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Photodissociation of Adsorbed Trimethylindium

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The photochemistry of trimethylindium (TMI) adsorbed on a quartz substrate at 150 K has been studied by time of flight mass spectrometry (TOF/MS) using electron impact ionization and resonance-enhanced multiphoton ionization techniques. Photolysis of adsorbed TMI at 222 nm results in the deposition of indium metal on the surface and the ejection of neutral and ionic fragments into the gas phase. The gas-phase photofragments observed were the neutral products $In(CH_3)_2$, $InCH_3$, In, and CH_3 and the ions In^+, CH_3^+, and $In(CH_3)^+$. The neutral product distribution observed from photolysis on the surface was significantly different from the reported distribution observed in gas-phase photolysis of similar metal alkyls, $M(CH_3)_3$ (M = Al, Ga). The neutral product TOF profiles were characterized by Maxwell–Boltzmann temperatures which were different for each photoproduct. Ions formed on the surface did not desorb with Maxwell–Boltzmann velocity distributions and had significantly higher kinetic energies (2 eV), suggesting the instantaneous presence of a high electric field during the laser-induced photodissociation on the surface. As the surface coverage of $In(CH_3)_3$ was increased, a gradual increase in the neutral product translational energies was observed. The increase in the product kinetic energy was associated with photodecomposition of adsorbed TMI clusters of increasing size on the surface.

Introduction

The study of laser-assisted chemical reactions on surfaces has become an active area of research motivated by both an interest in the fundamental processes involved in the laser surface interaction and the increasing use of laser-assisted processes in the fabrication of microelectronics. The fundamental chemistry has been expored recently in several studies on the photodissociation mechanism of physisorbed molecules.[1-8] These studies have shown that, while the decomposition process on the surface is similar to what is observed in the gas phase, the surface significantly alters the fragment energy distribution. In addition to photodissociation, photoinduced surface reactions of adsorbed species are likely to provide new details on oriented reaction dynamics since these species will be confined to narrow collision energies and impact parameters.[9-11]

A direct application of laser gas–surface chemistry involves the localization of chemical reactions on a surface. This spatial selectivity has led to the development of several new laser-assisted techniques in semiconductor device processing which involve deposition, etching, doping, and alloying.[12,13] In the fabrication of microelectronic devices, the goal is to produce well-defined features that are as small as possible. By taking advantage of the focusing capabilities of a coherent light source and nonlinear effects such as multiphoton processes, features on the order of 1–10 μm have been generated. To date there are very few mechanistic studies on the surface photochemistry relevant to these processes.[14-19] The study of surface photochemistry relevant to microelectronics is quite different from the more fundamental laser gas–surface interaction studies in that the photochemistry relevant to device fabrication takes place on a surface that is continuously being modified.

The laser-assisted chemical vapor deposition (LCVD) of group II and group III metals typically involves photodissociation of the corresponding metal alkyl.[20] In the gas phase, resonant excitation[21-23] results in the production of the gas-phase metal atom which deposits on the substrate. Recent mechanistic studies on the photolysis of trimethylgallium[19] and trimethylaluminum[23] showed the major gas-phase product to be the neutral species, MCH_3 (M = Ga,Al). Metal deposition has also been shown to occur for these organometallics adsorbed on a surface.[15]

Recently,[11,14] we have shown that time of flight mass spectrometry (TOF/MS) with electron impact ionization (EI) and multiphoton ionization (MPI) can be used to investigate the photochemistry of adsorbed molecules. The combination of these techniques enables us to identify the neutral products formed on the surface by the laser. In this study we have investigated the 222-nm photochemical decomposition of trimethylindium (TMI) adsorbed on quartz at 150 K. The TOF profiles of the photofragments ejected into the gas phase were measured. The measured product distribution is different from the reported gas-phase photolysis of $M(CH_3)_3$ (M = Ga, Al). Fragment translational energies were sensitive to surface coverage of TMI and were observed to increase with increasing coverage. The observed increase in the fragment translational energies and the relationship of the fragment mass to the observed translational temperature will be discussed in terms of a model involving cluster formation on the surface.

