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Optical Investigation of GaAs Growth Process in Flow-Rate Modulation Epitaxy

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Surface photo-absorption (SPA) is a newly developed in-situ optical monitoring technique for the epitaxial growth process. This method is based on the reflectivity measurement of P-polarized light incident at the Brewster angle. This configuration minimizes bulk GaAs contribution to the total light reflection. The small change in reflected light intensity between Ga and As atomic surfaces during Flow-rate Modulation Epitaxy (FME) of GaAs is thus detected with a high signal-to-noise ratio. By using this characteristic, GaAs growth rate can be monitored in-situ on an atomic scale. In addition to the in-situ monitoring of growth rate, the decomposition process of Ga and As precursors can be studied by SPA. We demonstrate the investigation of decomposition process of Ga organometals, and discuss the growth mechanisms of FME and atomic layer epitaxy.

1. Introduction

In-situ monitoring of the growth process is important in understanding the growth mechanism as well as in controlling the growth rate. Optical reflection from the growing surface is the powerful probe for monitoring the growth [1,2], especially in Metalorganic Chemical Vapor Deposition (MOCVD). The growth process occurs, however, within a very thin surface layer (~0.1 nm), and the signal from such a thin layer is quite low. Therefore, the optical investigation of the growth process suffers from a dominant bulk contribution to the total light reflection.

Recently, we developed a new in-situ optical monitoring technique called Surface Photo-Absorption (SPA)[3]. SPA is based on the reflectivity measurement of P-polarized light incident at the Brewster angle on the substrate surface. This configuration minimizes bulk contribution to the total light reflection, and makes it possible to detect small reflected light intensity variations caused by the surface photo-absorption change in the growing surface. This method is sensitive not only to the surface anisotropy along the principal axes in the growing plane, but also to the isotropic bonds perpendicular to the growing surface, because the incident P-polarized light includes E-vector components both parallel and perpendicular to the substrate surface.

In this paper, we apply SPA to the Flow-rate Modulation Epitaxy (FME) growth of GaAs. FME is an application of the principle of Migration Enhanced Epitaxy (MEE)[4] to MOCVD, and is based on an alternate supply of organometals and arsine in hydrogen carrier gas. In addition to the in-situ monitoring of growth rate, we demonstrate the investigation of decomposition process of Ga organometals by SPA, and discuss the growth mechanisms of FME and atomic layer epitaxy (ALE).

2. Experimental

Figure 1 shows the experimental setup of horizontal MOCVD reactor with SPA monitoring system. The source gases of triethyl gallium (TEG) or trimethyl gallium (TMG) and arsine, and hydrogen carrier gas flow perpendicularly in this figure. The P-polarized laser light or P-polarized monochromatic light irradiates the (001) GaAs substrate surface through the chopper at 70 degrees incidence angle. This is close to the Brewster angle. The light intensity at the surface is about 0.1 mW/cm^2 for the monochromatic light, and about 0.1 W/cm^2 for the laser light. Reflected light is detected by a Si p-i-n photodiode (PD), whose output is routed through a lock-in-amplifier and recorded on a time chart. The time constant of this system is about 0.3 s. The total flow-rate inside the reactor was 9 standard liters per minute and the

pressure was 30 Torr. Under these conditions, the composition of source gases over the substrate can be switched in less than 0.1 s. The hydrogen gas flows from the outer to the inner tubes to avoid deposits on the quartz windows through which the light passes.

3. Results and discussions

3.1 In-situ monitoring of GaAs FME growth by 325 nm laser light

Figure 2 shows the typical reflection intensity trace of P-polarized 325 nm He-Cd laser light for GaAs growth at the substrate temperature of 545°C. First, TEG and arsine were simultaneously supplied to grow a 200 nm-thick GaAs buffer layer on (001) GaAs substrate. During this growth, the growing surface is an As-stabilized one because of the arsine-rich growth condition. Next, the arsine supply was stopped and TEG was supplied for 5s, which corresponds to the growth of one Ga atomic layer. After a 5s purge with hydrogen, arsine was again supplied. The reflection intensity increased during the TEG flow and leveled off during the hydrogen purge. When arsine was supplied, the reflection intensity quickly decreased to its original level. A reflection intensity change of $\Delta R/R_{As}=(R_{Ga}-R_{As})/R_{As}$ exceeding 5% was observed, where R_{Ga} and R_{As} are, respectively, the reflection intensities of the Ga and As atomic surfaces. This result indicates that the signal-to-noise (S/N) ratio is sufficiently large in the SPA method. Both higher reflectivity of Ga atomic surface and $\Delta R/R_{As}$ value were independently of the incidence azimuth. This result indicates that SPA signal at 325 nm has an isotropic characteristic, which was confirmed by the measurement of spectral dependence, as described later.

