In-Situ Surface Photo-Absorption Study of Surface Structure and Desorption Dynamics for As-Stabilized GaAs MOCVD Surface

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To clarify the surface structure of As-stabilized (001) GaAs surface in metalorganic chemical vapor deposition (MOCVD), the spectral dependences of As-stabilized surfaces in MOCVD are *in-situ* measured using the surface photo-absorption method, and are compared with the spectra of well-defined As-stabilized surfaces in molecular beam epitaxy. It is shown that, in the practical growth condition, the As-stabilized GaAs surface has an c(4x4) like reconstructed structure, and that, at lower substrate temperatures than 500 °C, excess As adsorption occurs on the c(4x4) like surface. By stopping the arsine supply followed by an exposure to hydrogen flow, three distinct As desorptions from excess As, c(4x4), and (2x4) As surfaces are sequentially observed. The dynamics of As desorption from each As surface can be separately obtained by using a specific wavelength.

In-situ observation of a growing surface during metalorganic chemical vapor deposition (MOCVD) has been done using optical reflection methods such as reflectance difference (RD) spectroscopy¹⁾ and surface photo-absorption (SPA).²⁾ In this paper, we report on our measurement of the spectral dependencies of As-stabilized (001) GaAs surfaces in MOCVD using the SPA method, and our comparison of them to those observed for MBE As surfaces. In addition, we correlate As desorption dynamics observed as the temporal behavior of SPA signal during H₂ purging to the As surface defined by SPA.

The details of an SPA measurement system installed in an MBE chamber²⁾ and in horizontal³⁾ and vertical MOCVD reactors⁴⁾ have been previously reported. We used an optical multi-channel analyzer (OMA) to measure the SPA spectra. For this purpose, p-polarized light from a 150-W Xe-lamp directly irradiated the growing surface at an incidence angle of 70°.

In MOCVD, the working pressure was 10 kPa and the total flow-rate was 10 l/min. Triethylgallium and arsine were used as the source for GaAs growth. The MBE system consists of two K-cells for metal Ga and solid As, RHEED measurement equipment, and one pair of viewports with a synthesized quartz window for SPA measurement. The base pressure was less than $3x10^{-8}$ Pa when the shroud was cooled by liquid N₂. A (001) oriented semi-insulating GaAs substrate was used. All SPA measurements were done after the growth of an undoped buffer layer 200 nm thick.

We first measured the dependence of the SPA spectrum of an As-stabilized GaAs surface on substrate temperature (Ts) during MOCVD and compared it with the spectra observed for an MBE As surface. The reflectivity of a Ga surface is used as the standard in the spectrum measurement. In MBE, the Ga surface was formed by adding one Ga monolayer (ML) onto the As surface at each measured substrate temperature.

In MOCVD, the Ga surface is formed by As desorption instead of TEG supply, because at low substrate temperatures the slow decomposition rate of TEG⁵⁾ makes it difficult to precisely define the surface covered by a single Ga ML. The vertical axis of the SPA spectra shows (R_{As} - R_{Ga})/ R_{Ga} , where R_{Ga} and R_{As} denote the reflectivity of a Ga and an As surface, respectively. Figure 1 shows the typical SPA spectra observed for MOCVD (at Ts=600°C and 400°C) and MBE (at Ts=563°C and 483°C) at two incidence azimuths ([110]



Fig. 1: Typical SPA spectra observed for MOCVD (at Ts=600°C and Ts=400°C) and for MBE (at Ts=563°C and Ts=483°C) at two incidence azimuths ([110] and $[\overline{1}10]$).

and [T10]). For MOCVD, the arsine flow-rate was 20 cc/min, which corresponds to 3 μ mol/s and a partial pressure of 4 Pa. If we grow GaAs at a growth rate of 1 μ m/h at 600°C by using TEG and this arsine flow-rate, the V/III ratio is estimated to be about 10. Since the surface morphology of a GaAs epitaxial layer deteriorates at V/III ratios below 5 at 600°C, the arsine flow condition used here is not especially high, and is a common one for GaAs MOCVD growth.

For MBE, the As₄ beam flux intensity was 2.7×10^{-3} Pa, measured using an ion gauge at the growth position, which is a typical one used for GaAs growth at 1 µm/h at 580°C. At Ts=563°C, the As-stabilized surface showed a (2x4) reconstructed pattern, and at 483°C, a c(4x4) pattern with a half-order streak in both the [110] and [110] azimuths was observed.

Comparing the MOCVD and MBE surfaces in Fig. 1, although the absolute value on the vertical axis differs, presumably due to the slightly different optical configurations, the MOCVD As surface at 600°C is very similar to the MBE As surface at 483°C with c(4x4) reconstruction, while not to that with (2x4) reconstruction. SPA therefore shows the same result as that obtained by both *in-situ* RD spectroscopy⁶ and *in-situ* X-ray scattering⁷ measurement, that statically, an MOCVD As surface also reconstructs and has a c(4x4)-like structure under practical arsine partial pressure and Ts conditions. Thereafter, we call this c(4x4) surface.