Experimental Section

The experimental setup was similar to one described previously.[11] It consisted of a double differentially pumped and cryotrapped vacuum system with a base pressure of 1×10^{-8} Torr containing separately cryoshielded sample-dosing and detection

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chambers, a quadrupole mass spectrometer (Extrell), an excimer photolysis laser (Lumonics) operating on KrCl (222 nm, 5–20 mJ/pulse), and an excimer pumped dye laser (EMG102/FL2002). A quartz substrate was mounted on the end of a precision *x,y,z* manipulator which could be cooled with liquid nitrogen to ca. 150 K. The surface was set at an angle of 75° with respect to the central axis of the mass spectrometer. The flight distance from the substrate to the ionizer was 26 cm.

TMI was purified by vacuum distillation. Surface dosing was accomplished by flowing a dilute mixture of TMI in He over the cold quartz surface. TMI was seeded into the carrier gas by simply flowing He gas over solid TMI at room temperature. The equilibrium vapor pressure of TMI at room temperature is 1–2 Torr. The TMI/He mixture was directed onto the cold quartz substrate by a copper capillary positioned 1–2 cm from the substrate. This resulted in a pressure of 2×10^{-7} Torr in the detection chamber as measured by an ionization gauge. Under steady-state conditions, the surface coverage was estimated to be less than a monolayer for photolysis pulse rates between 10 and 30 Hz. In order to calculate the approximate surface coverage a 1% mixture of TMI in He was used at a constant mass flow of 1–3 sccm. An upper limit on the surface coverage was estimated by noting that under the above conditions (1% TMI/He at 1–3 sccm) the laser removed all of the sample in the irradiated volume with each laser pulse. Surface coverage was at a maximum 10^{14} molecules/cm^2 (assuming that all of the molecules that leave the capillary are adsorbed on 1 cm^2 of the substrate). The photolysis beam was focused to a rectangular spot 0.4 cm^2 on the substrate which resulted in an energy density of about 10^6 W/cm^2. Ion energies for electron impact were either 15 or 30 eV. EI/TOF profiles were obtained by digitizing and averaging the output from a Keithley 427 current amplifier with a transient digitizer and averaging module (DPS Technology 2001 and 4001) at a sampling interval of 1 μs. The time of flight distributions for CH_3 radicals and In atoms were obtained by resonance-enhanced multiphoton ionization (REMPI/TOF) using the transient digitizer and averaging memory, and a programmable delay generator operating under computer control. REMPI/TOF spectra were built up by stepping through a delay between photolysis and the probe beams (0–1000 μs following the photolysis pulse).

CH_3 radicals were detected by REMPI at 333.465 nm[24] (1–3 mJ/pulse) by focusing the output of the dye laser with a 15 cm focal length lens. Indium atoms were also detected by REMPI using the unfocused output of the frequency-doubled dye laser at 303.928 nm.[25] Photoproduct temperatures were calculated from the nonlinear least-squares fit of the time of flight profile to a Maxwell–Boltzmann distribution corrected for drift time in the quadrupole filter.

Results

The photochemistry of adsorbed trimethylindium was investigated by using time of flight (TOF) mass spectrometry with either electron impact (EI) or resonance-enhanced multiphoton ionization (REMPI). Electron impact resulted in the formation of ions by two main processes. These two processes were either collisional ionization or collision-induced fragmentation/ionization. In addition, ions were also produced photochemically by the laser/surface interaction. In this study, all charged species detected were positive ions. To simplify the discussion, the positive charge has been dropped from the reference of each individual species when the ion was formed by electron impact ionization or fragmentation/ionization of a neutral species. Whenever possible, the neutral product origin of the ion observed is identified.

Figure 1 is the gas-phase mass spectrum of TMI obtained with an electron impact energy of 15 and 30 eV. At 30 eV, fragmentation of TMI produced $In(CH_3)_2$, $InCH_3$, In, and CH_3. The parent molecule underwent extreme fragmentation and could not be seen. At 15 eV the parent molecule was still undetectable and the only fragment that could be detected was $In(CH_3)_2$.

