Laser Review

Excimer Laser Photolysis of Trimethylaluminum for Film Growth

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The photolysis of dimerized trimethylaluminum, $\text{Al}_2(\text{CH}_3)_6$, (TMA) by excimer laser irradiation was investigated. The valence electronic structure of TMA was determined by photoelectron spectroscopy and molecular orbital (MO) calculations. On the basis of time-resolved optical emission spectroscopy combined with MO calculations, a model for the UV photolysis of $\text{Al}_2(\text{CH}_3)_6$ was developed, in which Al and CH were produced in the gas phase through cascade one-photon absorption processes in $\text{Al}_2(\text{CH}_3)_6$ and $\text{Al}(\text{CH}_3)_n$ ($n = 1, 2, 3$). High-resolution electron-energy-loss spectroscopy (HREELS) was also used to study the adsorption and UV-laser-induced dissociation of TMA on the Si(100) 2×1 and Si(111) 7×7 surfaces. HREELS spectra from TMA single adlayers were consistent with those expected for nondissociatively adsorbed TMA dimers. No changes in the adlayer spectra were observed under KrF laser irradiation, while ArF laser irradiation caused the dissociation of adsorbed TMA and the desorption of some methyl ligands.

Key Words: Excimer laser, Photolysis, Trimethylaluminum.

1. Introduction

Trimethylaluminum (TMA) is an important organometallic molecule used as source material for metal and III - V compound film growth by chemical vapor deposition. Isolated TMA molecules absorb light at the commonly available excimer laser wavelengths of 248 nm (5eV, KrF) and 193 nm (6.4eV, ArF) with cross-sections of $\cong 10^{-19}$ and 10^{-17}cm^2 , respectively. Although "laser-induced" deposition of Al and III - V films has been reported, there has been relatively little work aimed at developing a detailed understanding of the mechanism of UV-laser photolysis of TMA.

In this article, I have summarized our recent works¹⁻⁶⁾ for the understanding of the mechanisms of UV-laser photolysis of gas-phase and

surface-adsorbed TMA. Ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) spectra from condensed TMA layers revealed three broad valence-band peaks centered at ~ 15.0 , 7.5 , and 4.5eV below the Fermi level. The peaks were assigned, based on molecular orbital (MO) calculations, to correspond primarily to $\text{C}(2s) + \text{H}(1s)$, $\text{C}(2p) + \text{H}(1s)$, and $\text{Al}(3p) + \text{C}(2p)$ bonding orbitals, respectively. The wavefunctions of the occupied upper MO levels, corresponding to the 4.5eV UPS peak, were predominantly composed of $\text{Al}(3p)$ orbitals. Time-resolved optical emission spectroscopy, with a resolution of $\sim 10 \text{ns}$, was used to analyze the formation of excited photo-fragments during KrF laser-irradiation of gas-phase TMA. The primary peaks observed were the $\text{Al } 4s^2S \rightarrow 3p^2P$ atomic transition and the

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$\text{CH A}^2\Delta \rightarrow \text{X}^2\Pi (0,0)$ band. The rise time of the Al and CH emission were both < 10 ns indicating that these are formed photolytically from TMA rather than through subsequent collisions involving photofragments. TMA adlayers were formed on Si (100) 2×1 and Si (111) 7×7 surfaces and the effects of KrF- and ArF-laser irradiation on adlayer chemistry were studied using high-resolution electron-energy-loss spectroscopy (HREELS). There were no detectable differences in the HREELS spectra from single adlayers on Si (100) 2×1 and Si (111) 7×7 . Three primary peaks due to C-H stretching modes ($\cong 362$ meV), C-H deformations modes ($\cong 170$ meV), and Al-C stretching modes (87 meV) were observed. KrF laser irradiation of single TMA adlayers were found to have no effect up to the highest laser intensity (200 mJ/cm^2) and dose (10^4 pulses) examined. ArF laser irradiation, on the other hand, rapidly monomerized adsorbed TMA dimer molecules, while continued irradiation resulted in the dissociation of methyl ligands, some of which were subsequently desorbed. However, the persistence of C-H stretch modes, even at the highest irradiation doses used, 200 mJ/cm^2 for 10^4 pulses, indicated some methyl ligands still remained.

