

## Invited

## In Situ Mass Spectrometric Analysis of Surface Chemistry in MOMBE Growth

Masahiro Sasaki and Seikoh Yoshida

*Optoelectronics Technology Research Laboratory (OTL)  
5-5 Tohkodai, Tsukuba, Ibaraki 300-26, Japan*

The surface chemistry in metalorganic molecular beam epitaxy (MOMBE) was studied by observing desorbed species with a mass spectrometer from controlled surfaces of GaAs(100) exposed to continuous and pulsed trimethylgallium (TMG) beams. We found that TMG molecules were temporarily (for ca. 1ms at 546K) trapped during the initial stage of the surface reaction on clean GaAs surfaces, although they were desorbed without a trapping from an oxidized GaAs surface (a mask for selective-area epitaxy). The trapping of TMG is considered to be essential for selective-area epitaxy. We further found that all the TMG molecules trapped on GaAs surfaces were desorbed from a (2×4)-reconstructed surface ( $\theta_{As}=0.75$ ), while they were efficiently decomposed on surfaces with other reconstructions, such as c(4×4) and (1×6). This structure-dependent behavior was interpreted in terms of the stability of the surface.

## 1. INTRODUCTION

Metalorganic molecular beam epitaxy (MOMBE) is applicable to the fabrication of three-dimensional structures of compound semiconductors by using a surface chemical reaction which is sensitive to the surface condition.<sup>1-6</sup> In order to obtain sufficient growth controllability for realizing nanostructures, such as quantum wires and dots, it is necessary to understand the surface chemistry in MOMBE. We have investigated the surface reaction of trimethylgallium (TMG) on differently prepared GaAs(100) surfaces using a mass spectrometer,<sup>7</sup> which is an effective tool for *in-situ* observations.<sup>8</sup> Furthermore, by using the incidence of a pulsed TMG beam, we have obtained information concerning the dynamical behavior of the surface reaction.<sup>9,10</sup> In this paper we discuss the role of the stoichiometry-dependent structure of GaAs surface in the MOMBE reaction and the mechanism of selective-area epitaxy in terms of the surface residence time during scattering and the energy exchange between TMG molecules and surfaces during scattering.

## 2. EXPERIMENTAL APPARATUS

The experiments were carried out in an ultrahigh vacuum (UHV) system comprising an MOMBE chamber and a pulsed molecular-beam scattering chamber. The MOMBE chamber was equipped with a quadrupole mass spectrometer (QMS) having a liquid-nitrogen-cooled sampling aperture as well as gas nozzles and effusion cells for continuous source material supplies.<sup>8</sup> Using this spectrometer, we observed the chemical species desorbed from substrate surfaces exposed to TMG, and obtained information concerning surface reaction, such as the TMG decomposition rate on surfaces.<sup>7</sup>

In order to observe the dynamical behavior of the surface reaction, we measured a time-of-flight (TOF) spectrum of TMG scattered from surfaces using a pulsed TMG beam in the scattering chamber.<sup>9,10</sup> The incident TMG pulse shape was reproduced by the velocity distribution of

a translationally drifted Maxwellian with a drift velocity of 457 m/s and a velocity spread of 103 m/s. From the TOF spectra of scattered TMG, we estimated the surface residence time and the amount of energy exchange during scattering, which determines the initial stage of the surface reaction of TMG.

## 3. RESULTS AND DISCUSSION

## 3-1 TMG Decomposition Rate as a Function of the As Coverage

We observed the TMG reaction as a function of the As coverage of GaAs(100) surfaces, which were prepared by depositing different amounts of Ga onto well-defined surfaces.<sup>7</sup> Figure 1 shows the signal intensity for the TMG desorbed without decomposition when GaAs was exposed to a TMG flux. The dashed line in Fig. 1 represents the signal intensity for the introduced TMG flux. The distance between the dashed line and the measured signal intensity in Fig. 1 corresponds to the amount of decomposed TMG. We found that the TMG decomposition rate is strongly dependent on the As coverage. It should be noted