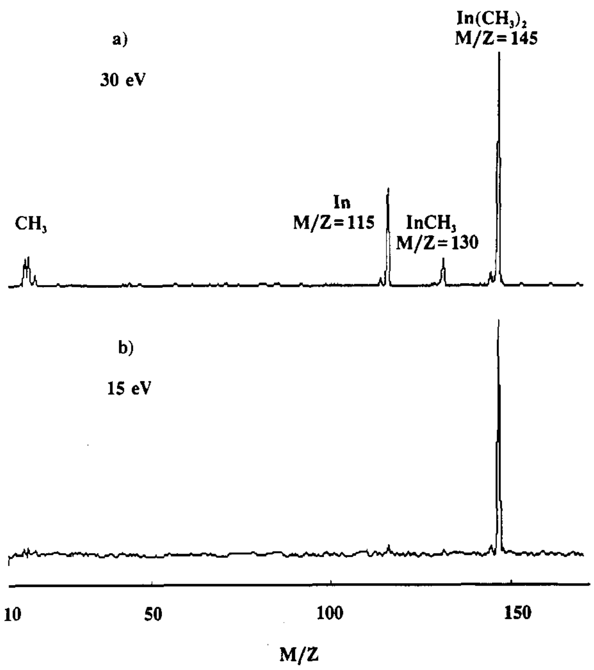

Figure 1. EI/MS for $In(CH_3)_3$ obtained at (a) 30 eV and (b) 15 eV.

In the gas phase, TMI absorbs strongly between 200 and 250 nm with a maximum at 213 nm.[15] When TMI is adsorbed on a substrate, the UV cross section has been reported to increase.[15] Photolysis of adsorbed TMI at 222 nm results in the deposition of a thin film of indium metal on the substrate. Figure 2 shows the EI/TOF profiles obtained at 30 eV for surface desorbed products observed in the 222-nm photolysis of TMI on a quartz substrate held at 150 K. The TOF profiles show four distinct arrival times. $In(CH_3)_2$ had a maximum at about 750 μs. $InCH_3$ and In had maximum arrival times which were shorter at 700 and 650 μs, respectively. CH_3 had a maximum at 300 μs. As in the gas-phase EI/MS, the parent ion was not observed under these conditions.

The TOF profiles shown in Figure 2 were reproducible under the conditions described with the exception of In. The TOF profile of In was found to vary depending upon the length of time the surface had been exposed to TMI and irradiated at 222 nm. The TOF maximum for In ranged from 500 to 650 μs. This was due to the deposition of In metal on the quartz substrate which increased with time.

Recently we have demonstrated that the technique of REMPI/TOF can be used to assign the neutral product origin of the ions observed in electron impact.[11,14] Laser ionization was used to selectively ionize a particular neutral molecule from the combined gas-phase fragments produced in the surface photolysis. In Figure 3 is shown a comparison of the TOF profiles for CH_3 formed by laser ionization at 333.465 nm ((2 + 1) photoionization of CH_3 radicals[24]) and electron impact ionization at 30 eV for the gas-phase species monitored at $m/z = 15$ in the 222-nm photolysis of adsorbed TMI. These two profiles are virtually identical and well described by a Maxwell–Boltzmann temperature of about 430 K. Mass and wavelength selectivity for REMPI are shown in Figure 4 for the detection of CH_3 radicals. These spectra were obtained at a delay of 300 μs from the photolysis laser which corresponds to the maximum in the TOF distribution of the CH_3 radical. It is important to note that the TOF profile for CH_3 did not contain any components of the TOF profiles observed for the $In(CH_3)_2$ or $InCH_3$ which had maxima at 750 and 700 μs, respectively. This indicates that the major source of the CH_3 ion signal was neutral CH_3 radicals formed as a result of the laser surface interaction and did not result from electron impact fragmentation of methyl-containing photoproducts in the ionizer of the mass spectrometer.