2. Electronic Structure^{1,2)}

2.1. Photoelectron Spectroscopy

The experiments were carried out in an ion, turbomolecular, and cryopumped ultrahigh vacuum ($< 10^{-10}$ Torr) system with separate chambers for sample introduction, preparation, and analysis. UPS spectra were taken using a He resonance lamp and a hemispherical analyzer with a resolution of 0.2 eV. XPS spectra were obtained using a separately ion-pumped and water-cooled $\text{Mg K}\alpha$ X-ray source. A gas doser coupled to an ion-pumped gas-handling system was used to provide controlled amounts of TMA

Fig.1 Typical UPS and XPS spectra of TMA layers condensed on clean substrates at -90°C . Binding energies were referenced to the Fermi energy. The solid lines are SCF- $X\alpha$ -SW calculated densities-of-states for $\text{Al}_2(\text{CH}_3)_6$ and $\text{Al}(\text{CH}_3)_3$. Note that the high binding-energy (or low kinetic-energy) region of the peak γ in the UPS spectrum includes a contribution of secondary electrons.

to the substrate surfaces.

The substrates used in these experiments were optically flat 7-13 $\Omega \text{ cm}$ p-type Si (100) wafers which, in a few cases, were coated with 300 nm of Au. The substrates were cleaned by *in situ* sputter etching with 5-keV Ne^+ ions until the surface was free from C and O contaminations, as judged by XPS. The samples were then cooled to -90°C and exposed to TMA. The thickness of the resulting condensed TMA layers on Si were estimated based upon the growth rate determined by the attenuation of the Si 2p XPS peak intensity. The results represented here were for

TMA films with a thickness of $\sim 5\text{nm}$ for UPS and $\sim 10\text{nm}$ for XPS. TMA was found to be extremely reactive with O_2 and H_2O , resulting in changes in both core-level and valence spectra when background pressures were $>10^{-9}$ Torr.

2.2. Results and Analysis

Typical UPS and XPS spectra, obtained using He II 40.8 eV and Mg K α 1253.6 eV photons, respectively, from condensed TMA films are shown in Fig.1. No differences were observed in spectra obtained from films on Si and Au substrates. There were three primary peaks, labeled α , β , and γ , located 4.5, 7.5, and 15.0 eV below the Fermi level. Molecular orbital calculations were employed to analyze these valence spectra. Since the TMA molecules are weakly bound in the condensed layer, the calculations were carried out for isolated TMA molecules using the self-consistent-field X α scattered-wave (SCF-X α SW) method.

The unit molecule in the condensed layers is dimerized with the structure shown in Fig.2. Two types of C atoms can be distinguished, bridging and terminating (C_b and C_t). The

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Fig.2 Molecular structure of dimerized trimethylaluminum, $\text{Al}_2(\text{CH}_3)_6$; the symmetry group is C_{2h} .

bridging C atoms form three-center electron-deficient bonds with the two Al atoms. C_{2h} symmetry was assumed for the molecular structure of $\text{Al}_2(\text{CH}_3)_6$. The bond lengths for Al-Al, Al-C $_t$, and Al-C $_b$ were set equal to 0.260, 0.197, and 0.214 nm, respectively. For each Al, C, and H atom in $\text{Al}_2(\text{CH}_3)_6$, an atomic sphere was assigned for which a muffin-tin potential was calculated using the X α approximation for the exchange-correlation term. Standard values were used for atomic sphere radii and X α parameters. The wavefunctions in the spheres were expanded in a series of partial waves using s, p, and d components for Al, s and p for C, and s for H. The occupied molecular orbitals were then calculated self-consistently and the gross s and p orbital populations in the atomic spheres were determined for each valence MO by the charge-partitioning method in which intersphere and outer-sphere charges were partitioned among the atomic spheres. The results are tabulated in Table I together with ionization energies of three MO levels calculated by the Slater-transition-state method.

