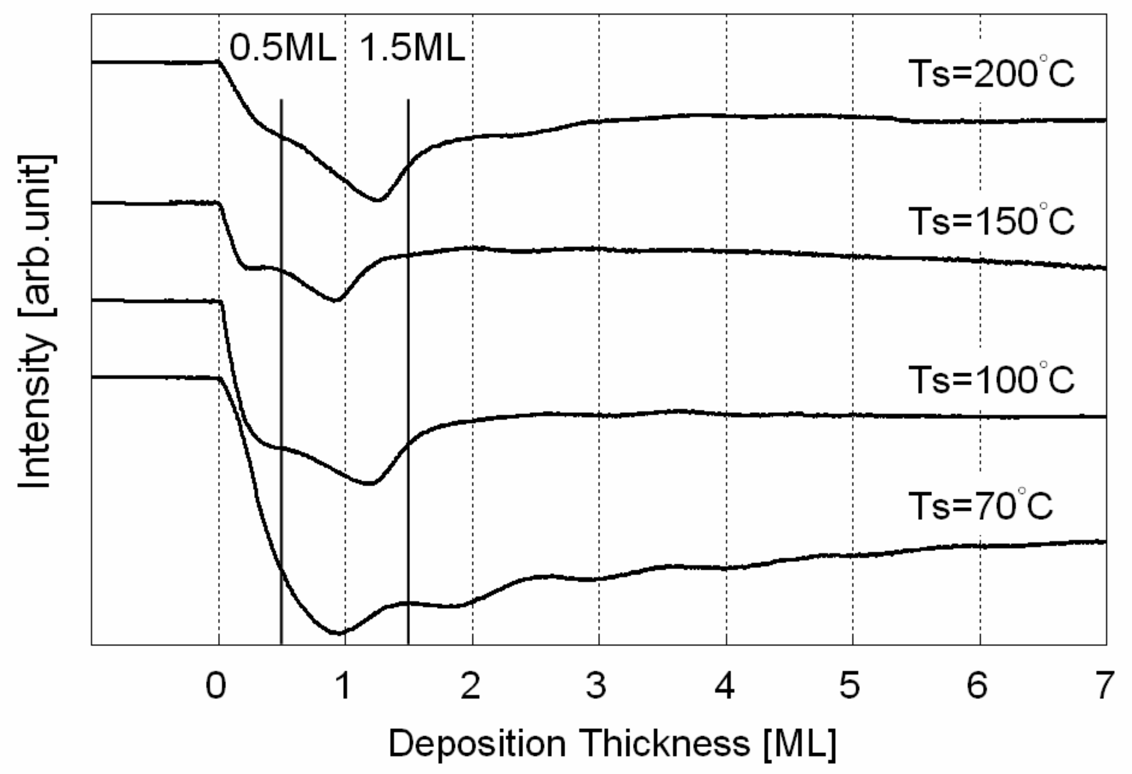
3.0x10-6
C60 BEP [Torr]

