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Laser Photodissociation of Trimethylaluminum and Trimethylindium on a Quartz Substrate: Laser-induced Fluorescence Study

Akihiko Sato, Kazuo Kasatani and Hiroyasu Sato*
Department of Chemistry for Materials, Faculty of Engineering, Mi'e University, Tsu 514, Japan

Laser photodissociation of trimethylaluminum and trimethylindium at 248 nm on a quartz substrate was studied by detecting aluminum and indium atoms appearing as reaction intermediates by laser-induced fluorescence. Photodissociation occurred predominantly in the adsorbed state in the experimental conditions. Kinetic energy distributions of the atoms were measured and were simulated by Maxwell–Boltzmann distributions in order to discuss photodissociation mechanisms.

Keywords: Photo-CVD, trimethylaluminum, trimethylindium, laser-induced fluorescence

INTRODUCTION

Photodissociation reactions of Group III alkyls such as trimethylaluminum [$Al(CH_3)_3$; TMA], trimethylgallium [$Ga(CH_3)_3$; TMG] and trimethylindium [$In(CH_3)_3$; TMI] are very important in relation to photo-CVD processes which are essential ingredients in present-day semiconductor technology.[1-3] In comparison with the very rapid industrial progress, however, fundamental research on the relevant reaction mechanisms is still sparse. In the beginning, Ehrlich *et al.*[4] studied deposition of aluminum films from TMA at 257.2 nm (the second harmonic of an argon-ion laser), together with that of cadmium films from $Cd(CH_3)_2$. A distinction was made between surface and gas-phase photodissociation, together with the manifestation of the important role of cluster formation in the deposition process. Higashi and co-workers[5,6] used an infrared technique to monitor the surface adsorbate during laser photochemical decomposition of TMA on oxide (Al_2O_3, etc.) surfaces at 248 nm and 193 nm.

Lasers are used effectively not only in photodissociation, but also in detection of reaction intermediates. Detection of intermediates is very important in the elucidation of reaction mechanisms. Highly sensitive and selective laser-based techniques, such as laser-induced fluorescence (LIF) and multiphoton ionization (MPI), are very effective in such investigations. For photodissociation in the gas phase, Mitchell and Hackett[7] detected aluminum, gallium and indium atoms produced by multiphoton dissociation of metal alkyls, using MPI by photolysis laser. Mitchell *et al.*[8] used MPI for detecting intermediates (gallium atoms and $Ga(CH_3)_n$ radicals, $n = 1, 2$) produced by multiphoton dissociation of TMG. Motooka *et al.*[9-11] used emission spectroscopy to detect photofragments produced in the excited states in the UV-laser photolysis of TMA. Zhang *et al.*[12] used laser mass spectroscopy for TMG. Beuermann and Stuke[13,14] photodissociated TMA, TMG and TMI by tunable UV laser light (190–310 nm), and detected fragments by one-photon ionization. Braun *et al.*[15] studied 193 nm photolysis of TMG by a unique quantum-yield measurement. The present authors[16] used MPI for detection of photofragments (gallium atoms and $Ga(CH_3)_n$, $n = 1$–3) in the laser photodissociation of TMG.

For photodissociation on solid substrates, the present authors probed gallium atoms produced on photodissociation of TMG on a quartz substrate at 248 nm.[17] It was concluded that thermally assisted photochemical dissociation in the adsorbed state occurred. Lubben *et al.*[18] studied ArF-laser photolysis of multilayered TMA on Si(100) 2 × 1 and Si(111) 7 × 7 surfaces by high-resolution electron energy loss spectroscopy (HREELS). Higashi[19] studied the 193 nm photolysis of TMA adsorbed on oxide surfaces (Al_2O_3, etc.). Zhang and Stuke[20,21] used laser time-of-flight (TOF) mass spectroscopy in the study of photodissociation of TMA, triethylaluminum and tri-isobutylaluminum. Orlowski and Mantell[22] measured TOF of fragments, $(Al(CH_3)_n$, $n = 0$–3

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* Author to whom all correspondence should be addressed.

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and CH_3) and obtained Maxwell–Boltzmann distributions. McCaulley *et al.*[23] studied XPS on TMG and triethylgallium adsorbed on GaAs(100). Hsu and co-workers[24,25] studied 222 nm photolysis of TMI adsorbed on quartz by MPI- and electron impact–TOF mass spectroscopy. Kawasaki and Nishi[26] found dependence of TOF distribution of fragments on the layer thickness on the 193 nm photolysis of TMG adsorbed on a quartz substrate cooled to 100 K. The present authors used MPI–TOF mass spectroscopy for the detection of reaction intermediates in the laser photodissociation of TMG in the gas phase and on a quartz substrate,[16] and of TMA on a quartz substrate.[27] They[28] reported an LIF study of photodissociation of TMG on a quartz surface at 20 °C. The results on TMA were also reported briefly. In the present paper, studies of photodissociation of TMA and TMI on quartz substrates are reported. The LIF technique has been used for the detection of aluminum and indium atoms, to obtain further insight into relevant reaction mechanisms.

