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Surface Stoichiometry and Reconstruction of GaP(001)

Masahiro YOSHIKAWA, Atsushi NAKAMURA, Takashi NOMURA, Kenji ISHIKAWA

Research Institute of Electronics, Shizuoka University
3-5-1 Johoku, Hamamatsu 432, Japan
TEL: +81-53-478-1322 FAX: +81-53-474-0630

The surface stoichiometry and reconstruction of GaP (001) are investigated by means of reflection high energy electron diffraction and surface photo absorption (SPA). The experiments were carried out using a conventional molecular beam epitaxy system with solid sources using a craker cell as a P source. The P induced oscillation and the SPA signal show that the state of excess Ga on the surface and the surface reconstruction are quite different from those on GaAs (001).

1. Introduction

Heteroepitaxial growth has received much attention because of its high potential for new device applications. An abrupt interface and a high quality epitaxial layer are required to realize such devices. In order to control the interface structure, it is necessary to clarify the conditions of the substrate surface prior to heteroepitaxial growth. Although GaP is a useful material to fabricate opto-electronic devices, the surface of GaP (001) is not clear due to different reconstruction from that of GaAs (001).

Reflection high energy electron diffraction (RHEED) is a useful tool as an in situ monitoring method for a molecular beam epitaxy (MBE) system. RHEED is sensitive to surface characteristics such as surface roughness on an atomic scale and surface atomic arrangement, but insensitive to a change of chemical species on the surface. On the other hand, in situ optical observation techniques such as reflectance difference spectroscopy (RDS)[1] and surface photo absorption (SPA)[2] provide chemical information on the surface which complements structural information provided by RHEED. This paper discusses the surface stoichiometry and reconstruction of GaP (001) by means of RHEED and SPA methods.

2. Experiments

The growth of GaP was carried out by a conventional MBE system with solid sources using a cracker cell as a P source. Prior to the measurement of the SPA signal, a GaP buffer layer about 500 nm in thickness was grown to obtain a well-defined surface. It was confirmed by RHEED pattern that the substrate surface was atomically flat.

The SPA measurements were performed using a He-Ne laser (633 nm) with the incident angle selected as 78 °, slightly higher than the Brewster angle. The incident azimuth was <100>. The measurements were carried out for various surface stoichiometries, which were changed as follows: the supply of P was stopped 30 seconds before the beginning of the Ga supply in order to decrease the background P pressure, and then Ga flux was supplied on the surface during the interruption of P flux, and the P flux was resumed after the Ga supply was stopped.

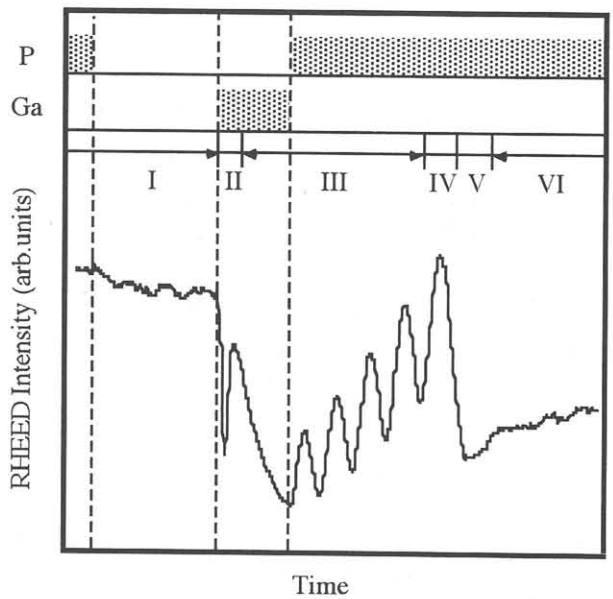

Fig. 1 Intensity of specular spot during alternating sequence of Ga and P flux. The deposition rate of Ga is 0.35 ML/s and the amount of Ga supplied is 6 ML. The substrate temperature is 650 °C. Roman numerals correspond to those in Table I.