Since hole-screening effects in the final states are weak in weakly-bound systems such as physisorbed and condensed molecular layers, and hole-state relaxation effects in the isolated TMA molecules are taken into account in the Slater transition-state energies, we can directly compare the calculated ionization energies with binding energies obtained by photoelectron measurements. In order to make this comparison, each MO level was broadened using a Gaussian distribution and the point of zero energy was adjusted using the Fermi level for p-type Si. The calculated valence density-of-states (DOS), represented by the solid line in Fig.1, reproduces the measured three-peak UPS spectra with good agreement except for a shift in the lowest binding-energy peak α . This shift may be

Table I Occupied $\text{Al}_2(\text{CH}_3)_6$ valence MO energy levels and their atomic orbital populations calculated by the SCF-X α -SW method. The Al 3d populations were negligible and are not shown. The H_t and H_b 1s population were obtained after averaging the components from the non-equivalent H atoms in the terminating and bridging methyl groups, respectively.

level	energy (eV)	Al		C_t		C_b		H_t 1s	H_b 1s	Remarks
		3s	3p	2s	2p	2s	2p			
α	7b _u	-4.1	—	—	0.001	0.017	0.280	0.001	0.010	Al 3p + C 2p
	5b _g (*)	-4.2(*)	0.0	0.172	0.006	0.131	0.0	0.005	—	
	5a _u	-4.3	0.0	0.178	0.005	0.124	0.0	0.005	0.005	
	7a _g	-4.9	0.010	0.187	0.002	0.073	0.011	0.005	0.002	Al 3s + C 2p
	6b _u	-6.4	0.176	0.035	0.001	0.082	—	0.036	0.006	
	6a _g	-8.7	0.261	0.011	—	0.034	—	0.005	0.010	
β	4b _g	-9.2	0.0	—	—	0.095	0.0	0.061	0.031	Ct 2p + H 1s
	4a _u	-9.2	0.0	—	—	0.099	0.0	0.053	0.033	
	5a _g	-9.3	0.001	—	—	0.110	—	0.031	0.036	
	3b _g	-9.4	0.0	0.001	—	0.123	0.0	0.006	0.040	
	3a _u (*)	-9.4(*)	0.0	—	—	0.126	0.0	—	0.041	
	5b _u	-9.4	0.001	0.004	—	0.125	—	—	0.040	
	4b _u	-9.5	—	0.005	—	0.124	0.001	0.001	0.040	Cb 2p + H 1s
	4a _g	-9.6	0.004	0.009	—	0.120	—	0.004	0.040	
	2b _g	-9.9	0.0	—	—	0.033	0.0	0.184	0.011	
	2a _u	-10.0	0.0	0.008	—	0.026	0.0	0.195	0.008	
	3a _g	-10.8	0.001	0.027	—	0.012	—	0.217	0.004	
	3b _u	-10.9	0.046	0.001	0.001	0.004	—	0.222	0.001	
γ	1b _g	-17.0	0.0	0.007	0.135	0.006	0.0	0.035	—	Ct 2s + H 1s
	1a _u	-17.0	0.0	0.008	0.135	0.006	0.0	0.035	—	
	2a _g (*)	-17.1(*)	0.005	0.022	0.002	0.032	0.006	—	—	
	2b _u	-17.1	0.012	0.002	0.134	0.005	—	0.034	—	C ₂ s + H 1s
	1b _u	-17.9	—	0.008	—	—	0.264	0.016	0.070	
	1a _g	-18.1	0.020	0.002	0.010	—	0.244	0.012	0.002	

(*) The Slater-transition-state energies for levels 5b_g, 3a_u, and 2a_g were -6.4, -11.8, and -19.5 eV, respectively.

attributed to interactions among the upper MO's, composed primarily of Al (3p) and C (2p) orbitals as described below, in the TMA molecular crystal. Such interactions are not accounted for in the calculated spectra.

The XPS valence spectrum exhibits three broad peaks centered at the same positions as those of the UPS peaks. However, the intensities of the XPS γ peak and the high-energy tail on the α peak are enhanced due to differences in photoionization cross-sections. That is, XPS and UPS are more sensitive to s-like and p-like orbitals, respectively. Thus, we conclude that the γ peak and the high-energy tail involves s orbital components while peaks α and β are predominantly composed of p orbitals. These

conclusions are consistent with the peak assignment described below.