EXPERIMENTAL

A schematic view of the experimental apparatus is given in Fig. 1. A quartz substrate was placed on a brass holder in a vacuum chamber, which was evacuated by an oil diffusion pump ($1400\,l\,s^{-1}$) backed by a rotary pump. The base pressure in the chamber was maintained below 10^{-4} Torr even when sample gas was introduced. The vapor pressures of TMA and TMI are very low at room temperature (*ca* 10 Torr and 2 Torr, respectively). For TMA, a 1:2 mixture of TMA and helium was prepared by bubbling helium gas through TMA. For TMI, a 1:40 mixture of TMI and helium was stored in a reservoir (20 l). The sample gas was injected into the vacuum chamber through a pulsed nozzle (a modified automobile fuel injector). A KrF excimer laser (Lambda Physik EMG 101 MSC, 50 mJ pulse^{-1}, 10 ns, 5 Hz) was used for photodissociation. The laser pulse was fired after an appropriate delay and irradiated onto the substrate surface. In some experiments a Nd:YAG laser [Quanta-Ray, DCR-2(10)] was used for photodissociation. All the experiments were carried out at room temperature.

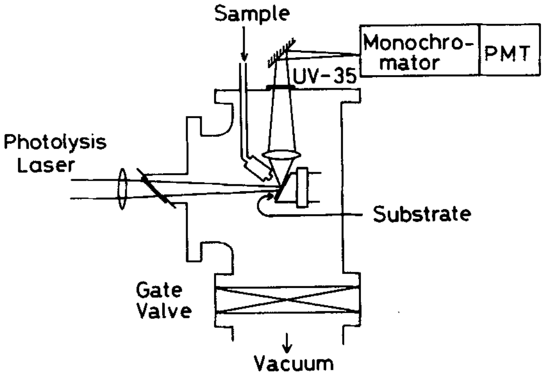

Figure 1 Schematic view of the experimental apparatus. PMT, photomultiplier.

The density of aluminum or indium atoms formed in the space above the substrate was monitored by LIF using a dye laser (Lambda Physik FL-3002) driven by another excimer laser (Lambda Physik EMG 105) operated at 308 nm. The dye laser light beam passed parallel to the substrate surface (perpendicularly to the plane of the paper). The light was focused after it traversed the space to be monitored in order to minimize unnecessary multiphoton absorption acts. The diameter of the dye laser light beam in the region just above the substrate was *ca* 2 mm. The LIF was detected by a gated multichannel plate (MCP) photomultiplier (Hamamatsu R204U) through a UV cutoff filter (UV-35) and a monochromator (Jobin Yvon H20). The signal was fed to a homemade gated integrator via an oscilloscope (Tektronix 7904) which worked simultaneously as an amplifier and a monitor scope, then stored and processed by a personal computer (NEC 9801 VX).

RESULTS

Trimethylaluminum

For TMA, LIF was detected by excitation by $4^2S_{1/2} \leftarrow 3^2P_{1/2}$ absorption at 394.4 nm. The observing wavelength was 396.2 nm corresponding to the $4^2S_{1/2} \rightarrow 3^2P_{3/2}$ transition (Fig. 2).

Observed LIF intensity ($I_{\rm LIF}$) values were plotted against laser power. A typical result is given in Fig. 3. $I_{\rm LIF}$ values at two delay times (2 and 9 μs) after the dissociation laser pulse are given. The exponent n in Eqn [1],

$$I_{\rm LIF} = kI_{\rm L}^{n} \qquad [1]$$

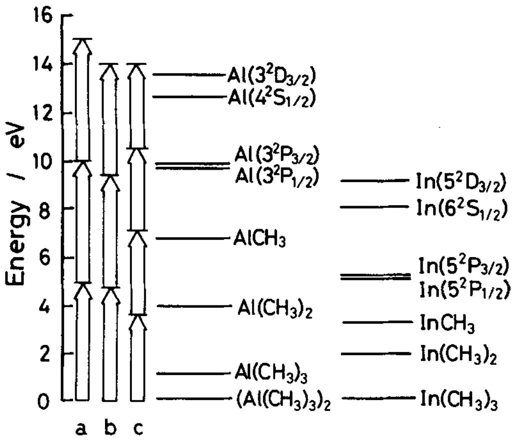

Figure 2 Energy levels of TMA, TMI and related radicals and atoms (drawn using the data of Ref. 8). The lengths of the arrows correspond to (a) 248, (b) 266 and (c) 355 nm.

where I_L is the dissociation laser power, was determined by a least-squares fit to be 4.5 and 3.7 for 2 and 9 μs after the dissociation laser pulse, respectively. Approximately four photons are needed to give aluminum atoms in this experimental condition.

