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Quantum Yield and Carbon Contamination in Thin-film Deposition Reaction by Core-electron Excitations

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The excitation energy dependence of the reaction quantum yield and the carbon contamination in synchrotron radiation-stimulated aluminum thin-film deposition using the low-temperature condensed layer of dimethylaluminum hydride (DMAH) were evaluated quantitatively in the vacuum ultraviolet region for the first time. It has been found that the core-electron excitation gives a few tens to hundreds of times higher a reaction quantum yield than the valence-electron excitations. This is explained qualitatively by the Auger-stimulated desorption model. The carbon contamination decreases due to a site-specific effect of the core-electron excitations.

Keywords: synchrotron radiation; dimethylaluminum hydride; core-electron excitation; thin-film deposition;

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1 INTRODUCTION

Photo-induced processes using lasers or discharge lamps as an excitation light source have been investigated actively during the last decade from the viewpoint of various applications such as photochemical vapor deposition,[1] new micro-fabrication techniques[2] and micromachining.[3] In these cases, the chemical reactions are induced thermally or by valence-electron excitations. Core-electron excitation has been regarded as one of the most important subjects in the field of photo- or electron-stimulated desorption (PSD, ESD) of surface absorbates[4] and decomposition of gas molecules.[5] In these fields, however, almost all the work on core-electron excitations has been done by detecting the fragment ions from the surface absorbates or the gas molecules. Eberhardt *et al.*[6] found site-specific effects for the first time in the core-electron excitation of simple gas molecules and suggested that this site-specific effect might play an important role in the reaction of condensed systems such as photochemical syntheses and photochemical thin-film depositions. Very few studies have been performed to verify this suggestion, however,[7,8] and the characteristics of this kind of condensed phase core-electron excitation chemistry are still unknown. Studies of synchrotron radiation (SR)-stimulated processes such as etching,[9] thin-film deposition,[10] and surface modification[11] have been studied extensively in recent years with the goal of developing a new field of application of SR or a new beam-induced process technique.[12] Fundamental knowledge regarding the core electron excitation chemistry is also useful for the study of the radiation damage with the biological materials.[13] Although these SR-induced chemical reactions are closely related to core-electron excitation, no experiments have been performed to elucidate the relationship. Even the excitation-energy dependence of the reaction quantum yield, a basic parameter of the chemical reaction, is completely unknown. One reason for this lack of investigation lies in the difficulty in obtaining tunable monochromatized light in the vacuum ultraviolet (VUV)

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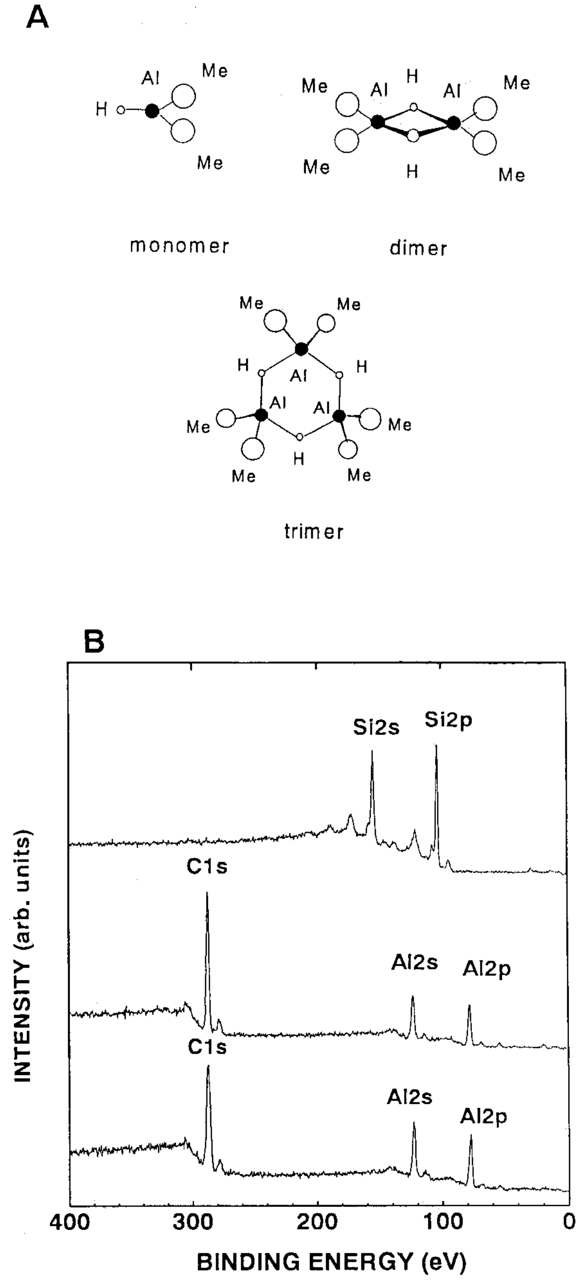