The valence DOS of the TMA monomer $\text{Al}(\text{CH}_3)_3$ with C_{3h} symmetry was also calculated based upon the molecular structure data given in reference 3. The results are shown in Fig.1. The Al and three C atoms in $\text{Al}(\text{CH}_3)_3$ form a planar configuration with D_{3h} symmetry, unlike $\text{Al}_2(\text{CH}_3)_6$, with no electron-deficient Al-C bonds. Thus the interactions between Al sp^2 and C sp^3 hybridized atomic orbitals are stronger in $\text{Al}(\text{CH}_3)_3$ resulting in more widely distributed MO levels.

The population analysis for $\text{Al}_2(\text{CH}_3)_6$ shown in Table I and the MO wavefunctions calculated based upon the SCF-X α -SW method were used

Fig.3 Contour plots for wavefunctions of occupied molecular orbitals: (a) $5a_u$ (-4.3 eV) . (b) $3b_g$ (-9.4 eV) , and (c) $2a_g$ (-17.1 eV) in the Y-Z plane (see Fig.2 for the coordinate system) . The contour spacing is 0.02 in units of a_0^{-3} (a_0 = Bohr radius) . Solid (dashed) lines represent positive (negative) parts of the wavefunction.

to derive a detailed bonding scheme for condensed TMA. Figure 3 shows wavefunction contour plots for three typical MO's- $5a_u$, $3b_g$, and $2a_g$ -belonging to the α , β , and γ peaks in the DOS spectra in Figure 1. Table I and Fig. 3a show that peak α corresponds to Al-C bonds formed primarily by Al ($3p$) and C ($2p$) orbitals. Bonds consisting of Al ($3s$) and C ($2p$) atomic orbitals also contribute to the tail on the high-energy side of peak α , β , and γ correspond to C-H bonds formed primarily by C ($2p$) and H ($1s$) atomic orbitals (see Table I and

Fig. 3c) respectively, in both bridging and terminating methyl groups.

The Al ($3p$)-C ($2p$) bonds are composed of two Al-C_t bonds, $5b_g$ and $5a_u$, one Al-C_b bond, $7b_u$, are one mixed Al- (C_t + C_b) bond, $7a_g$. More overlap change exists in the Al-C_t bond than in the Al-C_b bond consistent with the fact that the former is stronger than the latter. It should also be noted that the ratio of the total change populations (i.e., the sum of the appropriate columns multiplied by two to account full occupancy) of the C_b ($2p$) and C_t ($2p$) orbitals to that of the C_b ($2s$) and C_t ($2s$) orbitals is approximately 3 as expected for sp^3 hybridization.

These MO calculations indicated that the upper MO's in $Al_2(CH_3)_6$ and $Al(CH_3)_3$ as well as in $Al(CH_3)_n$ ($n = 1, 2$)³⁾ were predominantly composed of Al ($3p$) and suggested that UV transitions in TMA were Rydberg-like between Al $3p$ and Al $4s$ -like states⁴⁾.

3. Gas Phase Photolysis^{3,4,5)}

3.1. Experimental Procedure

Figure 4 shows a schematic diagram of the experimental apparatus which had a base pressure of 10^{-7} Torr. Two types of experiments were carried out in the stainless steel photoreaction chamber. Laser-induced optical emission spec-

Fig.4 Schematic illustration of the experimental apparatus.

tra were obtained using a static gas fill in which TMA was allowed to flow into the system through a leak valve until the desired pressure was achieved. In the case of time-dependent intensity measurements, however, TMA has introduced as a pulsed molecular beam using a solenoid valve with a nozzle diameter of 0.76 mm. The molecular beam pulse width and frequency were 500 μ s and 8 Hz, respectively. The maximum chamber pressure P during operation in the pulsed mode was $\sim 10^{-5}$ Torr and the pumping speed was such that P was reduced to less than 10^{-6} Torr between gas pulses. The TMA cylinder and gas handling manifold were maintained at 60°C, for which the TMA vapor pressure is ~ 40 Torr. under these conditions, the dominant TMA species was the dimer $\text{Al}_2(\text{CH}_3)_6$.

