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RHEED Studies on TEGa Decomposition during TEGa-As_4 Alternate Supply Growth of GaAs

Makoto UNETA, Yoshio WATANABE and Yoshiro OHMACHI

NTT Applied Electronics Laboratories

3-9-11, Midori-cho, Musashino-shi, Tokyo, 180, Japan

The RHEED intensity variation during TEGa and As_4 alternate supply is investigated. The measurements of the RHEED intensity recovery after supplying As_4 molecules on the Ga deposited surface and the growth rate of GaAs by TEGa and As_4 alternate supply demonstrate that the Ga deposition time T_0, at which the RHEED intensity rises to a maximum, corresponds exactly to the Ga monolayer formation time. The decomposition rate of TEGa molecules is studied using T_0 as a measure of Ga monolayer formation time. The TEGa decomposition reaction takes place in the substrate temperature range of 350-450 °C. In this reaction limited region, the decomposition rate tends to saturate as TEGa flow rate increases. This phenomenon is well explained by a rate equation that considers the surface coverage of adsorbed TEGa molecules.

1. Introduction

Metalorganic molecular beam epitaxy (MOMBE), which combines some advantages of metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE), is expected to clarify the mechanism of crystal growth which uses metalorganic compounds as source materials.[1] Recently, Chiu et al measured the variation in intensity of reflection high energy electron diffraction (RHEED) during GaAs growth by chemical beam epitaxy (CBE).[2] The measurements showed that the RHEED intensity variation during Ga deposition can provide direct information on surface reactions of metalorganic compound. This work investigates the RHEED intensity behavior during the growth of GaAs by the alternate supply of triethylgallium (TEGa) and arsenic vapor (As_4). The monitoring technique of this RHEED behavior is used to estimate the decomposition rate of TEGa.

2. Experimental

TEGa and solid arsenic were used as sources of Ga and As. The TEGa vapor was directly introduced to the growth chamber without using any carrier gases. The flow rate of TEGa vapor was precisely controlled by the mass flow meter. The TEGa flow rate was from 0.2 to 1.5 standard cubic centimeters per minute (sccm). The TEGa was not cracked at the outlet of the tube, so the TEGa molecules decomposed on the heated substrates. Arsenic vapor (As_4) was evaporated from a conventional effusion cell. The growth chamber was surrounded with liquid nitrogen shrouds. The background pressure was 3×10^{-10} Torr and the pressure during growth was typically about 2×10^{-6} Torr. Semi-insulating GaAs substrates exactly oriented (001) were used for the growth. The substrate temperature was measured with an optical pyrometer through a heated window, to avoid arsenic deposition. For RHEED intensity measurements, the 15-keV electron beam was aligned along the [100] axis. No enhancement of the GaAs growth or the decomposition of TEGa molecules on the electron beam irradiated area was observed.

3. Results and Discussion

A typical scan of the RHEED intensity measurements with the experimental sequence of TEGa and As_4 supply is shown in Fig.1.

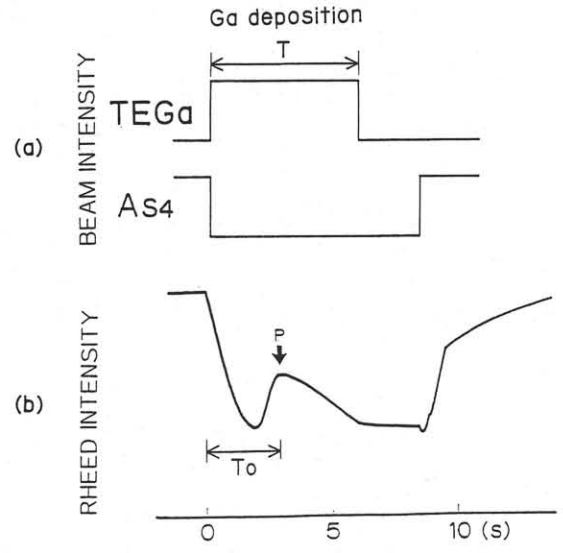

Fig.1. RHEED intensity variation during TEGa and As_4 alternate supply. (a) shutter operation sequence, and (b) corresponding RHEED intensity variation.

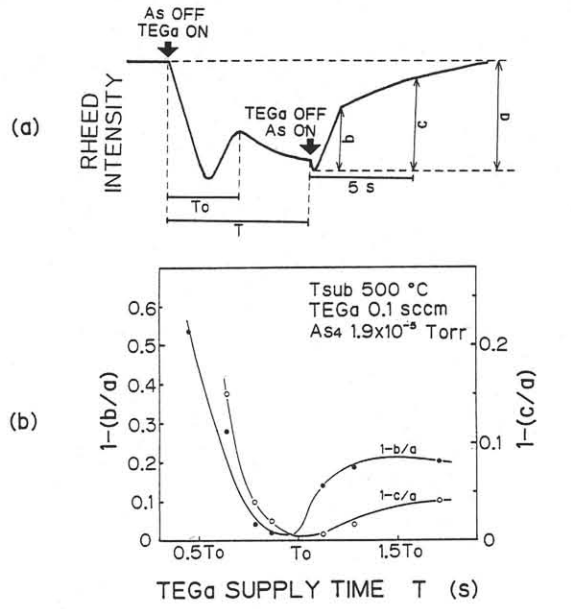

Fig.2. Recovery characteristic of RHEED intensity as a function of TEGa supply time. (a) RHEED intensity recovery after resupplying As_4 molecules, and (b) recovery as a function of the TEGa supply time.