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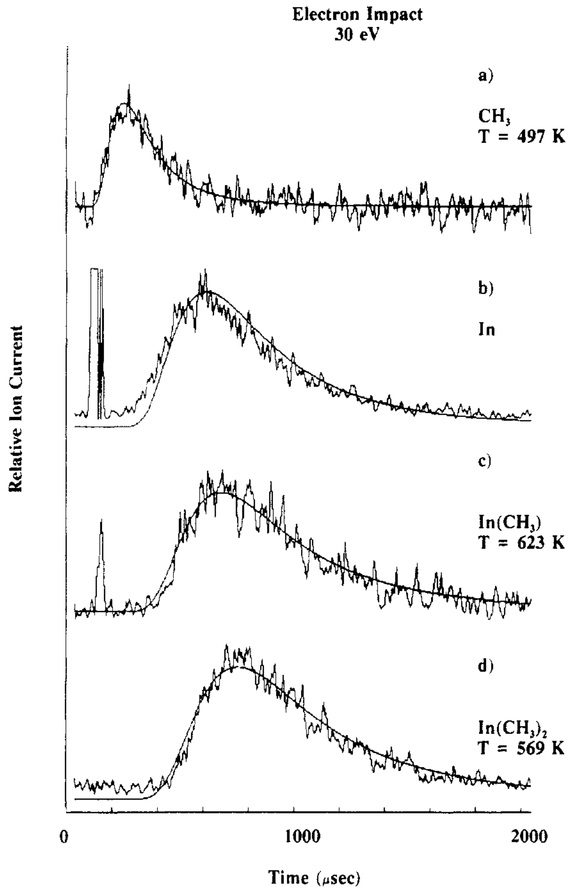

Figure 2. EI/TOF profile detected for the 222-nm photolysis of TMI on quartz at 150 K. The solid line represents the nonlinear least-squares fit to a Maxwell-Boltzmann velocity distribution. Temperatures were calculated for products assuming that the ion is formed by the corresponding neutral species. For In ions, the solid line represents a single-component fit which was found to be unsatisfactory due to electron impact ionization/fragmentation of heavier In-containing species. The temperature associated with this was not meaningful. In TOF analysis is treated in more detail in Figure 5 and the associated discussion.

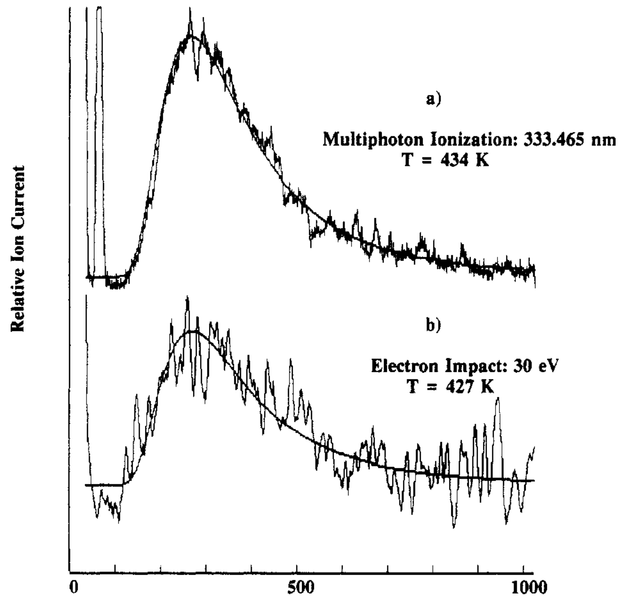

Figure 3. TOF profiles for CH_3 detected in the 222-nm photolysis of TMI on quartz at 150 K: (a) REMPI/TOF of CH_3 radicals at 333.465 nm; (b) EI/TOF at 30 eV.