Fig. 2.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1.5ML
Ts=200°C
Ts=150°C
Ts=100°C
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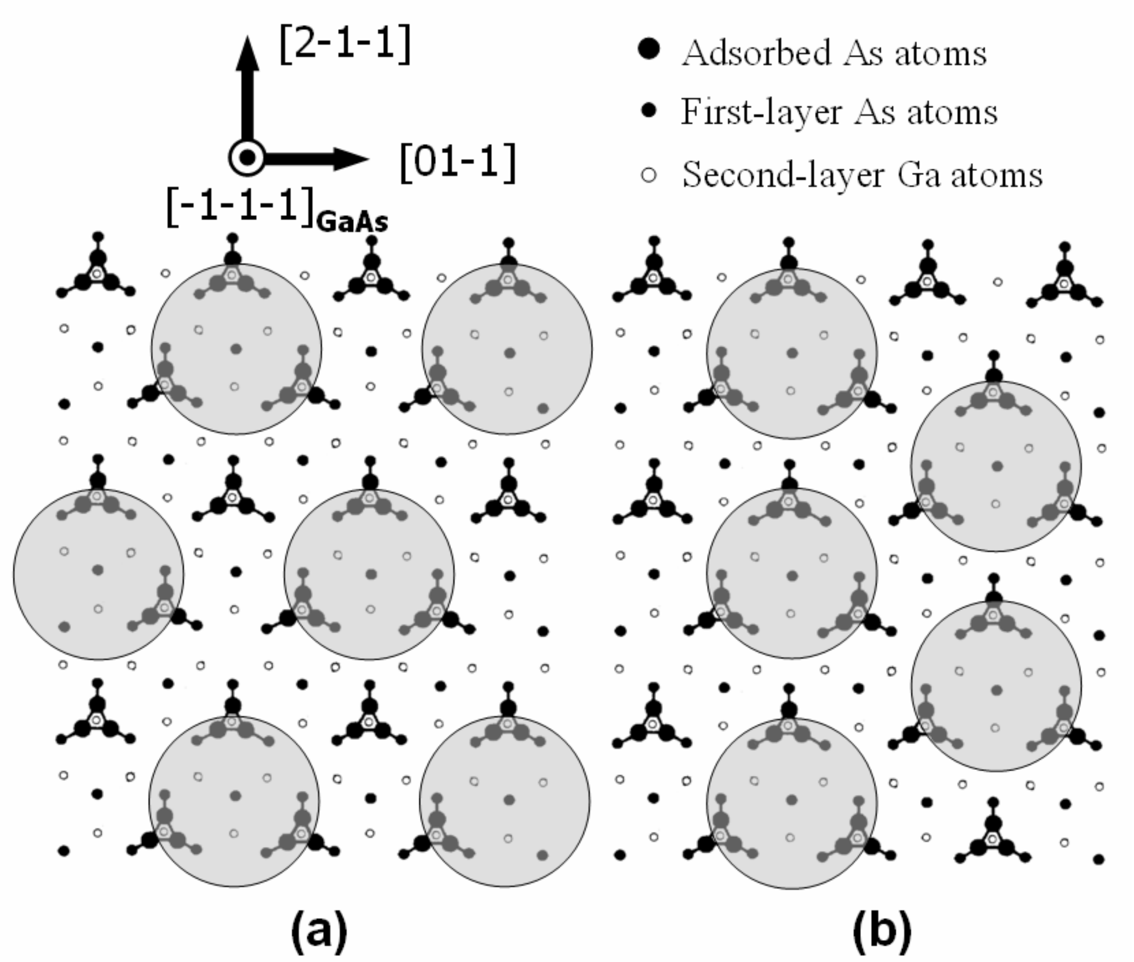
1
2
3
4
5
6
7
Deposition Thickness [ML]

Fig. 3.


[2-1-1]
[01-1]
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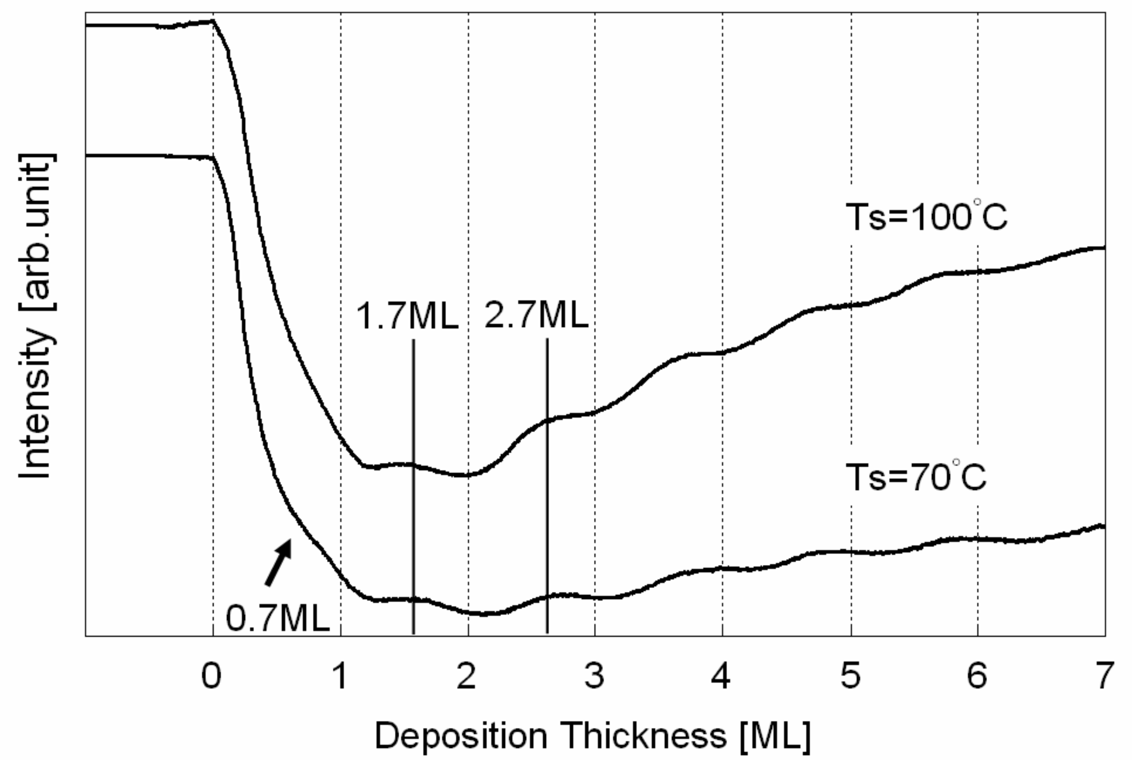
• First-layer As atoms
○ Second-layer Ga atoms
(a)
(b)

Fig. 4.