Optical irradiation was provided orthogonal to the molecular-beam direction by a KrF excimer laser. The laser pulse width was ~ 15 ns and the energy per pulse was 80 mJ. The laser beam was focused by a suprasil spherical lens with a 100 cm focal length to yield a peak intensity $I_{h\nu} \cong 7 \times 10^{10} \text{ Wcm}^{-2}$. In these experiments, the laser beam was allowed to intersect the molecular beam at increasing distances x from the nozzle (the number density N_d of molecules decreased as x^{-2}) and fluorescence intensities were measured along a direction perpendicular to both the laser and molecular beams.

The fluorescence was focused using a $f/1$ lens and dispersed in a 0.75 m spectrometer with a 1200 lmm^{-1} grating blazed at 400 nm. Time-dependent signals were detected by a photomultiplier with a 3 ns rise time and recorded by a transient recorder with a 10 ns sampling time. The apparatus was computer controlled to synchronize the laser and molecular beams and time-resolved fluorescence intensities were recorded over a time window from 10 ns to 3 μ s.

Fig.5 Fluorescence spectrum of TMA excited by 248 nm KrF laser irradiation at 100m Torr; the spectral resolution is 1 nm.

Fig.6 The fluorescence intensities I of the $\text{Al } 2\text{S} \rightarrow 2\text{P}$ atomic transition and $\text{CH } 2\Delta \rightarrow 2\Pi(0,0)$ molecular band of photo-excited TMA as a function of the KrF laser intensity $I_{h\nu}$.

3.2. Results and Discussions

A typical fluorescence spectrum with a resolution of 1 nm in the near UV to blue region is shown in Fig. 5 for TMA. The two peaks at

394.4 and 396.2 nm correspond to the $\text{Al } 4s^2S \rightarrow 3p^2P_{1/2}$ and $4s^2S \rightarrow 3p^2P_{3/2}$ atomic transitions, respectively. The band structure near 430 nm was due to the (0,0) band of the $\text{A}^2\Delta \rightarrow \text{X}^2\Pi$ transition of CH with a band head at 431.4 nm and rotational structure at shorter wavelengths. Emission from other excited radicals such as CH_3 , CH_2 , and CH do not have absorption bands at the KrF laser wavelength.

The fluorescence intensities of the Al and CH emission peaks were also measured as a function of the incident laser beam intensity $I_{h\nu}$ between 2×10^{10} and $7 \times 10^{10} \text{ W cm}^{-2}$. The results are shown in Fig. 6 to yield the same behavior with an approximately linear dependence for both Al and CH suggesting a common precursor for both species.

Time-resolved fluorescence measurements were at various positions x along the molecular beam axis with $I_{h\nu} \cong 7 \times 10^{10} \text{ W cm}^{-2}$. Data were taken at distances from the nozzle ranging from $x \cong 0$ to 40 mm, corresponding to particle number densities from $N_d \cong 3 \times 10^{16}$ to $1 \times 10^{14} \text{ cm}^{-3}$, and the rise times for I_{Al} and I_{CH} were always 10 ns, the experimental resolution. Typical data for I_{Al} and I_{CH} are shown in Fig. 7.

The decay time for I_{Al} was found to be non-exponential at all x positions. This was expected since the radiative lifetime of the Al^2S state, 6.8 ns, was shorter than the laser pulse width, ~ 15 ns. The CH fluorescence intensity decay was, however, a strong function of position along the molecular beam axis. In all cases, there was a component of the measured intensity due to Al emission which decayed rapidly as shown in Fig. 7. Further decay in the CH intensity was exponential allowing τ_{CH} to be determined as the time at which I_{CH} reached its 1/e value, τ_{CH} increased with increasing x and then saturated at $x \sim 40$ mm where N_d was sufficiently low, $\leq 10^{14} \text{ cm}^{-3}$, that the collisional quen-

Fig. 7 Time-resolved fluorescence of the $\text{Al } ^2S \rightarrow ^2P$ atomic transition and $\text{CH } ^2\Delta \rightarrow ^2\Pi$ (0,0) molecular band of photo-excited TMA at various positions x along the molecular beam axis. The dashed line represents fitted exponential decays. The excitation source was a 248 nm KrF laser pulse.

ching time was longer than the radiative lifetime. The decay time in the saturated region was determined to be 530 ± 20 ns in agreement with the reported radiative lifetime of CH.