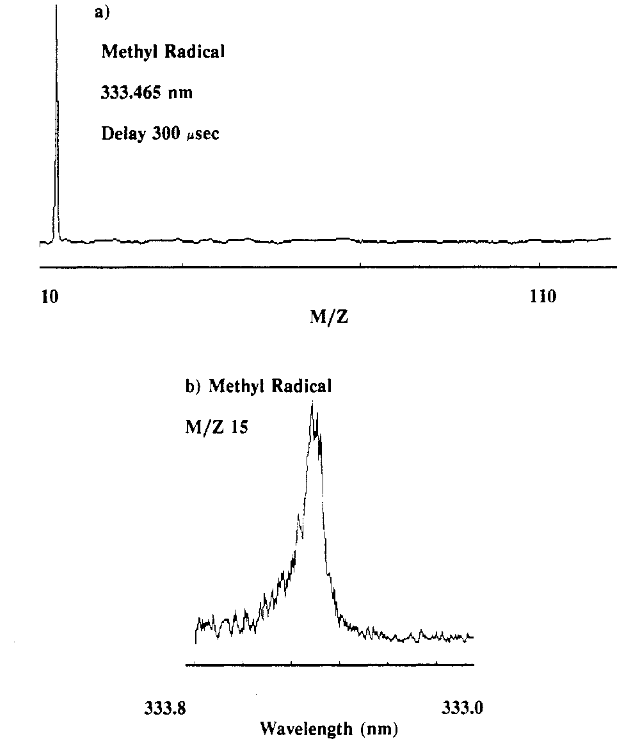

Figure 4. REMPI mass and wavelength spectra obtained for CH_3 radicals observed in the 222-nm photolysis of TMI adsorbed on quartz at 150 K. Laser ionization was at 333.465 nm. Spectra were obtained at a fixed delay of 300 μs from the photolysis laser.

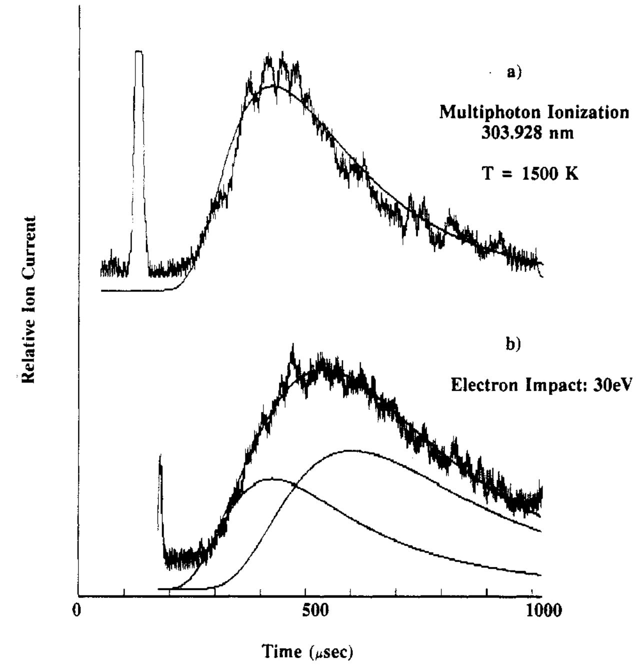

Figure 5. TOF profiles for In detected in the 222-nm photolysis of TMI on quartz at 150 K. (a) REMPI/TOF of In atoms at 303.936 nm. The solid line represents a Maxwell-Boltzmann temperature of 1500 K. (b) EI/TOF obtained at 30 eV. The solid lines represent a fit of the velocity distribution as arising from two species, one of which was assumed to be indium atoms at 1500 K.