The large anisotropy observed in the SPA spectra of c(4x4) surfaces can be explained qualitatively by using the electronic transition of the As dimer bond. An As submonolayer attached to an one-ML As surface has [110]-oriented As dimer bonds. The electrical vector of p-polarized light in SPA interacts efficiently with this dimer bond at a [110] azimuth incidence. As a result, the reflectivity



Desorption Time

Fig.2: Transients of SPA reflectivity at a [Π 0] azimuth using 470 nm monitoring light when arsine supply was stopped and the surface was then exposed to H₂ carrier gas flow.

of As surface at a [110] azimuth increases due to the strong photo-absorption by the upmost As dimers. From the c(4x4) surface spectra, a c(4x4) As dimer bond is expected to have a large photo-absorption coefficient in the wavelength range from 460 nm to 520 nm. This is confirmed by the simultaneous comparison between SPA and RD spectra for c(4x4) As surface in MBE⁸⁾ which indicates that the peak position at 470 nm in SPA coincides with that observed in the RD spectrum. At Ts=400°C in MOCVD, the spectrum is unlike the other three spectra in Fig. 1, but with careful comparison, the negative isotropic signal in the region below 400 nm and the positive isotropic signal at around 550 nm can be seen as an overlap with the anisotropic spectrum of the c(4x4) surface. This isotropic signal clearly appears below 500°C. An excessive adsorption of As on the c(4x4)surface is the most probable as the origin of this isotropic signal.

When TEG was supplied onto the c(4x4) As-stabilized surface, the SPA reflectivity increases linearly with the increase in TEG flux, and it saturates near one-ML Ga deposition.^{3,9)} The saturation is caused by the formation of large-sized droplets by the rapid agglomeration of smallsized ones. As a result, most of the Ga surface has the coverage of one-ML and the reflectivity saturates because of the low areal density of large-sized droplets. The linear increase in reflectivity indicates that Ga atoms do not enter into two-layer As structure of c(4x4) to form GaAs, but instead the upmost submonolayer As dimers desorb spontaneously during the formation of the Ga surface. This hypothesis was confirmed by the dynamic RD observation during the formation of Ga-stabilized surface.¹⁰⁾

So far, we have reported the As and P desorptions from (001)-oriented GaAs, GaP, InAs, and InP surfaces,¹¹⁾ in which the desorption rate correlated well with the standard heat of tetrahedral binary III-V compound formation and, from the observed desorption activation energies, the desorption species was speculated. In this report, the detailed desorption process of As from GaAs is investigated.

Figure 2 shows the transients of SPA reflectivity at a [110] azimuth using 470 nm monitoring light when the arsine supply was stopped and the surface was then exposed to the H₂ carrier gas flow. This wavelength is sensitive to the As dimer of a c(4x4) surface, but insensitive to the excessively adsorbed As on c(4x4) surface. The initial stage was As-stabilized surface. At 460°C, the desorption of excess As adsorbed on a c(4x4) surface was observed almost as a plateau having a duration of about 25 s. Next, the desorption from a c(4x4) surface was observed. The plateau showing the excess As desorption becomes shorter as Ts increases. The desorption from a c(4x4) surface also becomes more rapid as Ts increases. If a wavelength of 370 nm, which is sensitive to excess As adsorbed on a c(4x4) surface, is used, the excess As desorption process can be measured. Figure 3 shows a comparison of SPA reflectivity transients at 370 nm and 470 nm for the As desorption at 460°C. The plateau continues for about 25 s



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at 470 nm. In contrast, at 370 nm, it can be seen that within 25 s, the reflectivity increases and tends to saturate and the excess As desorbtion is almost completed.

In addition, the remarkable point in Fig. 2 is that two desorption processes with different rates are clearly observed above 520° C. At first, the desorption occurs from the c(4x4) surface and then slows as a Ga-stabilized surface is obtained. Figure 4 shows the first-order kinetic plots of the SPA reflectivity transients shown in Fig. 2, assuming that the initial and final As coverages are 1 and 0, respectively. Above 540°C, kinks denoted by arrows can be seen near the half coverage point of the initial surface. This result indicates that in MOCVD, there is a metastable As surface other than c(4x4) and excess As surfaces. A (2x4) surface is the most probable metastable As surface because the



Fig.4: First-order kinetic plots of SPA reflectivity transients corresponding to the As desorptions shown in Fig. 2.

spectra corresponding to the (2x4) surface can be seen in the time-resolved spectra during the As desorption. Therefore, it is considered that As desorption from a c(4x4) As surface to a Ga-stabilized surface occurs via a metastable (2x4) As surface. Assuming that the kink point in Fig. 4 corresponds to a (2x4) surface with As coverage of 0.75, a c(4x4) As surface in the Ts range from 540°C to 595°C may have a 1.5 coverage.

In conclusions, we measured the spectra of As-stabilized (001) GaAs surfaces in MOCVD using SPA method, and compared them with those observed for an MBE As surface. The results obtained by SPA were the same as those obtained using *in-situ* RD spectroscopy and *in-situ* X-ray scattering, that statically, an MOCVD As surface reconstructs and has a c(4x4) structure under practical arsine partial pressure and Ts conditions. We found that, below 500°C, excessive As is adsorbed on c(4x4) As surface. Using As desorption measurement, we found a metastable As surface other than the two As surfaces. This surface is considerd to be a (2x4) surface. We also determined, by using different wavelengths, the As desorption dynamics for each As surface separately.

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