The LIF intensity was measured as a function of time after the dissociation laser pulse, for various values of the height l of dye laser beam above the substrate surface. Typical results are given in Fig. 4. The peak of LIF intensity shifts to a later time for a larger value of l. Evidently, photodissociation occurred predominantly on the substrate surface, and aluminum atoms diffused into the space above the substrate surface. Observed LIF intensity curves represent the distribution of time of flight (TOF) of aluminum atoms from the substrate surface to the region probed by the dye laser light. (When injection of the sample gas was stopped, the LIF intensity decreased to less than 10%, which was due to laser ablation of the aluminum film formed beforehand.)

The TOF curves of aluminum atoms were simulated by assuming a Maxwell–Boltzmann distribution. A translational temperature of 2000 K was obtained, although the experimental curve accompanies an extra tail corresponding to some lower-energy components.

Trimethylindium

In the LIF detection of indium atoms from photodissociation of TMI, the atoms were excited through the transition $6^2S_{1/2} \leftarrow 5^2P_{1/2}$ at 410.1 nm, and detected by another transition $6^2S_{1/2} \rightarrow 5^2P_{3/2}$ at 451.1 nm. LIF of indium atoms was much weaker than that of aluminum atoms from TMA, leading to a poorer signal-to-noise ratio. Laser power dependence of I_{LIF} was measured using the third (355 nm) and fourth (266 nm) harmonic of the Nd:YAG laser. A typical result is given in Fig. 5. The value of the exponent n in Eqn [1] was determined by a least-squares fit to be 1.36 and 1.25 for 355 and 266 nm, respectively, as shown in Fig. 5. Two photons are needed in the photodissociation. The deviation of observed values can

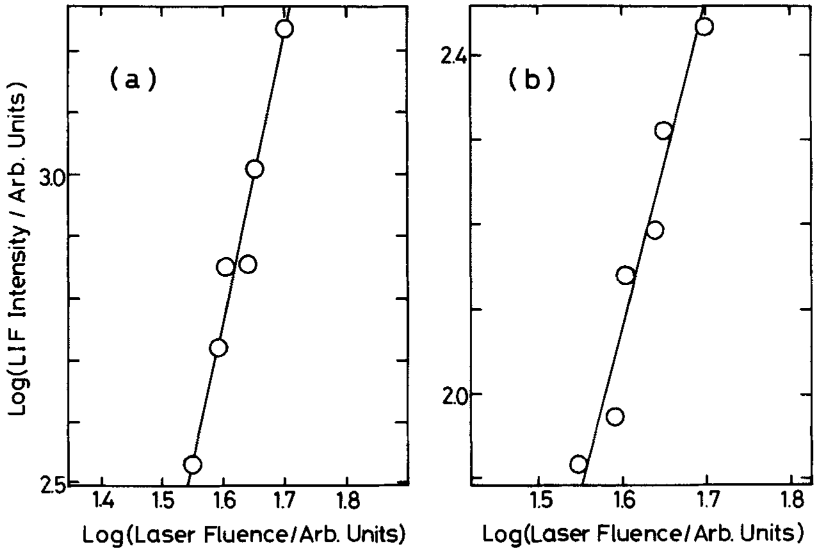

Figure 3 Dependence of LIF intensity of aluminum atoms on the fluence of the 248 nm dissociation laser light, measured at (a) 2 and (b) 9 μs after the dissociation laser pulse.

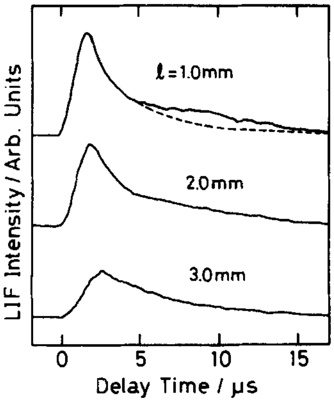

Figure 4 Temporal variation of the LIF signal of aluminum atoms after a 248 nm photodissociation laser pulse, probed at various vertical distances (*l* mm) from the substrate surface. Broken line: simulated curve with a translational temperature of 2000 K.

be attributed to the presence of dissociation path(s) competitive in the intermediate excited state of resonant 1 + 1 photon excitation, among other possible origins.