Intensity [arb.unit]
Deposition Thickness [ML]
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4
5
6
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Ts=70°C
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2.7ML
0.7ML

Fig. 5.

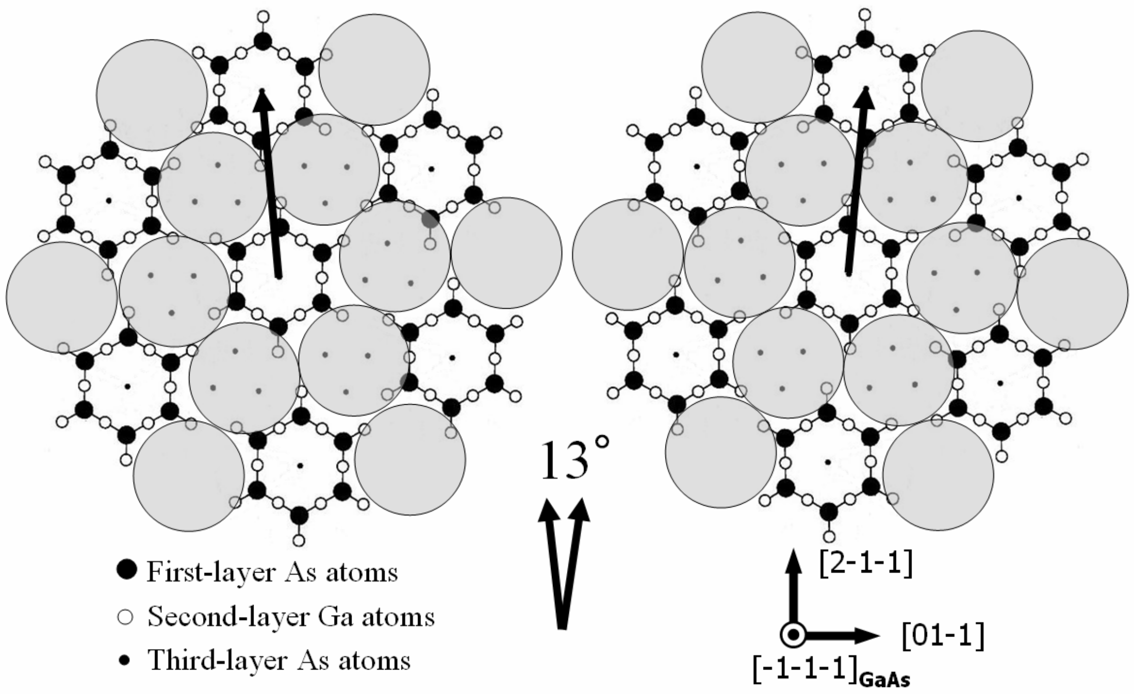

13°
● First-layer As atoms
○ Second-layer Ga atoms
• Third-layer As atoms
[2-1-1]
[01-1]
$[-1\text{-}1\text{-}1]_{\mathrm{GaAs}}$

Fig. 6.