3. Results and Discussion

Figure 1 shows the RHEED intensity of the specular spot from the GaP (001) surface. The shutter sequences of Ga and P flux are also given in the figure. The substrate temperature was 650 °C and the deposition rate of Ga was 0.35 ML/s. The total amount of the Ga supply was chosen to be 6 ML. No change of RHEED pattern and specular intensity during interruption of P flux was observed. It suggests that the P terminated surface reconstruction is stable at 650 °C with background P pressure. The intensity increased at 0.75 ML after a sharp decrease at the beginning of the Ga supply, then decreased until the supply of Ga was resumed. The intensity oscillation of five cycles was observed during the supply of P flux. The intensity oscillation results from the successive layer by layer growth by the incorporation of group V atoms consuming the excess Ga on the surface[3]. The incorporation

Table I Change of the reconstruction during alternating sequence of Ga and P flux.

supply of P	2 × 4	I
interrupt of P		
begnning of Ga →	4 × 4	II
Up to 2ML →		
end of Ga start of P	2 × 4	III
Up to 4ML →		
Up to 5ML →	4 × 4	IV
Up to 6ML →	4 × 1	V
after 6ML	2 × 4	VI

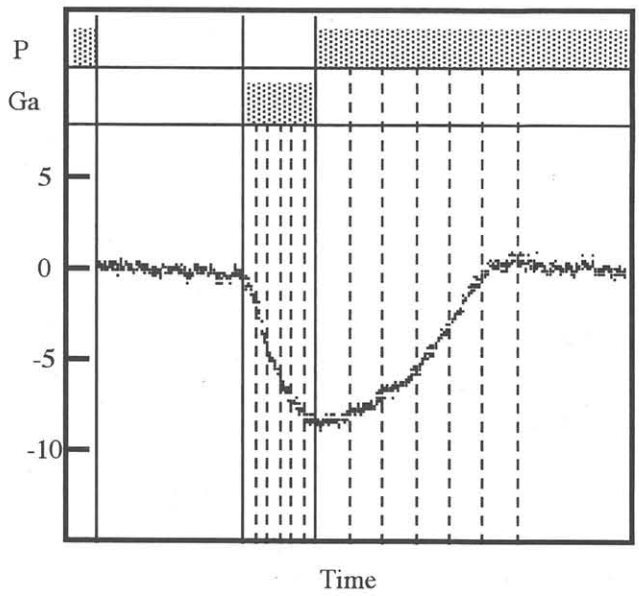

Fig. 2 Change of the SPA signal during alternating sequence of Ga and P flux. The incident azimuth is <100> and the amount of Ga supplied is 6 ML. The substrate temperature is 650 °C.

rate of group V is calculated to be 0.13 ML/s from the period of the intensity oscillation. This oscillation clearly shows the existence of excess Ga on the surface.

Table I shows the changes in surface reconstruction observed by RHEED. Roman numerals in the table correspond to the periods of the reconstruction in Fig. 1. The 2×4 pattern was observed during the interruption of the P supply. The pattern changed to 4×4 at the onset of the Ga supply, then changed to 2×4 at 2 ML of the Ga supply. The 2×4 pattern was maintained up to 4 ML in the supply of P. Then the pattern changed to 4×4 and 4×1 after 5 ML of the P supply. It returned to the P stabilized 2×4 after 6 ML of P was supplied. The Ga terminated reconstruction such as 4×2 reported for GaAs (001) was not observed for GaP (001) although the presence of excess Ga on the surface was clearly shown by the intensity oscillation during the supply of P. Only 4×4 and 4×1 were observed up to 2 ML of excess Ga. These results indicate that the state of Ga on the GaP (001) surface is quite different from that on the GaAs (001) surface.