Figure 1 (A) Structure of DMAH. It is reported that DMAH vapor consists of a mixture of trimer and dimer species at 80 °C and only dimer species at 170 °C.[14] The detailed structure of dimer species is determined by electron diffraction.[15] The low-temperature condensed layer consists of only trimer above 130 K.[16] (B) X-ray photoelectron spectra of the substrate surface just after cleaning (top), just after DMAH deposition at 150 K (center), and after SR irradiation at a 800 mA min dose using an A1 filter. All observations were made at about 150 K.

range with a sufficiently high photon flux to detect the neutral reaction products.

Dimethylaluminum hydride (DMAH, Fig. 1A)[14–16] is an important organometallic compound for the thermal CVD of aluminum thin film, in which carbon contamination is known to be low owing to the desorption of methyl groups by the reaction[17]

$$-CH_3(s) + H(s) \longrightarrow CH_4(g)$$

In photo-CVD with DMAH, where experiments using excimer lasers have been actively carried out, however, severe carbon contamination is known to occur, although its mechanisms are not sufficiently elucidated.[18]

In this study of SR-stimulated aluminum thin-film deposition using a low-temperature condensed layer of DMAH, the excitation-energy dependences of the reaction quantum yield and the carbon contamination were investigated quantitatively in the VUV region for the first time.

2 EXPERIMENTAL

Experiments were carried out in the beamline 4A of the SR facility (UVSOR) of the Institute for Molecular Science. The SR ring energy was 0.75 GeV. The spectrum distribution of the white beam and the transmittance characteristics of the LiF (thickness 2 mm), aluminum thin film (thickness 150 nm), and carbon thin film (thickness 120 nm) filters used in the present experiment are shown in Fig. 2. Here, the photon flux spectrum (Fig. 2A) was calculated by using Schwinger's equation[19] for the 100 mA ring current and ±0.5 mrad horizontal and ±0.5 mrad vertical divergence angles, the beam of which irradiated the $4.7 \times 4.7\ mm^2$ area at the center of the sample surface. This area was almost equal to the observation area for the X-ray photoelectron spectroscopy (XPS; VSW Ltd, model Class 150) used in the present experiments. After cleaning by the conventional wet process, the $10 \times 12\ mm^2$ Si(100) substrate, covered by SiO_2, about 0.3 nm thick was inserted into the ultrahigh-vacuum (UHV) reaction chamber (the base pressure was 7.5×10^{-10} Torr), and then heated to about 600 K. This heating almost completely removed the carbon contamination on the sample surface, as verified by the XPS spectrum shown in Fig. 1B. After this surface cleaning process, DMAH was deposited on