After annealing the surface in the As_4 beam, we closed the As-cell shutter and simultaneously opened the TEGa-cell shutter to start the Ga deposition. The Ga deposition continued for T seconds. After closing TEGa-cell shutter, we reopened the As-cell shutter. As shown in Fig.1(b), the RHEED intensity dropped steeply at the start of Ga deposition. The intensity then rose to a maximum (at point P) after T_0 seconds from the start of the Ga deposition. It then decreased again monotaneously until the TEGa-cell shutter closed. The intensity recovered to the initial level when As-cell shutter reopened. This RHEED intensity behavior has been observed by Chiu et al. They compared it with the conventional RHEED intensity oscillation and concluded that the intensity peak during Ga deposition appears when the deposited Ga amounts to approximately one monolayer on the surface.[2] However, the relation between Ga surface coverage and the corresponding RHEED intensity during the Ga deposition has not been clarified directly.

Information about the Ga surface coverage at the RHEED intensity peak (P) was directly obtained by two experiments. The recovery charactaristic of the RHEED intensity after resupplying As_4 molecules on the Ga deposited surface and the growth rate of GaAs by TEGa and As_4 alternate supply were investigated. First, we observed the RHEED intensity recovery after resupplying As_4 molecules for various Ga deposition times. This intensity recovery process is sensitive to the initial surface coverage of Ga atoms.[3] As shown in Fig.2(a), the recovery itself consisted of two parts. A fast recovery appeared soon after reopening the As-cell shutter and a slow recovery appeared after the fast recovery. According to ref.3, the fast recovery corresponds to the adsorption of supplied As atoms on the Ga-rich surface and the slow recovery corresponds to the surface migration of GaAs molecules. If the number of Ga atoms is almost equal to the surface site number and if they are distributed in one atomic sheet on the surface, then very quick RHEED intensity recovery can be expected after the As-cell shutter reopens. The two parts of the RHEED intensity recovery are plotted in Fig.2(b) as a

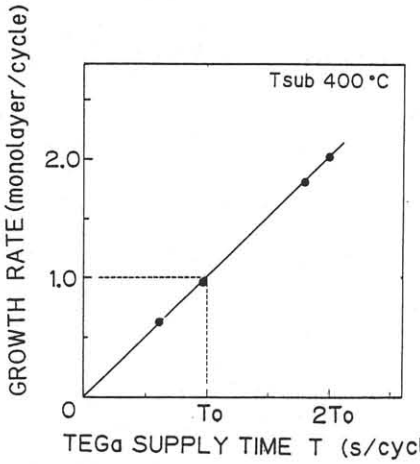

Fig.3. Growth rate per one cycle as a function of TEGa supply time.

function of the TEGa supply time T. This figure clearly shows that the RHEED intensity recovers rapidly when the TEGa supply time is close to T_0. This result means that the Ga monolayer is formed near the RHEED intensity peak (P).

Next, we measured the growth rate of GaAs by TEGa and As_4 alternate supply. Figure 3 shows the GaAs growth rate per one cycle as a function of the TEGa supply time T. The substrate temperatures were approximately 400 °C. At this substrate temperature the desorption of TEGa molecules can be neglected. As shown in Fig.3, the growth rate per one cycle increases linearly with increasing TEGa supply time T and is exactly one monolayer of GaAs when the TEGa supply time is T_0. This result demonstrates that the deposited Ga amounts exactly to one monolayer at the the RHEED intensity peak (P). These two experimental results clearly show that the RHEED intensity peak (P) during Ga deposition corresponds to Ga monolayer formation.

In MOMBE, TEGa molecules decompose on the substrate surface, so T_0 is the time for the number of Ga atoms provided by the decomposition of TEGa molecules to reach a monolayer unit. Thus, the TEGa decomposition can be estimated quantitatively by T_0. Here, we use $1/T_0$ as a measure of the TEGa decomposition rate, which represents the number of decomposed Ga atoms per second, normalized by the monolayer unit. By measuring $1/T_0$, we investigated the dependences of the TEGa decomposition rate on the substrate temperature and on the TEGa flow rate. The relationships between $1/T_0$ and the substrate temperature for four different TEGa flow rates are shown in Fig.4. The TEGa flow rates were chosen as 0.24, 0.48, 0.9 and 1.5 sccm. For a substrate temperature below 450 °C, the thermal pyrolysis of the adsorbed TEGa molecules becomes energetically unfavorable, and $1/T_0$ rapidly approaches zero near 350 °C. This substrate temperature dependence is almost the same as the results of GaAs growth rate in MOMBE using TEGa as a Ga source.[4,5] But comparing the experimental results of the TEGa gas phase decomposition in H_2 and N_2,[6] the reaction-limited region in the present result is 50-100 °C higher than that in the gas phase decomposition. This difference may be caused by the difference in reaction mechanism between surface and gas phase decomposition.