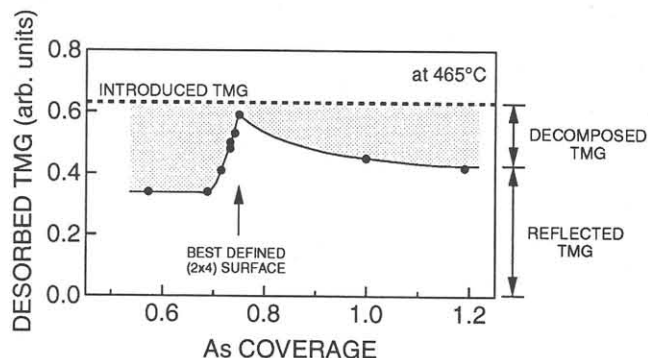


Fig. 1 Signal intensity for TMG desorbed without decomposition as a function of the As coverage. The dashed line shows the flux of incident TMG. The difference between the dashed line and the signal intensity corresponds to the fraction of decomposed TMG.

that the TMG decomposition rate is lowest on a surface with an As coverage of 0.75, and that even a small As coverage change of a few percent remarkably enhances the TMG decomposition.<sup>7)</sup>

The structure of a GaAs(100) surface with an As coverage of 0.75 is reported to consist of three As dimers and one missing dimer in a surface unit cell, which is energetically stable.<sup>11)</sup> The obtained results suggest that TMG decomposition is suppressed on a surface having a stable structure.

### 3-2. Scattering of Pulsed TMG Beam from GaAs Surfaces

To understand the As-coverage-dependent reaction of TMG in detail, we examined the scattering of a pulsed TMG beam from epitaxially-prepared GaAs surfaces having different As coverages: c(4×4)-reconstructed surface ( $\theta_{\text{As}} \approx 1.2$ ), (2×4)-reconstructed surface ( $\theta_{\text{As}} = 0.75$ ) and (1×6)-reconstructed surface ( $\theta_{\text{As}} \approx 0.2$ ).<sup>10)</sup> Figure 2 shows the TOF spectra obtained at 546K on these surfaces. It was noticed that these spectra have a long tail which corresponds to the surface residence of TMG molecules during scattering. We analyzed these spectra by curve-fitting to the sum of the components for scatterings with and without surface residence, where these components are represented by the convolution of the surface residence time and the velocity distributions of the incident and scattered TMG. The solid lines in Fig. 2 are the results of curve-fitting. All the measured TOF spectra were well reproduced by the theoretical fittings.

The obtained residence time ( $\tau$ ) was about 0.9ms and the velocity distribution of scattered TMG showed thermal equilibrium for the substrate temperature, independent of the As coverage. However, we observed a large difference in the fraction of the two components; the component for the scattering with surface residence was dominant for the (2×4) surface, while this component was extremely small for the c(4×4) and (1×6) surfaces.

The sticking coefficients of TMG can be estimated by integrating the TOF spectrum for a split dosage. The obtained sticking coefficient was zero on the (2×4) surface and about 0.7 on the c(4×4) and (1×6) surfaces.<sup>10)</sup> These results are consistent with the TMG decomposition rates measured using a continuous TMG beam, as described in the previous subsection.

Surface chemical reactions are often discussed by taking into account the precursor state.<sup>12)</sup> In this framework, molecules are temporarily trapped in a precursor state during the initial stage of surface reaction. While being trapped, a certain fraction of the molecules move into a chemisorbed state, resulting in dissociation. The long residence time obtained from an analysis of the TOF spectra indicates the existence of precursor states with a deep trapping potential. We observed no permanent sticking on the (2×4) surface, although a long residence time generally gives a high probability of chemisorption. This anomalous feature is considered to be caused by a high potential barrier to chemisorption or a high stability of this surface.

On the c(4×4) and (1×6) surfaces, we observed only a small fraction of the component with surface residence in the TOF spectra (Fig. 2). This result does not necessarily indicate a small density of trapping sites which generate a long surface residence. We speculate that, although there exist the trapping sites also on these surfaces, molecules