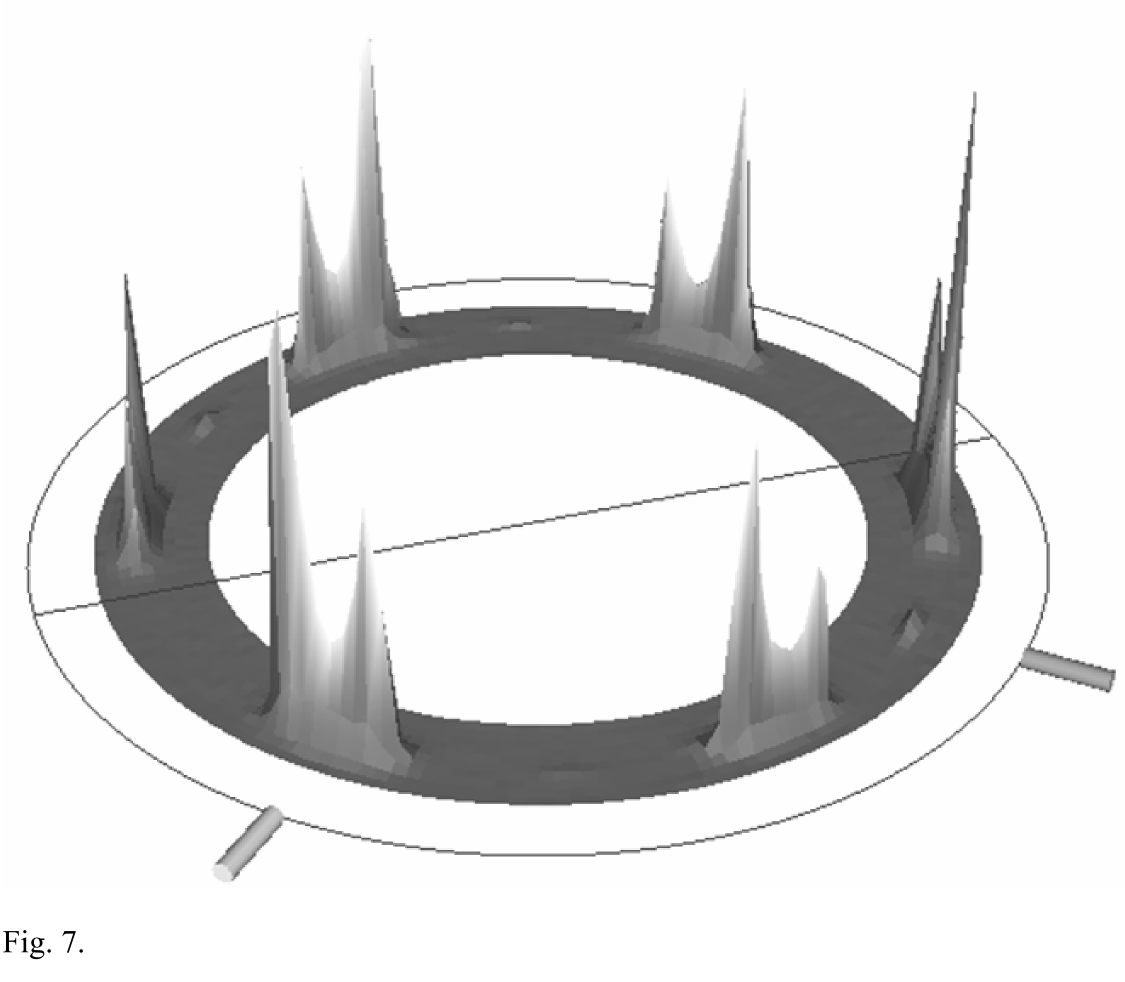
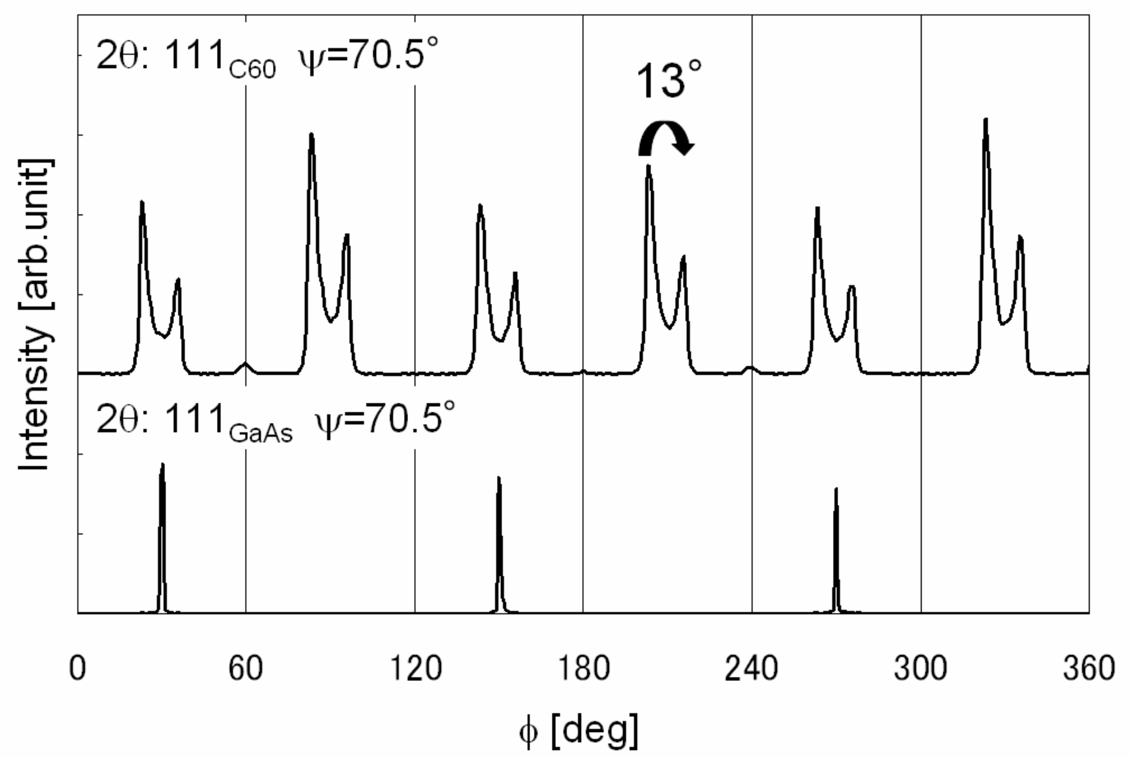