Figure 5 shows the dependences of $1/T_0$ on the TEGa flow rate for five different substrate temperatures from 350 °C to 470 °C.

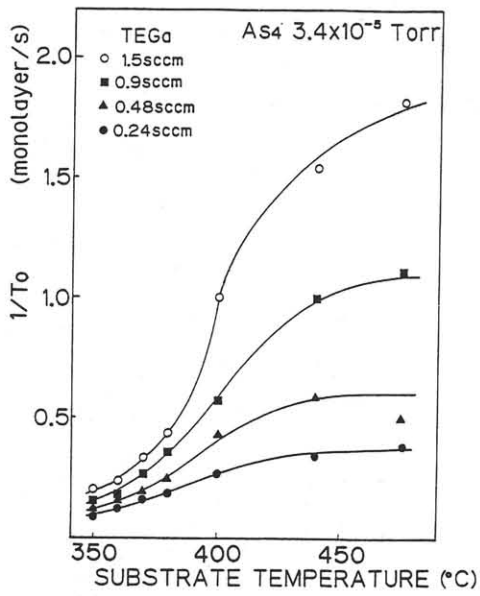

Fig.4. Dependence of $1/T_0$ on the substrate temperature.

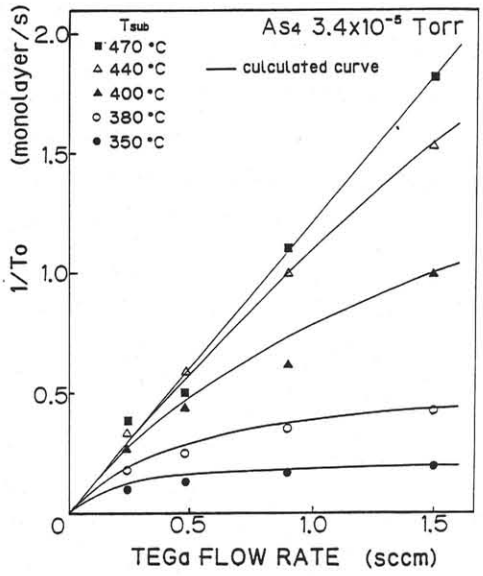

Fig.5. Dependence of $1/T_0$ on the TEGa flow rate.

At 470 °C, $1/T_0$ increases linearly with the TEGa flow rate. As the substrate temperature decreases below 440 °C, $1/T_0$ tends to saturate as the TEGa flow rate increases. This saturation can not be explained only by the decrease in the decomposition rate.

Assuming that the surface coverage of adsorbed TEGa molecules is limited, and that the TEGa sticking coefficient is unity on GaAs and zero on a TEGa covered surface, then we can derive an expression for the time dependence of the TEGa coverage.[7,8]

$$\frac{dX(t)}{dt} = sF(1-X(t)) - X(t)\left(\frac{1}{\tau_{dcp}} + \frac{1}{\tau_{dsp}}\right)$$

where X is the surface coverage of adsorbed TEGa molecules, F is the incident TEGa flux, s is the sticking coefficient of TEGa on GaAs, τ_{dcp} is the decomposition time constant and τ_{dsp} is the desorption time constant. Here, since we consider the reaction-limited region, the substrate temperature is low enough to neglect the desorption of TEGa molecules. So we assume $\tau_{dsp} \longrightarrow \infty$. Using realistic values for sF and τ_{dcp}, a reasonable fit to the experimental data is obtained as shown in Fig. 5 (solid curves). The model reproduces the non-linear dependence of the decomposition rate on the flow rate.

4. Summary

We investigated the RHEED intensity variation during TEGa and As_4 altenate supply growth of GaAs. The measurements of the RHEED intensity recovery after resupplying As_4 molecules on the Ga deposited surface and the growth rate of GaAs by TEGa and As_4 alternate supply demonstrated that the RHEED intensity peak appears when the Ga monolayer is formed on the GaAs surface. From this RHEED intensity peak observation, the TEGa decomposition rate on the GaAs surface was directly estimated as functions of the substrate temperature and the TEGa flow rate. The decomposition takes place in the substrate temperature range of 350-450 °C. In this reaction-limited region, the decomposition rate tends to saturate as the TEGa flow rate increases. This phenomenon can be well explained by the rate equation that considers the suface coverage of adsorped TEGa molecules.

Acknowledgements

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