Shown in Figure 5 is a comparison of the TOF profiles for In ions observed by EI at 30 eV and REMPI at 303.936 nm. At this wavelength the laser selected only In atoms to be ionized by (1 + 1)[25] photoionization. Mass and wavelength selectivity for REMPI detection of In atoms is shown in Figure 6. The REMPI/TOF had a maximum at 450 μs while the EI/TOF is broader and had a maximum at 500 μs. The EI/TOF for In was most likely a combination of In atoms formed on the surface and electron impact fragmentation of higher molecular weight photoproducts which contain In (e.g., $(InCH_3$ or $In(CH_3)_2)$. An

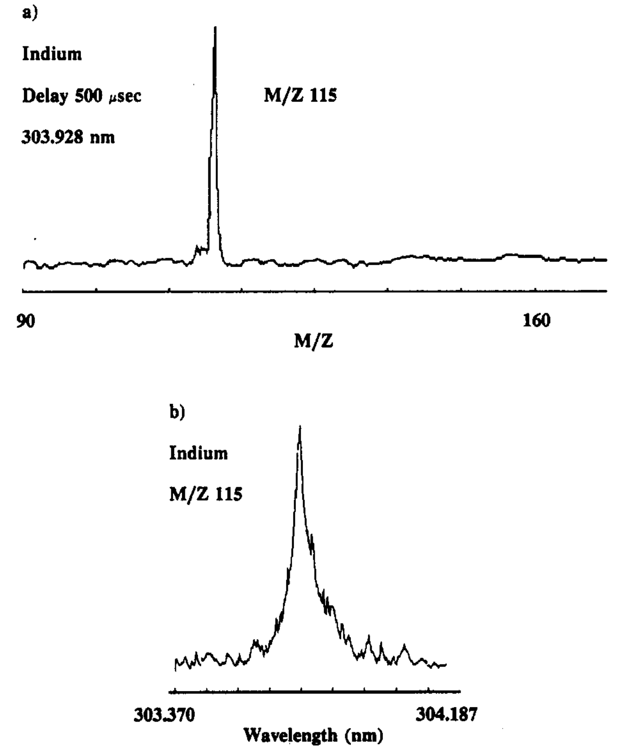

Figure 6. REMPI mass and wavelength spectra obtained for In observed in the 222-nm photolysis of TMI adsorbed on quartz at 150 K. Laser ionization was at 305.928 nm. Spectra were obtained at a fixed delay of 500 μs from the photolysis laser.

analysis of the REMPI/TOF for indium atoms produced on the surface yielded a Maxwell–Boltzmann temperature of 1500 K.

In addition to the ions formed by electron impact of neutral photoproducts, two ions were observed which were formed on the surface. A very short and intense TOF maximum at 170 μs was observed for In. This TOF was assigned as arising from In^+ ions formed photochemically on the surface. Similarly, the $InCH_3^+$ ion was also detected. These ions, originating directly from the surface, were detected when the mass spectrometer ionizer was turned off. The high velocity of the ions formed on the surface (relative to the neutral products) is an indication of a local charge created by the photolysis laser. This local charge could be produced by assuming that, during the laser surface interaction, electrons produced on the surface left fast enough to leave a large positive charge on the surface. This high charge density resulted in an explosion of charged species from the surface. These ions were then accelerated toward the detector as a result of electrostatic interactions with the surface. The ions had translational energies which were calculated to be on the order of 2 eV based on arrival times. The TOF for the ions is much narrower than that would be predicted by Maxwell–Boltzmann statistics. The detection of ions as a surface photochemical product was found to be very sensitive to the orientation of the surface with respect to the axis of the quadrupole filter. At near-normal angles, the ions were most intense.

Mass spectra were obtained at fixed delays relative to the photolysis laser. Shown in Figure 7 is a comparison between the 30-eV electron impact mass spectra observed at 300- and 1000-μs delay and the spectra observed from the gas-phase TMI. These two times were chosen by examining the TOF profiles shown in Figure 2. There appeared to be two distinct arrival times, one at about 300 μs corresponding to CH_3 radicals, and one at longer times, between 600 and 800 μs. At short times, only CH_3 radicals were detected. At long delays, only $In(CH_3)_2$, $InCH_3$, and In were observed. Very little ion current could be detected at 1000 μs for CH_3. This strongly suggests that the methyl radical was formed as result of complete photochemical decomposition of TMI on the surface. If TMI was desorbed by the laser it would fragment following electron impact to produce both $In(CH_3)_2$ and CH_3 (as was seen in the gas-phase EI/MS) resulting in the CH_3 TOF profile having a slow component. This clearly cannot be the case because the CH_3 EI/TOF profile (Figure 2) showed only one component which was much faster than the EI/TOF profiles of the other fragments. Since TMI was completely decomposed by the laser, the source of $In(CH_3)_2$ ion could only have been the neutral radical $In(CH_3)_2$. Similarly, the difference in the arrival times in the EI/TOF profiles for $In(CH_3)_2$ and $InCH_3$ indicated that the $InCH_3$ radical was also formed on the surface by the laser.