Fig. 7.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13°
2θ: 111$_{GaAs}$ ψ=70.5°
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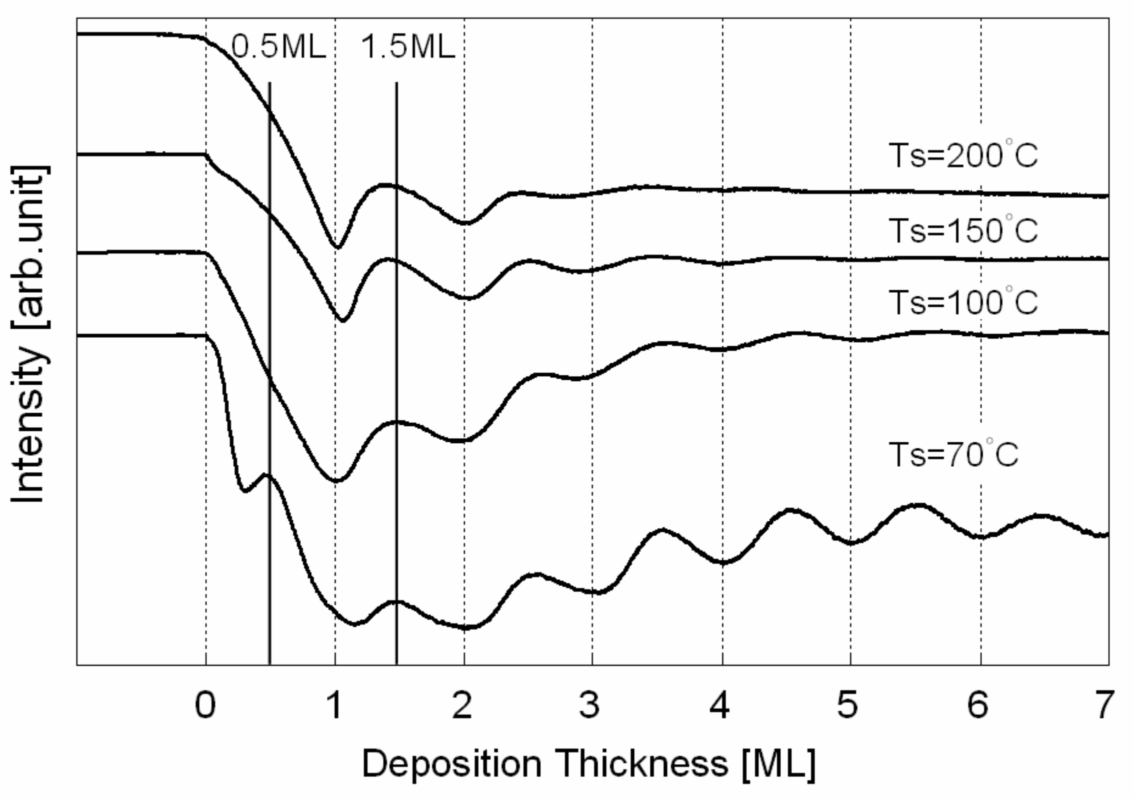
180
240
300
360
ϕ [deg]

Fig. 8.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1.5ML
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Ts=150°C
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Intensity [arb.unit]
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1
2
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5
6
7
Deposition Thickness [ML]

Fig. 9.