The results presented showing that Al is a primary photolytic product from KrF laser-irradiated TMA and that the emission intensity of the $\text{Al } 4s^2S \rightarrow 3p^2P$ transition varies linearly with the laser intensity are consistent with the following model for the UV photolysis of TMA proceeding as a cascade single-photon absorption process;

Moreover, since the time of the CH fluorescence was, as in the case of Al, less than 10 ns, it can be concluded that CH was also produced photo-lytically rather than during subsequent collisions. Thus, in addition to reactions (1) - (4), other photo-induced side reactions must

occur leading to the photolytic generation of CH.

While more complex reaction channels may play a role, a simple model for producing CH which is consistent with all results presented so far may be formulated by assuming that the monomethyl radical Al(CH₃) is the common precursor for CH as well as for Al. Figure 8 is a schematic diagram describing the proposed reaction path for the UV photogeneration of the excited species Al* and CH* from Al(CH₃). The absorption of one KrF laser photon excited the molecule into state 1 where it spontaneously relaxes to produce Al* (4s²S), resulting in Al fluorescence, and CH₃. State 1 consists of an Al 4s-like Rydberg state overlapped with an Al-C antibonding state. A second radiative pathway, requiring the absorption of two photons is also available. In this case, after the one-photon absorption, state 1 spontaneously relaxes to 1', a local minimum in the same excited-state energy surface. The absorption of a second photon by the bound state 1' excites the molecule into state 2 to produce Al, CH* (²Δ), and H₂. CH* then emits spontaneously.

The ground state energies of Al + CH₃ and Al + CH + H₂, also shown in Fig. 8, were estimated based upon known bond energies for Al-CH₃ (~3 eV), CH₂-H (4.9 eV), CH-H (4.2 eV), and H-H (4.5 eV). The proposed model for the production of CH is consistent with these results. Since the energies associated with the fluorescence from Al and CH are both ~3 eV, the energy balance indicates that the initial state of Al(CH₃) is highly vibrationally excited and located ~1 eV above its ground state as shown in Fig. 8.

There was a spatial variation in the laser intensity over the region in which fluorescence was observed. Thus, a detailed analysis of the dependence of the Al and CH fluorescence yields on the laser intensity is difficult. Nevertheless, based upon the photolysis model described

Fig.8 Schematic diagram describing the proposed reaction path for the KrF laser photogeneration of the excited species Al* (²S) and CH* (²Δ) from Al(CH₃).

above, we conclude that each single-photon absorption step in the cascade process is nearly saturated except the rate limiting step. For the production of Al and CH, the rate limiting step is the transition from the initial level to state 1 in Al(CH₃).

4. Adlayer Photolysis⁶⁾

4.1. Experimental Procedure

The UHV system used in these experiments, shown schematically in Fig. 9, had separate chambers for sample preparation and analysis. The preparation chamber was equipped with turbomolecular and ion pumps, as well as a liquid-N₂-cooled Ti sublimator, and had a base pressure of 1×10^{-10} Torr. The sample stage could be cooled with liquid N₂ or heated to temperatures in excess of the Si melting point (1685 K). Highly-polished Si(100) and Si(111) substrates were degreased and rinsed with distilled water before being inserted into the preparation chamber, where they were further cleaned by sputtering with 1 keV Ne ions followed by annealing at 1300 K for one minute. After

Fig.9 Schematic diagram of the HREELS system used in the experiments.

annealing, the Si (100) wafers exhibited a 2×1 reconstruction as determined by LEED, while the Si (111) samples produced 7×7 LEED patterns. Both LEED patterns were well defined and sharp.

Adsorption was accomplished by flowing electronic grade TMA from Alpha Corporation via a metal-sealed, bakeable gas-handling system through a gas jet directed at the Si surface. In these experiments, the Si substrate temperature T_s during adsorption was maintained at $T_s \approx 200\text{K}$, allowing the formation of a single stable layer. The thicknesses of the adsorbed TMA layers were estimated based on the attenuation of the substrate Si 2p XPS intensity, as described in section 2-1.