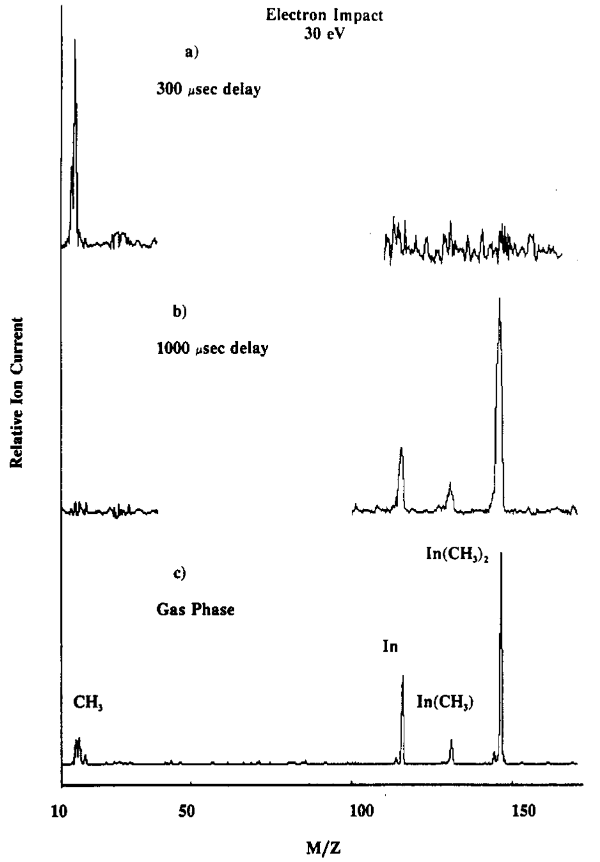

Figure 7. EI/MS obtained at 30 eV for the gas-phase species observed in the 222-nm photolysis of TMI on quartz at 222 nm at a fixed delay relative to the photolysis laser: (a) 300 μs; (b) 1000 μs; and (c) gas phase.

As was mentioned earlier, the EI/TOF profile for In, shown in Figure 5, was composed of In atoms formed on the surface and electron impact fragmentation of another indium-containing species in the ionizer of the mass spectrometer. The EI/TOF profile could be described by a combination of two Maxwell–Boltzmann distributions. One of these distributions was obtained from the REMPI/TOF data which yielded an indium atom temperature of 1500 K. The EI/TOF was best described as a combination of neutral In atoms and the neutral $In(CH_3)$ radical formed photolytically at the surface. Similarly, we tried to fit the TOF profiles for $In(CH_3)_2$, $InCH_3$, and CH_3 as combinations of Maxwell–Boltzmann distributions. The detected species could have been formed by electron impact fragmentation of neutral photoproducts in addition to direct electron impact ionization of photoproducts produced on the surface. However, these TOF profiles were best described by *single* Maxwell–Boltzmann distributions indicating a unique pathway for production of the detected species.