The LIF intensity was measured as a function of time after the dissociation laser pulse for various values of *l*. The results are given in Fig. 6. Because the observed LIF was very weak, the false signal near $t = 0$ due to scattered light was rather pronounced. The shift in the peak positions to later times with the increase in *l* indicates that the photodissociation occurred predominantly on the substrate surface. Simulation of the observed distribution was attempted by assuming the Maxwell–Boltzmann distribution. Although the fit was much poorer than in the TMA case, a more or less reasonable fit was obtained with a translational temperature of 2500–3000 K. The poor fit is undoubtedly due to the poor signal-to-noise ratio of the data.

DISCUSSION

The energy levels of TMA, TMI and related radicals and atoms are shown in Fig. 2, which has been drawn using the data of Mitchell *et al.*[8] The arrows in the figure correspond to the 248, 266 and 355 nm light used. Absorption bands of TMA and TMI, with a maximum near 200 and 215 nm, respectively, extend to *ca* 260 nm.[1] Therefore, the first photon is in resonance with the absorption bands.

Motooka and co-workers[9-11] proposed for TMA a cascade of one-photon processes (Eqns [2]–[5]):

$$(\mathrm{Al(CH_3)_3})_2 + h\nu \rightarrow 2\mathrm{Al(CH_3)_3} \qquad [2]$$

$$\mathrm{Al(CH_3)_3} + h\nu \rightarrow \mathrm{Al(CH_3)_2} + \mathrm{CH_3} \qquad [3]$$

$$\mathrm{Al(CH_3)_2} + h\nu \rightarrow \mathrm{AlCH_3} + \mathrm{CH_3} \qquad [4]$$

$$\mathrm{AlCH_3} + h\nu \rightarrow \mathrm{Al} + \mathrm{CH_3} \qquad [5]$$

in which a total of four photons are necessary to yield aluminum atoms. Orlowski and Mantell[22]

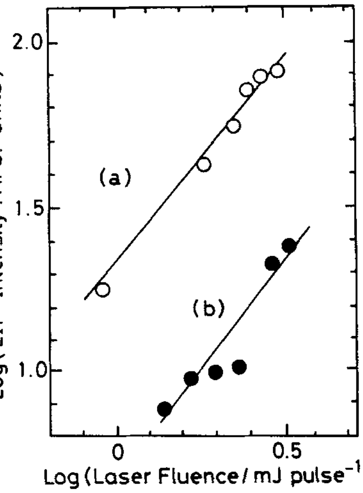

Figure 5 Dependence of the LIF intensity in indium atoms on the fluence of (a) 266 and (b) 355 nm photodissociation laser light.

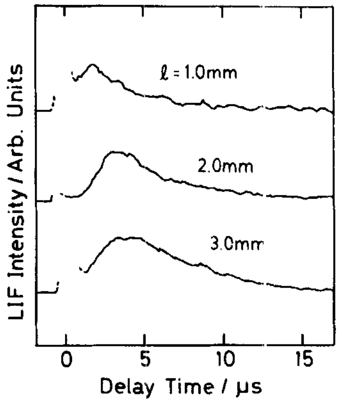

Figure 6 Temporal variation of the LIF signal of indium atoms after a 248 nm photodissociation laser pulse, probed at various vertical distances (*l* mm) from the substrate surface. The signals indicated by broken lines near $t = 0$ are due to scattered laser light.

considered the threshold behavior they found on $Al(CH_3)_2$ and $AlCH_3$ fragments as suggestive of the stepwise removal of methyl fragments. However, Beuermann and Stuke[13,14] put forward a one-photon decomposition process such as that represented by Eqns [6]–[8],

$$M(CH_3)_3 + h\nu \rightarrow M(CH_3)_3^* \qquad [6]$$

$$M(CH_3)_3^* \rightarrow M(CH_3)_2^\ddagger + CH_3 \qquad [7]$$

$$M(CH_3)_2^\ddagger \rightarrow M + C_2H_6 \qquad [8]$$

where M = Al, Ga, In, to explain the energy threshold for the metal atom generation, which is considerably below the sum of all three metal–carbon bond energies. $M(CH_3)_2^\ddagger$ is a dimethylmetal species with large internal energy. (The metal atoms were detected by laser ionization.) In their mechanism the monomethylmetal species is produced by Eqn [9].

$$M(CH_3)_3^* \rightarrow MCH_3 + CH_3 + CH_3 \qquad [9]$$

The MCH_3 species may absorb another photon to give metal atoms (Eqn [10]),

$$MCH_3 + h\nu \rightarrow M + CH_3 \qquad [10]$$

although this is not included in their scheme. A total of one photon and two photons is required in production of metal atoms in Eqns [8] and [10], respectively. Recent results of quantum yield measurements by Braun *et al.*[15] are in accord with these mechanisms.