The dependence of TEG flow duration on $\Delta R/R_{As}$. $\Delta R/R_{As}$ increased in proportion to the surface coverage of Ga until full coverage is accomplished. This observation indicates that SPA can monitor fractional layer growth. When S-polarized light was used, the reflection intensity difference between Ga and As atomic surfaces was not detected. This is due to both low S/N ratio by the large bulk contribution in S-polarized light reflection and weak absorption of S-polarized 325 nm light by Ga atomic surface.

3.2 Spectral dependence of SPA signal

Figure 3 shows the spectral dependences of the SPA signal for incidence azimuths of [$\bar{1}$10] and [110] during GaAs growth at 560°C. Signals were plotted as $|R_{Ga}-R_{As}|/R_{As}$ versus the energy of incident light. At the [$\bar{1}$10] azimuth, R_{Ga} is higher than R_{As} in the spectral region between 2.2 eV and 3.7 eV. On the contrary, R_{As} is higher than R_{Ga} in the range from 2.1 eV to 3.2 eV, and R_{Ga} is higher than R_{As} above 3.2 eV when [110] azimuth is used.

The anisotropic signal is caused by the interaction of the parallel E component of the P-polarized incident light with anisotropic surface chemical bonds. To confirm this, the spectra were measured using S-polarized light, where only the anisotropic signal is expected. Although the S/N ratio in S-polarized light is lower than in P-polarized light due to the large contribution of bulk GaAs reflection, only anisotropic signals were obtained in the spectral range from 2.1 eV to 3.2 eV. Since the E-vector of S-polarized light incident in the [$\bar{1}$10] azimuth has only the [110] component, the observed anisotropy should be equivalent to that observed in the [110] azimuth experiment for the P-polarized light. Indeed, the S-polarized light incidence in the [$\bar{1}$10] azimuth showed $R_{As}>R_{Ga}$ as with the result of P-polarized light in the [110] azimuth. Therefore, these spectra can be divided into two regions. One is the anisotropic signal region corresponding to the spectral range from 2.1 eV to 3.2 eV, and the other is the isotropic signal region above 3.2 eV.

These spectra can be ascribed to the optical absorption of the chemical bond between surface Ga (or As) atom and underlying As (or Ga) plane in the anisotropic region and, in the isotropic region, the optical absorption of chemical bond related to the surface Ga atom, which is perpendicular to the (001) GaAs surface.

3.3 Investigation of the decomposition process of Ga organometals

SPA has a large advantage of observing the phenomenon occurred at the surface in the real growth condition, as compared with infrared spectroscopy and mass spectroscopy. We investigated the decomposition process of TEG and TMG on GaAs surface by SPA using 325 nm laser light. Figure 4 shows the $\Delta R/R_{As}$ as a function of Ga organometal flow duration

corresponding to the growth of one Ga atomic layer. SPA signal intensity during the decomposition of Ga organometal has a substrate temperature dependence, and its characteristic differs between TEG and TMG. In order to compare the substrate temperature dependence, $\Delta R/R_{As}$ value at 10 s flow duration is plotted in Fig.5. TEG and TMG show a similar dependence, but the peak of TMG shifts to higher substrate temperature by about 150°C than TEG. This temperature difference seems to correspond to the decomposition energy difference between TEG and TMG. These dependence can be divided into three regions as denoted by region I, II and III.