Although the total amount of Ga supplied was 6 ML, the intensity oscillated only five cycles. It should be noted that the intensity increased at 0.75 ML after a sharp decrease at the beginning of the Ga supply and the surface reconstruction from RHEED was changed from 2×4 P stabilized to 4×4 at the same time. After the oscillation, the intensity decreased gradually during the supply of Ga. The oscillation and the change of the surface reconstruction suggest that the first one monolayer Ga is used for changing the surface reconstruction from 2×4 to 4×4. The decrease of the intensity after the increase results from the formation of Ga droplets.

The SPA signal was measured to obtain chemical information on the surface for various surface stoichiometries. Figure 2 shows the intensity of the SPA signal from the GaP (001) surface obtained simultaneously with the RHEED measurement. The dotted lines in the figure indicate one monolayer supplies of Ga and P calculated from the RHEED oscillation. The SPA signal decreased monotonously during the supply of Ga, then increased during the P supply. The intensity increased to the value of the P stabilized surface after the P supply of 5 ML which corresponds to the amount of the P supply estimated from the number of P induced oscillation. It suggests that the surface state recovers to the P stabilized surface before the supply of Ga.

The dependence of the change in the SPA signal on the incident azimuth was measured to clarify the origin of the SPA signal change. Figure 3 shows the changes of the SPA signal for various incident azimuths. The shutter sequences of Ga and P flux are also given in the figure. The dotted lines in the figure indicate one monolayer supplies of Ga and P calculated from the RHEED oscillation. The total amount of Ga supplied was 5ML. The substrate temperature was 640 °C and the deposition rate of Ga was 0.37 ML/s. The incorporation rate of P is estimated to be 0.40 ML/s from the intensity oscillation of the specular spot during the supply of P. The SPA signal decreases during the supply of Ga and increases during the supply of P for all incident azimuths. The changes in the SPA signal during the alternating sequence of Ga and P flux show no difference among all incident azimuths. The isotropic property in the SPA signal indicates that the signal change at this wavelength is mainly originated from metallic Ga because Ga droplets have an isotropic nature.

McIntyre and Aspnes studied theoretically the optical properties of very thin surface films whose thicknesses are much less than the wavelength[4]. This calculation is based on a three-layer model. The change in the reflectivity, $\Delta R/R$, of p-polarized light when the surface is covered with a thin film of thickness d is calculated by following equation

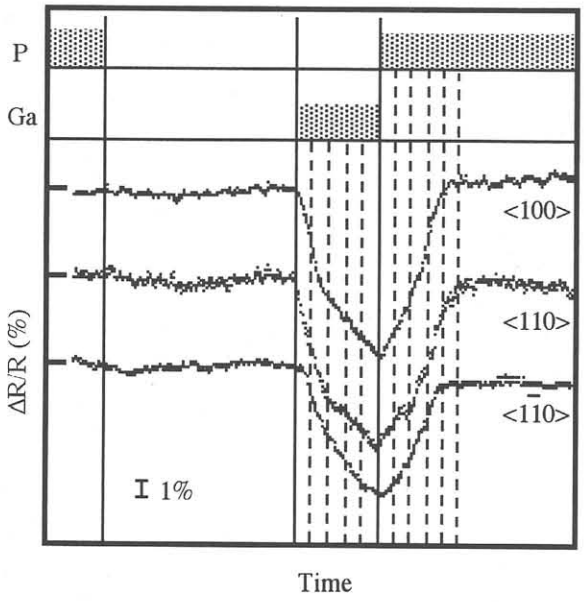

Fig. 3 Changes of the SPA signal during alternating sequence of Ga and P flux for various incident azimuths. The deposition rate of Ga is 0.37 ML/s and the amount of Ga is 5 ML. The substrate temperature is 640 °C.