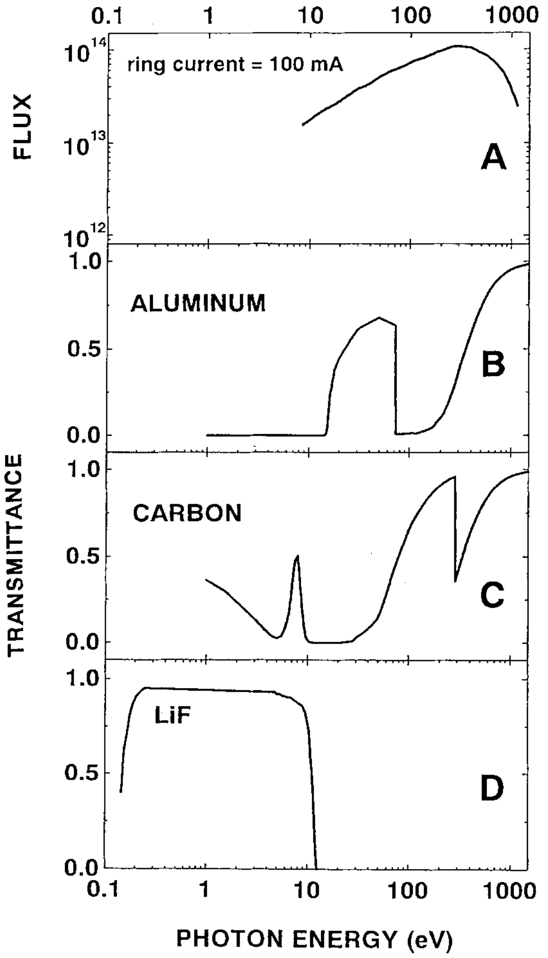

Figure 2 Calculated photon flux spectrum of the beamline 4A of UVSOR (A), and the transmission spectra of aluminum (150 nm thickness) (B), carbon (120 nm thickness) (C) and LiF (2 mm thickness) (D) filters. The photon flux is calculated for nonmonochromatized total photons emitted for 1 mrad horizontal × 1 mrad vertical divergence angles, 10% bandwidth and 100 mA ring current.

it at about 150 K by introducing DMAH gas purchased from Tri Chemical Lab. Inc., and purified using liquid nitrogen freeze–thaw cycles in the reaction chamber via a nozzle set close to the sample surface through a variable-leak valve. The SR beam was reduced in size by a slit in order to make sure that places other than the $10 \times 12\ \mathrm{mm}^2$ sample surface were not irradiated; furthermore, it was attenuated in intensity to about 8% by a stainless steel mesh to protect the filters from thermal destruction. This attenuation was also necessary to suppress any increase in the substrate temperature caused by irradiation, and to keep the substrate below 160 K, since our preliminary experiments of temperature-programmed desorption had shown that the low-temperature condensed layer of DMAH started to desorb thermally at 160–170 K. It should be noted that the condensed layer of DMAH deposited at less than 130 K is a metastable mixture of dimers and trimers (Fig. 1A) and changes irreversibly to the stable structure, composed of only trimers, at a temperature above 130 K.[16] Thus, to work with a stable structure, the deposition temperature was kept at 150 K in the present experiments.

The composition ratios between C and Al (C/Al) of the as-deposited and the SR-irradiated films were determined by measuring the intensity of the C 1s (Ic) and the Al 2p (Ia) peaks from the XPS as shown in Fig. 1(B). The measurement time, as far as monitoring XPS was concerned, was limited to less than 45 min to keep the decomposition of DMAH by the MgK_α line irradiation itself at an ignorable level. The sensitivity calibration factor β, defined by $\mathrm{C/Al} = \beta(\mathrm{Ic/Ia})$, was determined to be 0.57 by assuming that the C/Al ratio for the as-deposited film was 2. This calibration agrees well with the value (0.54) obtained by the calculation using the reported atomic sensitivity factor values.[20] XPS for the SR-irradiated samples, after desorbing all unreacted species by increasing the substrate temperature to 600 K, was used to determine the thickness *d* of the deposited aluminum film (containing carbon) from the peak intensity ratio between the Al 2p and the Si 2s peaks (obtained from the deposited film and the silicon substrate, respectively).

3 RESULTS AND DISCUSSION

The values obtained for the C/Al ratio and the deposited film thickness *d* are shown for each filter in Fig. 3A. To understand the relationship between these data and the excitation energy in more detail, the number of photons absorbed per DMAH molecule, *f*, during the irradiation time *T* in the energy band *E* to ($E + \Delta E$) was calculated from Eqn 1:

$$f = \int^{E} \int^{T} p(E,t)\sigma(E)\mathrm{d}t\mathrm{d}E \qquad [1]$$

Here, *p(E,t)* is the photon flux per unit area on the

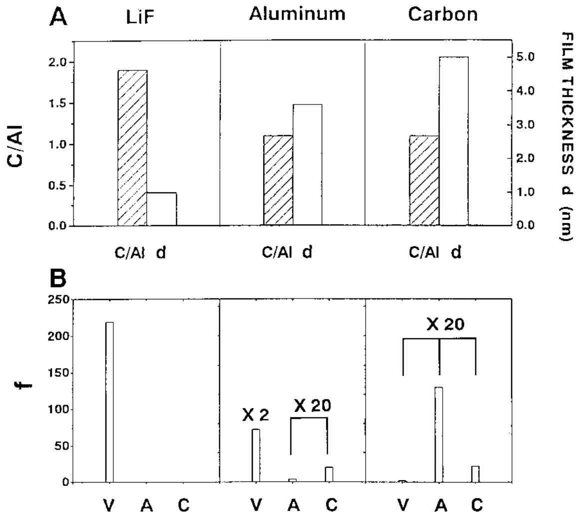

Figure 3 (A) The composition ratio (C/Al; hatched bars) of the condensed layer just after the filtered SR beam irradiation, and the deposited film thickness (*d;* empty bars) are given for the LiF (left), aluminum (center) and carbon (right) filters. (B) The dependence on the excitation energy of *f* (the number of absorbed photons per DMAH molecule during the irradiation in each energy region of V, A and C in Fig. 4) when using LiF (left), aluminum (center) and carbon (right) filters.

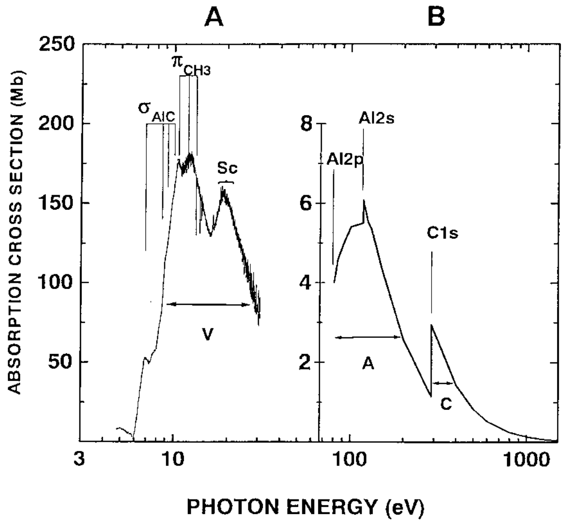

Figure 4 Absorption cross-section spectra for the valence-electron excitation region (A) and the core-electron excitation region (B). The valence-electron excitation region spectrum was measured in the beamline 2A of UVSOR. Details of the experiments and the assignment of the bands are described in Ref. 20. σAlC, πCH$_3$ and Sc denote the transitions of $\sigma_{\mathrm{AlC}} \rightarrow$ 4s, 5s and 6s Rydberg states and ionization states, $\pi_{\mathrm{CH_3}} \rightarrow$ 3s and 4s Rydberg states and ionization states, and Sc$\rightarrow$Rydberg states and ionization states, respectively. The spectrum in the core-electron excitation region was calculated by using the photoionization cross-section data reported in Ref. 22, and A12p, A12s and C1s mean the transitions from the corresponding core-electronic states.

sample surface at time *t* and photon energy *E*. σ (*E*) is the absorption cross-section at energy *E*. As necessary data for the calculation using Eqn 1, the absorption cross-section spectra of DMAH, measured for the valence electron excitation region (5–33 eV) with gas-phase molecules at room temperature[21] and calculated for the core-electron excitation region by using the reported atomic subshell photo-ionization cross-section data,[22] are shown in Figs 4(A) and 4(B), respectively. Although the spectrum shown in Fig. 4(A) is for gas-phase molecules, it is assumed here that it will also be valid for the condensed phase in the following analysis. The electronic spectrum of condensed-phase DMAH has not been reported, to our knowledge. It is, however, known that differences in the absorption spectra between the vapor and condensed phases are small in many molecules (for example, gas-phase and condensed phase spectra of H_2O are compared.