In region III, SPA signal intensity was very close to the value obtained by MBE growth of GaAs. Therefore, region III shows the formation of Ga metal surface by the complete cracking of Ga organometals. The temperatures in region III are above 500°C for TEG and above 670°C for TMG. Therefore, the enhanced surface migration of Ga atoms is expected above 500°C, when TEG is used. This is an important characteristic of FME. The extremely sharp single-quantum-well luminescence of GaAs/AlGaAs was observed from the sample grown by FME at 570°C[4]. This result indicates that the heterointerface is very flat due to the enhanced surface migration of Ga and Al atoms. (Fig.6) In region II, a higher reflectivity was observed than Ga metal surface of region III. SPA signal in region II was unstable, i.e., when the substrate temperature was increased after the supply of Ga organometal, $\Delta R/R_{As}$ decreased to the value of region III. These results indicates that alkyl-Ga surface is partially formed due to the incomplete cracking of organometals and, when the substrate temperature increases, the surface becomes Ga metal surface by alkyl-group desorption. Monoalkyl-Ga is the most probable as the surface chemical bond absorbing 325 nm light in region II, because SPA signal at 325 nm is sensitive to the chemical bond perpendicular to the surface.

In region I, both the growth rate and $\Delta R/R_{As}$ saturated, when the organometal flow duration increased. This self-limiting characteristic of growth rate has been reported by many authors[5-8]. In fact, ALE growth (one GaAs monolayer per one cycle of source gases supply) was observed at 500°C for TMG. Therefore, ALE mode dominates the growth process of region I. It is easily expected that the incomplete cracking ratio of organometal becomes higher in region I than in region II, because of lower substrate temperatures. Dialkyl and/or trialkyl-Ga species are considered to be favorably formed on the surface. Low SPA signal in region I is probably due to the weak interaction of P-polarized light with the alkyl-Ga bond not perpendicular to the surface, or the low absorption coefficient of these alkyl-Ga species at 325 nm, or the low surface coverage by steric hindrance. Therefore, the self-limiting characteristic of growth rate in ALE seems to be caused by no adsorption of the excess organometals supplied on the alkyl-Ga surface.

4. Conclusions

SPA method was applied to FME growth of GaAs. In-situ monitoring of growth rate is possible on an atomic scale with high S/N ratio. Furthermore, we measured the spectral dependences of SPA signal, which correspond to the absorption spectra of surface chemical species on the growing surface. We investigated the decomposition process of Ga organometals on GaAs surface. The enhanced surface migration of Ga atoms is expected above 500°C in the FME growth of GaAs using TEG. This was confirmed by the extremely sharp luminescence of GaAs/AlGaAs single-quantum-wells grown by FME. The result supporting the well-accepted ALE mechanism, i.e., no adsorption of the excess organometal supplied on the alkyl-Ga surface, was obtained.

Acknowledgement

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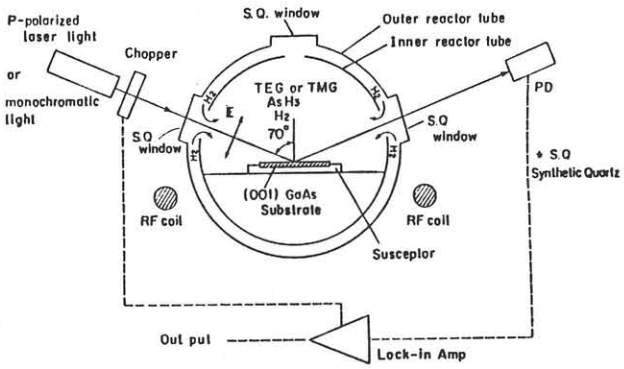

Fig 1: Horizontal MOCVD reactor with SPA monitoring system.

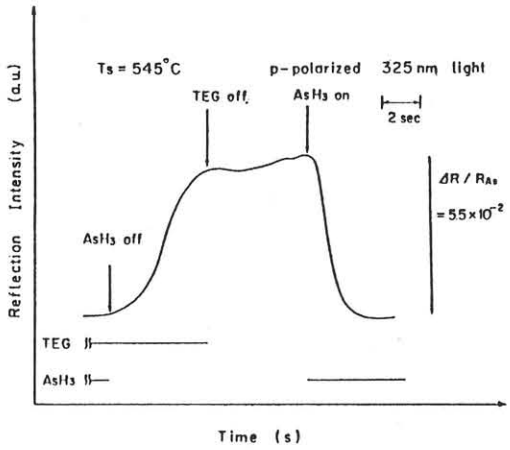

Fig 2: Typical reflection intensity trace for a gas-flow sequence consisting of a 5s TEG flow period, a 5s hydrogen purge period and an arsine flow period. TEG and arsine flow rates were 3.0×10^{-7} mole/s and 1.0×10^{-5} mole/s, respectively.