Motooka and co-workers[9–11] reported that one photon is necessary to monomerize a TMA dimer, and Zhang and Stuke[29] mentioned the photomonomerization reaction, although it was not taken into consideration in Beuermann and Stuke's treatments.[13,14] By taking into account this extra photon for monomerization in addition to the mechanisms reported by Stuke's group (Eqns [6]–[10]), a total of two or three photons is required in production of one aluminum atom from a TMA dimer.

Four photons are consumed for the production of aluminum atoms in our experiments. Therefore, four-photon absorption is assumed in the energy balance considered below. The metal atoms are considered to be given by two paths, represented by the sequence of Eqns [2]–[6]–[9]–[10] and [2]–[6]–[7]–[8]. With the dimerization energy (E_{dimer}) of 0.87 eV,[30] we have for production of one aluminum atom from one dimer molecule (Eqn [11] or [12]).

$$E_{\mathrm{AVL}} = 4N_0h\nu - 3D_0 - E_{\mathrm{dimer}} = 1004\ \mathrm{kJ\ mol^{-1}} \qquad [11]$$

for the [2]–[6]–[9]–[10] path, or

$$E_{\mathrm{AVL}} = 4N_0h\nu - 3D_0 - E_{\mathrm{dimer}} + E_{\mathrm{ethane}}$$
$$= 1380\ \mathrm{kJ\ mol^{-1}} \qquad [12]$$

for the [2]–[6]–[7]–[8] path.

In the equations above, N_0 is Avogadro's number, D_0 is the averaged dissociation energy of three Al—C bonds ($2.9\ \mathrm{eV} = 280\ \mathrm{kJ\ mol^{-1}}$ from Ref. 31) and E_{ethane} is $D_0(CH_3\text{—}CH_3) = 3.9\ \mathrm{eV} = 376\ \mathrm{kJ\ mol^{-1}}$ from Ref. 14. Distribution of this E_{AVL} into various degrees of freedom is considered in two cases.

(1) For an even distribution of E_{AVL} among the translational energy of an aluminum atom ($3RT/2$), and the translational ($6RT$), vibrational ($51RT$) and rotational energy ($6RT$) of three methyl radicals plus one trimethylaluminum radical, $64.5RT = 1004$ or $1380\ \mathrm{kJ\ mol^{-1}}$ yields $T = 1870$ or 2570 K.

(2) An even distribution among the translational energy of an aluminum atom and the translational and rotational energy of three methyl radicals plus one trimethylaluminum radical gives $T = 8950$ or $12\,300$ K.

Case (1) gives a reasonable fit of the translational temperature with the experimental value.

For the TMI case, the energetic situation was considered with Eqn [13] or [14],

$$E_{\mathrm{AVL}} = 2N_0h\nu - 3D_0 \qquad [13]$$

or

$$E_{\mathrm{AVL}} = 2N_0h\nu - 3D_0 + E_{\mathrm{ethane}} \qquad [14]$$

for the [6]–[9]–[10] path or the [6]–[7]–[8] path, respectively.

Using $D_0 = 1.8$ eV,[31] we obtain $E_{\mathrm{AVL}} = 444$ (Eqn [13]) or $820\ \mathrm{kJ\ mol^{-1}}$ (Eqn [14]). Again we consider two cases:

(1) When we assume an even distribution of E_{AVL} among the translational energy of an indium atom ($3RT/2$) and the translational ($9RT/2$), vibrational ($18RT$) and rotatio-

nal ($9RT/2$) energy of three methyl radicals, we obtain $T = 1870$ or 3460 K.

(2) An even distribution of E_{AVL} among the translational energy of an indium atom ($3RT/2$), and the translational ($9RT/2$) and rotational ($9RT/2$) energy of three methyl radicals, gives $T = 5090$ or 9390 K.

Again, case (1) gives a reasonable fit to the observed translational temperature.

CONCLUSIONS

UV laser photolysis of TMA and TMI on quartz substrates was studied by LIF measurements of aluminum and indium atoms, respectively. Translational energy distributions of these atoms were fitted to the Maxwell–Boltzmann distribution. Translational temperatures of 2000–3000 K were obtained. Plausible energy disposal in the dissociation processes is discussed.

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