To compare the effect of the core-electron excitation with that of the valence-electron excitation, *f* in Eqn 1 was calculated for three regions of the spectrum as shown in Fig. 4; the valence-electron excitation region (V), the Al core-electron excitation region (A), and the C core-electron excitation region (C) are defined as the full width at half the maximum height of each absorption band. The calculated *f* value for each filter is shown in Fig. 3(B), as compared with the results of the deposited film thickness and the C/Al ratio (Fig. 3A). In these figures, the calculated *f* values for regions V, A and C, the deposited film thickness *d* and the C/Al ratio are given by the bar graph. It is clearly concluded from the comparison between Figs 3(A) and 3(B) that: (1) the core-electron excitation gives an extremely high reaction quantum yield compared with the valence-electron excitations; and (2) the core-electron excitation decreases the carbon contamination, although it is difficult to discuss the difference between the core-electron excitations of Al and C. The number (*N*) of Al atoms deposited is given by $N = nfY$, where *n* is the number of as-deposited DMAH molecules per unit area and *Y* is a quantum yield (number of molecules decomposed per excitation of DMAH). *N* values for the LiF, Al and C filters are calculated to be about 6×10^{15}, 2.2×10^{16} and 3×10^{16}

cm^{-2}, respectively, from the data shown in Fig. 3(A). The value of n estimated from the XPS data is $4 \times 10^{16}\ \mathrm{cm}^{-2}$ From these values and the f values in Fig. 3(B), the quantum yield Y is determined as 6.8×10^{-4}, 0.025 and 0.52, for valence-electron excitation (V), Al core-electron excitation (A), and C core-electron excitation (C) regions, respectively. Although these values are not better than the order estimations, it is clearly concluded that the core-electron excitation has a few tens to hundreds times higher a quantum yield than the valence-electron excitations.

Several reaction models are proposed for the photo- or electron-stimulated desorption. The Menzel–Gomer–Redhead (MGR) model[24,25] for the dissociation induced by Frank-Condon valence excitation, and the Knotek-Feibelmann (KF) model[26] for the dissociation or desorption induced by the core-electron excitations in highly ionic systems, are well known. For the photolysis of the covalent bond species, the Auger-stimulated desorption (ASD) model proposed by Ramaker[27] is considered to give a good explanation. According to this model, multivalence hole states are generated through Auger processes induced by the Al or C core-electron excitations in the present case. The hole–hole repulsive energy is considered to be much larger than the valence bandwidth of the condensed (physisorbed) system of DMAH, which is a molecule composed of covalent σ-bonding; thus the multivalence hole states remain localized until the molecule is decomposed along the repulsive Coulomb force potential.[26] This might explain the significantly high reaction quantum yield of the core-electron excitations observed in the present case. The excitation energy dependence of the carbon contamination (C/Al) is also explained, as follows. By the site-specific effects[6] in core-electron excitations, the Al–C bond is selectively broken by the Al or C core-electron excitations, reducing the carbon by its desorption in the form of $-\mathrm{CH}_3$ radicals or ions or CH_4 molecules. On the other hand, in the case of the valence-electron excitations where the transition from the π_{CH_3} orbital is dominant, the C–H bond is efficiently broken and the Al–C compound is formed.

The clearly observed excitation-energy dependence indicates that the contribution of the secondary electrons to the deposition is minor or ignorable. In fact, the observed secondary-electron emission current from the substrate surface in white beam irradiation, which was in the order of 10^{14} electrons $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$ for the 100 mA ring current, only gives an f value of a similar order of magnitude to that of the valence excitation in the case of the Al filter, if the excitation cross-section of the electron with 10–20 eV kinetic energy is asuumed to be 10^{-15}–$10^{-16}\ \mathrm{cm}^2$.

4 CONCLUSION

Excitation energy dependence on the carbon contamination and the deposition quantum yield in SR-stimulated aluminum thin-film deposition using the low-temperature condensed layer of DMAH was evaluated experimentally by irradiating with a filtered SR beam using LiF, Al and C filters. It has been found that the Al and/or C core-electron excitations give lower levels of carbon contamination and much larger quantum yields compared with the valence-electron excitations. These results are explained by the ASD reaction model. The contribution of secondary electrons from the substrate was evaluated as minor or ignorable.

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