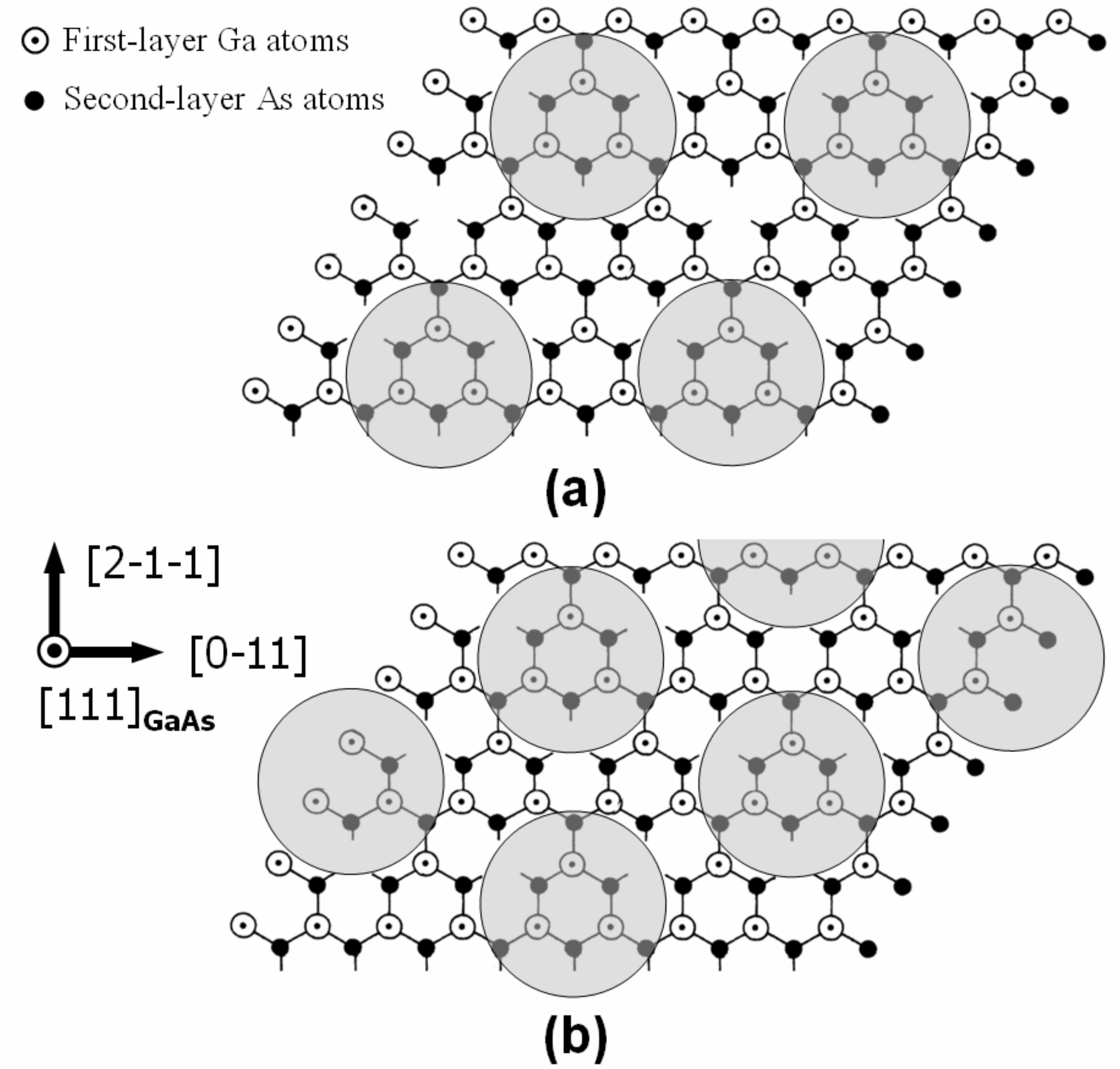
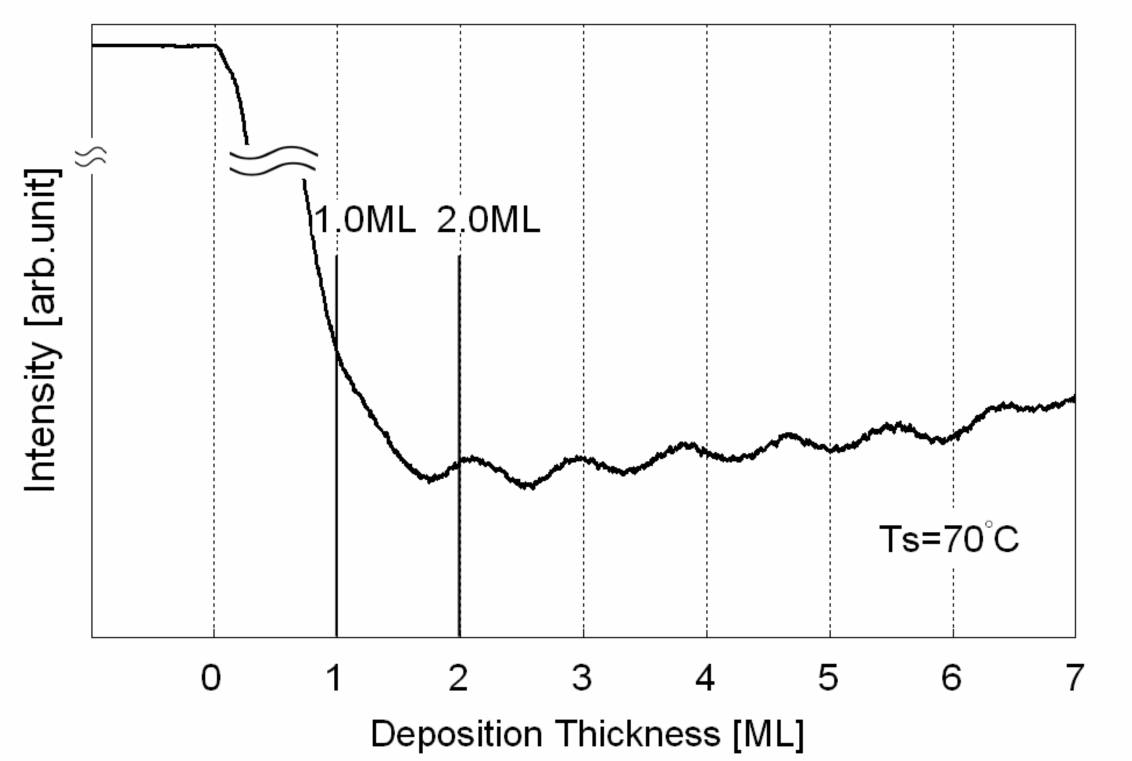