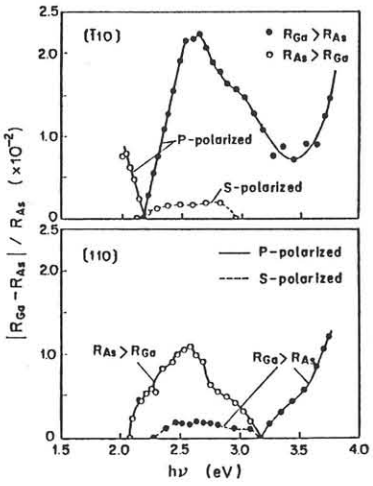

Fig 3: Spectral dependences of SPA signal for incidence azimuths of [$\bar{1}$10], [110] during GaAs growth at 560°C.

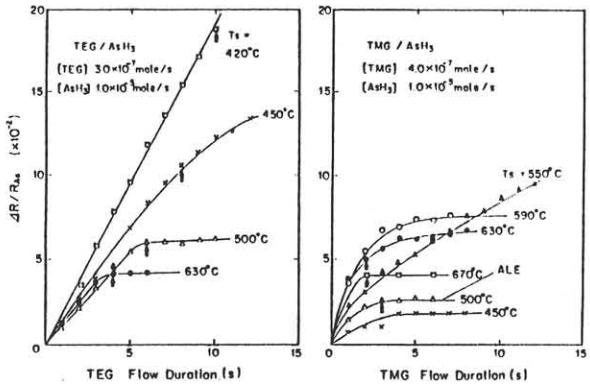

Fig 4: $\Delta R/R_{As}$ as a function of the Ga organometal flow duration for several substrate temperatures.

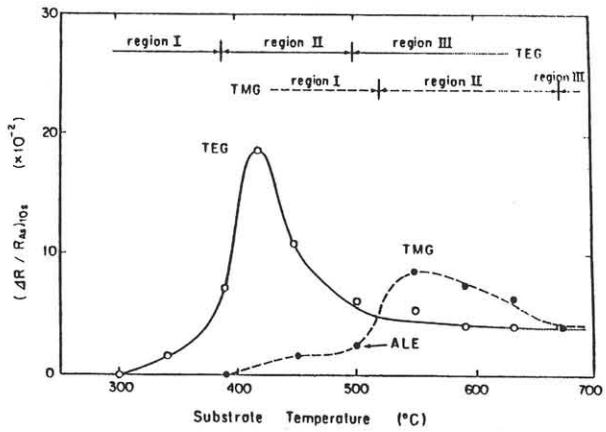

Fig 5: Substrate temperature dependences of $\Delta R/R_{As}$ at 10s flow duration for TEG and TMG.

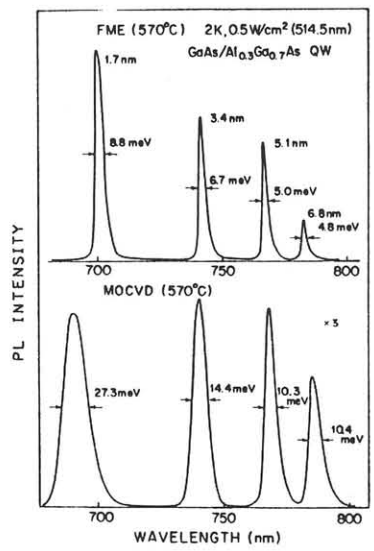

FIG. 6: Comparison of a 2-K photoluminescence spectra of quantum-well heterostructures for GaAs well widths of 1.7, 3.4, 5.1, and 6.8 nm sandwiched with 50-nm $Al_{0.3}Ga_{0.7}As$ barrier layers between FME and MOCVD.