The analysis chamber containing the HREELS spectrometer and LEED system was evacuated

by an ion-pump together with a liquid- N_2 cooled Ti sublimator. The system base pressure was $\approx 5 \times 10^{-11}$ Torr. The HREELS spectrometer consisted of a single-pass monochromator and analyzer capable of 8 meV resolution for clean metal surfaces and was operated with a primary electron beam energy of 7 eV. The resolution for Si surfaces was, however, decreased to ≈ 19 meV at room temperature (16 meV at 200 K).

4.2. Results and Discussions

The HREELS spectrum in Fig. 10a contains three major groups of overlapping peaks located near 87 meV, 170 meV, and 362 meV. Peak assignments were made based upon previous

Fig.10 HREELS spectra obtained in the specular direction of a TMA adlayer (a) as-deposited at $T_s = 200\text{K}$, (b) after 10 $20\text{-mJ}\cdot\text{cm}^{-2}$ ArF laser pulses, (c) after 1000 $20\text{-mJ}\cdot\text{cm}^{-2}$ and 1000 $200\text{-mJ}\cdot\text{cm}^{-2}$ ArF laser pulses, and (d) after the above laser treatments followed by heating to 650 K for 10 minutes.

infrared absorption measurements from isolated TMA dimer molecules in a frozen Ar matrix. The high-energy peak labeled α was due to C-H stretching modes (359 and 364 meV) while the peak near 170 meV was composed of two components β_1 and β_2 resulting from antisymmetric (178 meV) and symmetric (155 and 148 meV) deformations of the methyl groups. The 87-meV Γ peak corresponds to several overlapping modes associated with both bridging and terminating Al-CH₃ bonds. These include bridging and terminating methyl rocking modes and Al-terminating-C (Al-C^t) stretching modes. Finally, there is a poorly resolved peak Γ' near 62 meV due to Al-bridging-C (Al-C^b) stretching.

HREELS spectra were also obtained after rotating the samples from 3 to 20° away from the specular direction in order to determine the primary scattering mechanisms responsible for the various loss peaks. For dipole scattering, signal intensity is peaked in the forward or specular direction, while the impact scattering regime leads to a much broader angular distribution. The results indicate that Γ , corresponding to Al-CH₃ vibrational modes, is predominantly due to dipole scattering, α and β , on the other hand, primarily arise due to impact scattering, a finding which is consistent with the general behavior of C-H vibrational modes.

No changes were detected in the HREELS spectra following KrF laser irradiation at intensities up to 200 mJ·cm⁻² for 10⁴ pulses. However, ArF laser irradiation (for which the absorption cross-section of gas-phase TMA exceeds that for KrF by a factor of 100) was found to have an immediate effect on both the intensities and positions of the peaks in the adlayer HREELS spectrum. Peak intensities are plotted in Fig. 11 as a function of the number of laser pulses.

Even with relatively low laser fluences (20

Fig.11 HREELS peak intensities of a TMA adlayer deposited at 200K plotted as a function of the number of 20 and 200-mJ·cm⁻² laser pulses.

mJ·cm⁻²), a comparison of Fig. 10a and 10b shows that Γ decreased in intensity and shifted to lower energy (from 87 to 85 meV) after just 10 pulses while the elastic peak both decreased and broadened. β_2 also decreased and shifted from 155 to 152 meV, while α and β_1 exhibited little change. The intensity of the weak substrate (2×1) LEED pattern decreased. After 1000 pulses, Fig. 11 shows that both Γ and the elastic peak regained some of their lost intensity while α and β decreased slightly. Subsequent irradiation at higher laser fluence (200 mJ·cm⁻²) resulted in no further changes in the elastic peak height, but all of the loss peaks decreased. In addition, Fig. 10c shows that a shoulder began to accumulate on the high-energy side of Γ . These trends,

including an increase in the Γ shoulder feature, continued with further $200 \text{ mJ}\cdot\text{cm}^{-2}$ irradiation.

Following laser irradiation, the samples were heated to $T_s \approx 650 \text{ K}$, slightly above the pyrolytic threshold for TMA dissociation, for 10 minutes in order to determine whether thermal processing would result in further desorption or chemical reactions. A typical HREELS spectrum is shown in Fig. 10d. The intensity of the elastic peak decreased by a factor of 30 and the angular width of the elastic peak increased from $\approx 1.7^\circ$ for unirradiated samples to $\approx 10^\circ$. In addition, no LEED pattern, not even the weak 2×1 substrate pattern observed before heating, was obtained. Thus, the disordered adlayer has been densified to more completely cover the Si surface. The β_1 , β_2 , and α peaks corresponding to C-H modes have essentially disappeared. However, as discussed below, Al and C are still primary species on the surface. Thus the disappearance of the C-H modes signifies that most of the H has been driven off. The Γ peak has shifted to higher energies, 100 meV, following the evolution of H and broadened considerably.