First-layer Ga atoms
Second-layer As atoms
(a)
[2-1-1]
[0-11]
$[111]_{GaAs}$
(b)

Fig. 10.


Intensity [arb.unit]
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Ts=70°C
0
1
2
3
4
5
6
7
Deposition Thickness [ML]

Fig. 11.

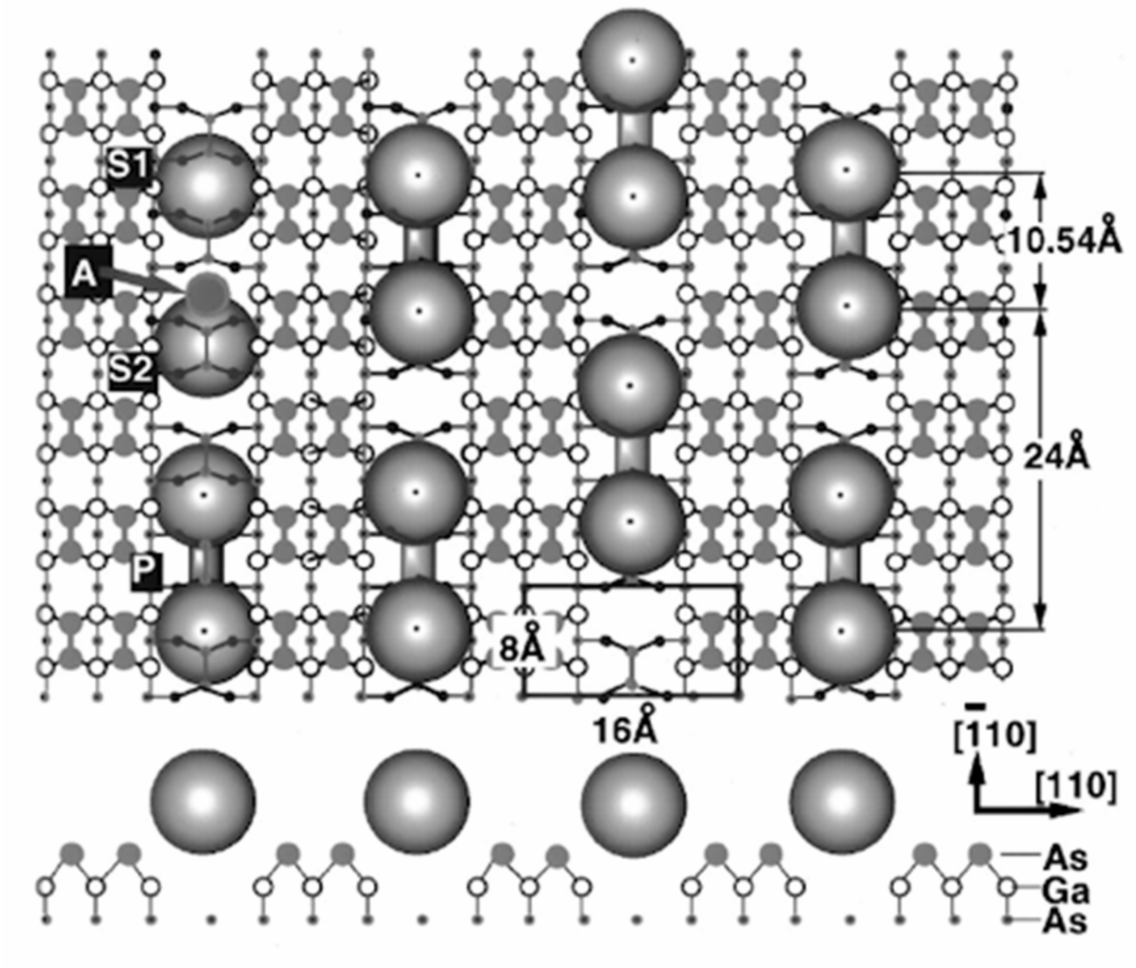
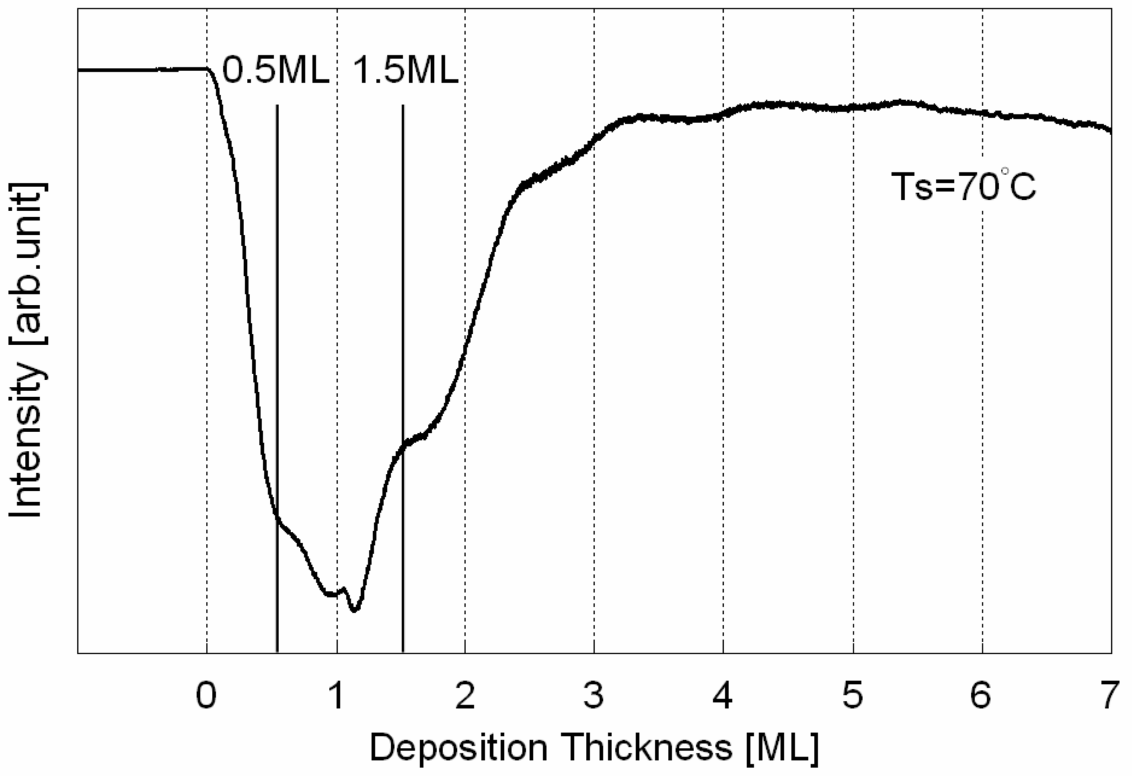


Fig. 12.



0.5ML
1.5ML
Ts=70°C
Intensity [arb.unit]
0
1
2
3
4
5
6
7
Deposition Thickness [ML]

Fig. 13.