$$\frac{\Delta R}{R} = \frac{8\pi d n_1 \cos\varphi_i}{\lambda} \mathrm{Im}\left[\left(\frac{\varepsilon_2-\varepsilon_{sub}}{\varepsilon_1-\varepsilon_{sub}}\right) \times \left\{\frac{1-(\varepsilon_1/\varepsilon_2\varepsilon_{sub})(\varepsilon_2+\varepsilon_{sub})\sin^2\varphi_i}{1-(1/\varepsilon_{sub})(\varepsilon_1+\varepsilon_{sub})\sin^2\varphi_i}\right\}\right]$$

where d is the thickness of the thin film on the substrate, n_1 the refractive index of the atmosphere, λ the wavelength of the incident light, φ_i the angle of incidence, ε_1 the dielectric constant of the atmosphere, ε_2 and ε_{sub} the complex dielectric constants of the thin film and the substrate, respectively. Figure 4 shows the calculated reflectivity change for a GaP substrate with a thin film of metallic Ga using p-polarized light of 600 nm in wavelength. The complex dielectric constant of GaP is 8.53-0.04i for 600 nm[5]. Since the complex dielectric constant of one monolayer Ga is not known, we assume the value of bulk metallic Ga to be valid for one monolayer thickness. The complex dielectric constant of metallic Ga is estimated to be -10.64-10.8i for 600 nm[6]. The incident angle of the present experiments was selected as 78°. The change in the reflectivity is negative at this angle as shown in Fig. 4. This results in the SPA signal decreasing with the deposition of metallic Ga on the GaP substrate. The decrease of the SPA signal during the supply of Ga in Fig. 2 may be interpreted as the Ga atoms supplied on the GaP (001) surface having metallic behavior.

These results from the RHEED and SPA methods suggest the formation of Ga droplets on the surface of GaP (001). Under the formation of Ga droplets on the surface, however, the reconstruction observed by RHEED shows the 2×4 structure which corresponds to that of the P stabilized surface as shown in Table I. These results are explained by the following process; the Ga atoms supplied on the P stabilized surface of GaP (001) are used for the change of the surface reconstruction up to the first 2 ML and then Ga atoms aggregate to form droplets and the surface returns to the P stabilized reconstruction during the supply of Ga.

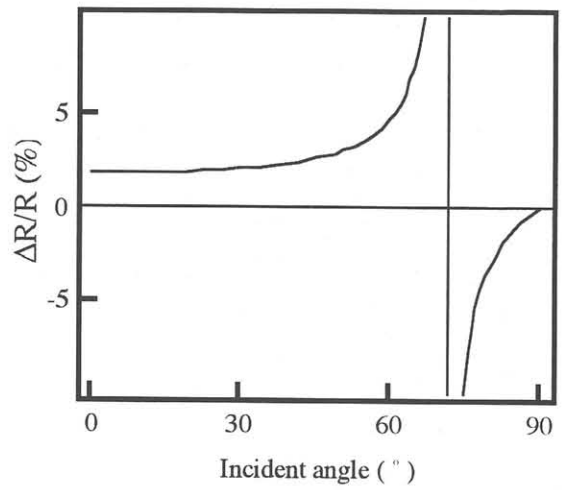

Fig. 4 Reflectivity change on the GaP substrate with a thin film of a metallic Ga as a function of the incident angle.

4. Conclusion

The surface stoichiometry and reconstruction of GaP (001) were investigated by means of RHEED and SPA methods. The presence of excess Ga is clearly shown by P induced oscillation and the change in the SPA signal. The change in the SPA signal and the calculation indicate that the Ga atoms supplied on the GaP (001) surface show metallic behavior. However, reconstruction relating to the Ga stabilized surface was observed only up to the 2 ML supply of Ga. The change in the RHEED pattern may be interpreted as the surface is a Ga terminated structure up to 2 ML supply of Ga, then Ga moves to some nonperiodic sites such as Ga droplets since the dimer structure of P is very stable. These results indicate that the state of excess Ga on the surface and the surface reconstruction are quite different from those on the surface of GaAs (001).

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