We propose the following model to explain the above set of data. The primary effect of the low-intensity ArF laser irradiation is to break the dimer bond to form $\text{Al}(\text{CH}_3)_3$ monomers, most of which remain on the surface as discussed below. (The bond strengths of the dimer and Al-C^t bonds are ≈ 1 and 3 eV, respectively.) The corresponding initial decrease in the intensity of Γ , which has a strong dipole scattering character, is due primarily to a surface roughening since the α and β_1 peak intensities, which have significant impact scattering character, remain approximately constant consistent with the assumption that most of the $\text{Al}(\text{CH}_3)_3$ remains on the surface. The intensity of β_2 has contributions from vibrational modes at 148 and 155 meV

resulting from CH_3^t and CH_3^b symmetric deformation, respectively. As the adlayer becomes monomerized, the component due to CH_3^b is reduced, resulting in a reduction in β_2 intensity and a shift to lower energies. The shift of Γ to lower energy ($\approx 85 \text{ meV}$) is also consistent with monomerization since the main vibrational component for the dimer (Al-C^t stretch) is located at 87 meV, while the main component for the monomer (Al-C_3 antisymmetric stretch) lies at 85.5 meV.

As the irradiation dose is increased, the monomer population begins to dominate resulting in a more uniform overlayer. Thus, the elastic peak intensity, and hence the Γ peak intensity, increases and β_2 gradually shifts toward 148 meV. There are, of course, other photofragments produced such as $\text{Al}(\text{CH}_3)_n$ ($n=1,2$) and some desorption occurs. Nevertheless, we believe that the primary effect of low-intensity ArF irradiation of absorbed TMA is monomerization.

Increasing the ArF laser power density to $200 \text{ mJ}\cdot\text{cm}^{-2}$ produced no further significant changes in the elastic peak intensity even after 10^3 pulses. However, the intensities of all loss peaks decreased with increasing irradiation dose and a high-energy shoulder appeared on the Γ peak at approximately 105 meV. Independent XPS analyses of TMA overlayers on Si(100) before and after the same irradiation schedule show no measurable decrease in the amount of Al in the surface overlayer. From this, together with the fact that the elastic peak intensity is constant, we conclude that the decrease in Γ with high intensity ArF irradiation is due to breaking of Al-CH_3 bonds rather than $\text{Al}(\text{CH}_3)_n$ ($n=1,2,3$) desorption. Subsequent methyl desorption and H evolution give rise to the observed decrease in α and β intensities.

Annealing the irradiated samples at 650 K for 10 min resulted in the disappearance of the α

and β C-H vibrational modes. The lack of a corresponding decrease in the C KLL AES line intensity indicates that the disappearance of the α and β modes was due to H evolution rather than CH_3 desorption. Moreover, the change in the C AES KLL line shape together with the broadening and increase in the relative intensity, with respect to Γ , of the HREELS shoulder peak, may be an indication of the initiation of carbide formation.

5. Summary

UV laser photolysis of gas-phase and adsorbed trimethylaluminum, $\text{Al}_2(\text{CH}_3)_6$, (TMA) has been investigated using photoelectron spectroscopy, optical emission spectroscopy, and electron-energy-loss spectroscopy combined with molecular orbital (MO) calculations. The electronic structure of TMA was determined and the upper MO's were found to be predominantly composed of Al 3p. Optical emission spectra from KrF laser excited TMA showed that Al and CH were generated in the gas-phase. Based on MO calculations, primary UV transitions were suggested to be Rydberg-like between Al 3p and Al 4s-like states. ArF laser irradiation on TMA adsorbed

on clean Si surfaces led to monomerization and further decomposition of the adlayer and partial removal of some of the dissociated methyl ligands, while some of the ligands remained on the surface.

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