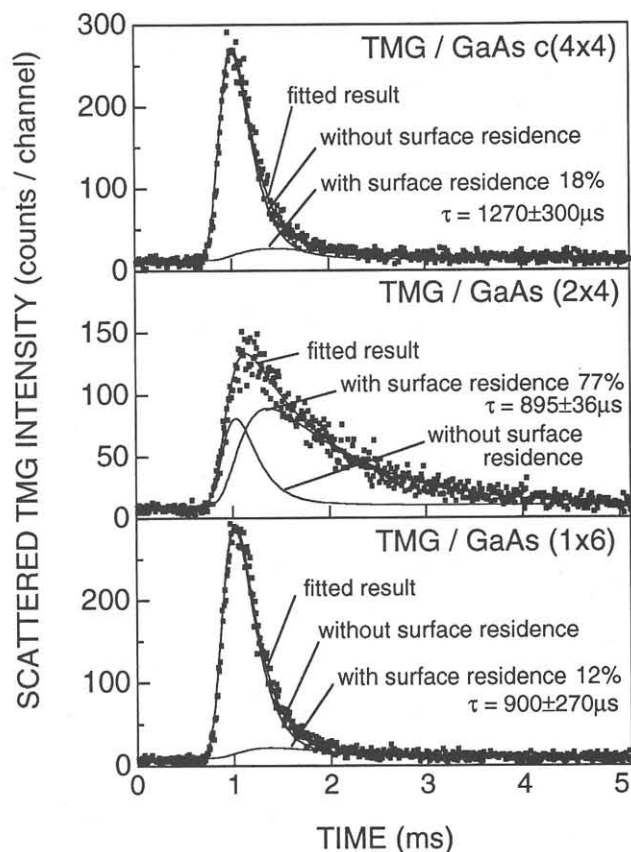


Fig.2 Time-of-flight spectra of TMG scattered from epitaxially-prepared GaAs surfaces with c(4×4), (2×4) and (1×6) reconstructions. The solid lines show the result of curve-fitting. The fractions of scattering with surface residence and the residence time obtained by curve-fitting are given.

trapped in precursor states efficiently move into the chemisorbed states since the surface stability of these surfaces is not very high. (The trapped molecules do not appear in the TOF spectra.)

The rapid increase in the TMG decomposition rate caused by a change in the surface stoichiometry (shown in Fig. 1) can be interpreted as follows. We consider that TMG molecules trapped on the (2×4) surface can migrate over a wide area during a long surface residence. When an As coverage change generates active sites, TMG molecules can efficiently reach the active sites. Consequently, the TMG decomposition can be remarkably enhanced.

### 3-3. TMG Scattering from a Mask Surface of Selective-Area Epitaxy

We investigated the scattering of a pulsed TMG beam from photo- and dark-oxidized GaAs surfaces, which both act as masks of selective-area growth since TMG decomposition is suppressed on them. The photo- and dark-oxidized GaAs surfaces were prepared by exposing the (2×4)-GaAs surface to pure oxygen, with and without halogen-lamp irradiation, respectively. The photo-oxidized GaAs surface has been shown to be more effective as a mask for the selective-area growth than a dark-oxidized surface.

Figure 3 shows the TOF spectrum measured for a dark-oxidized surface at 546K. This spectrum does not have a long tail. We carried out curve-fitting to the single com-

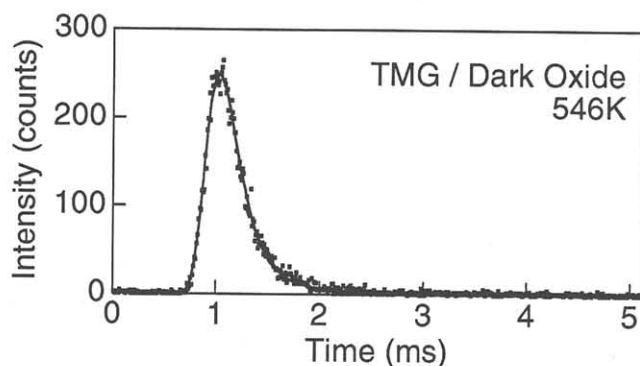


Fig.3 Time-of-flight spectrum of TMG scattered from dark-oxidized GaAs surfaces. The solid line shows the result of curve-fitting without surface residence.

ponent in which TMG is scattered with a velocity distribution of a translationally drifted Maxwellian. The solid line in Fig. 3 is the result of the curve-fitting, which well reproduces the spectrum without taking into account any surface residence. For a photo-oxidized surface, we obtained a similar result to that for a dark-oxidized surface, except for the values of the parameters (velocity spread

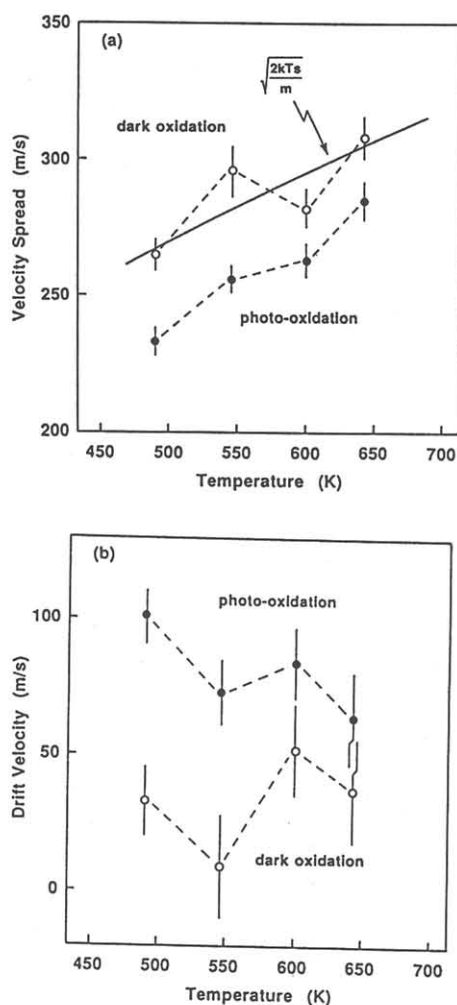


Fig. 4 (a) Transitional velocity spread and (b) drift velocity of the velocity distribution of TMG scattered from photo- and dark-oxidized GaAs surfaces at different substrate temperatures. The solid line corresponds to complete thermal equilibrium.

and drift velocity).

In Fig. 4, the velocity spread (a) and the drift velocity (b) obtained from curve-fitting are plotted as a function of the substrate temperature for photo- and dark-oxidized surfaces. If complete thermal equilibrium is maintained, the velocity spread would be equal to the solid line in Fig. 4(a), and the drift velocity in Fig. 4(b) would be zero. On the other hand, if there is no interaction, the pulse shape of the incident beam would not change after scattering. We found in Fig. 4 that the scattering from a dark-oxidized surface proceeded under conditions near to thermal equilibrium, and that the energy exchange during scattering from the photo-oxidized surface is smaller. From the results concerning the dark-oxidized surface, we can conclude that TMG molecules do not decompose even when they receive thermal energy from the substrate in equilibrium. Therefore, the decomposition selectivity, which provides a basis for selective-area epitaxy, cannot be caused only by the difference in the energy transfer during scattering. We speculate that the deep precursor state, which was observed only in the scattering from GaAs surfaces, causes an efficient TMG decomposition on a GaAs surface.

In practical selective-area epitaxy, complete suppression of TMG decomposition is required. We found that the energy transfer from the photo-oxidized surface to TMG molecules is small, which gives a higher suppression of decomposition. The behavior of the photo-oxidized GaAs is a favorable characteristic to the mask used in selective-area epitaxy.

#### Acknowledgment

The authors would like to thank Dr. C. Yamada, Dr. M. Tamura, Dr. Y. Katayama and Dr. I. Hayashi for their helpful discussions and continuous encouragement.

#### References

- 1) E. Tokumitsu, Y. Kudou, M. Konagai, and K. Takahashi, *J. Appl. Phys.* **55** (1983) 3163.
- 2) J. Nishizawa, T. Kurabayashi, H. Abe, and A. Nozoe, *Surf. Sci.* **185** (1987) 249.
- 3) A. Watanabe, T. Isu, M. Hata, T. Kamijo, and Y. Katayama, *Jpn. J. Appl. Phys.* **28** (1989) L1080.
- 4) Y. Hiratani, Y. Ohki, Y. Sugimoto, K. Akita, M. Taneya and H. Hidaka, *Jpn. J. Appl. Phys.* **29** (1990) L1360.
- 5) S. Yoshida and M. Sasaki, in *Proc. 19th Int. Symp. GaAs & Related Compounds, Karuizawa, Japan, 1992*, eds T. Ikegami, H. Hasegawa and Y. Takeda (Inst. Phys., London-Bristol, 1993) p49.
- 6) Y. Nomura, Y. Morishita, S. Goto, and Y. Katayama, *J. Electronic Materials* **23**, (1994) 97.
- 7) M. Sasaki and S. Yoshida, *J. Vac. Sci. Technol.* **B10** (1992) 1720.
- 8) Y. Ohki, Y. Hiratani, and M. Yamada, *Jpn. J. Appl. Phys.* **28** (1989) L1486.
- 9) M. Sasaki and S. Yoshida, *Jpn. J. Appl. Phys.* **33** (1994) L884.
- 10) M. Sasaki and S. Yoshida, to be published in *Surf. Sci.*
- 11) D. J. Chadi, *J. Vac. Sci. Technol.* **A5** (1987) 834.
- 12) J. B. Hudson, in *Surface Science; An Introduction* (Butterworth Heinemann, Boston, 1992).