These results indicate the differences between the gas-phase and the surface photochemistry of the group III metal alkyls. In the visible and UV laser photolysis of $M(CH_3)_3(g)$,[21,23] the major product has been shown to be the neutral radical, MCH_3 (M = Al, Ga). It was argued that the dimethyl fragment would have too much internal energy to be stable. Here we have shown in the UV photolysis of adsorbed $In(CH_3)_3$ that the neutral species, $In(CH_3)_2$, was formed apparently stabilized by the surface. The $In(CH_3)_2$ radical was stable with respect to electron impact

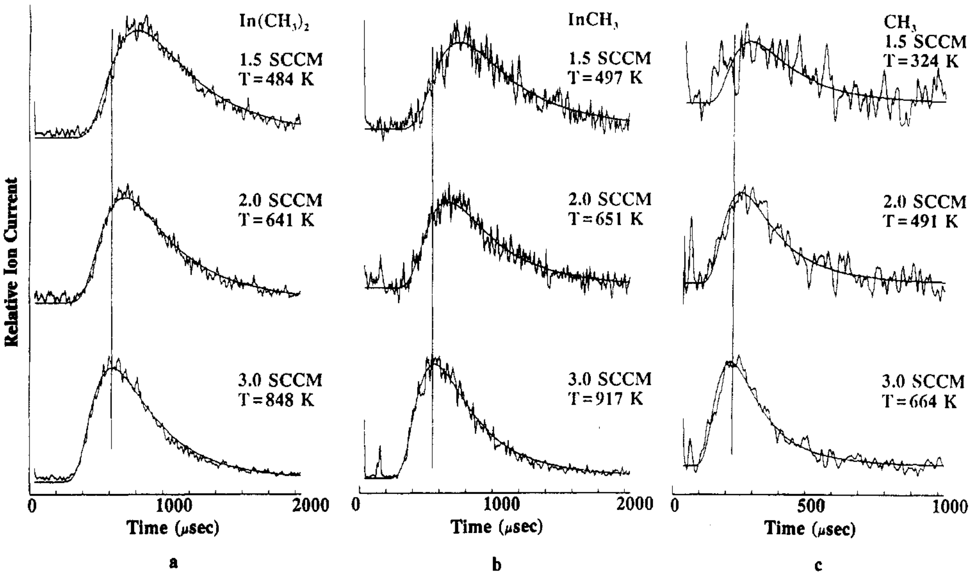

Figure 8. EI/TOF profiles for (a) In(CH$_3$)$_2$, (b) InCH$_3$, and (c) CH$_3$ as a function of surface coverage. The surface was continuously dosed with a 1% mixture of trimethylindium in He at the indicated mass flow. The solid curve is the calculated Maxwell–Boltzmann temperature. The vertical line is drawn at the maximum in the TOF distribution at 3.0 sccm.

TABLE I: Photoproduct Translational Temperatures as a Function of Surface Coverage

mass flow, sccm	photoproduct temp, K		
	CH$_3$	InCH$_3$	In(CH$_3$)$_2$
1.5	324	497	484
2.0	491	651	461
3.0	664	917	848

ionization which produced the corresponding ion instead of fragmenting to form CH$_3$ ions and InCH$_3$ ions.

In addition to the primary photoproducts formed by photolysis of TMI, we also looked for secondary chemistry on the surface in the production of CH$_4$ or C$_2$H$_6$. These species were observed in the gas-phase thermal CVD reactions[26,27] but were not detected even at times up to 2 ms following the photolysis laser pulse in the present experiment. We have not found any evidence for the formation of these species in our experiment. It has been shown that, in thermally activated CVD under very low pressure conditions, CH$_4$ and C$_2$H$_6$ are not formed on the surface.[28] This suggests that these species observed in the high-pressure CVD reactions were formed as a result of collisions in the gas phase.

At submonolayer coverages, the TOF maxima were found to be sensitive to the amount of TMI on the surface. As the coverage increased, the TOF maxima were shifted to shorter times, indicating a gradual increase in the kinetic energy of the photofragment. For a 1% mixture of TMI in He, the translational temperature of In(CH$_3$)$_2$ increased from 484 to 848 K as the mass flow (TMI + He) to the surface was increased from 1.5 to 3 sccm. Similarly, for CH$_3$ and InCH$_3$ increases from 324 to 664 K and 497 to 917 K were observed, respectively. Representative TOF profiles for In(CH$_3$)$_2$, InCH$_3$, and CH$_3$ illustrating this gradual increase in translational energy are shown in Figure 8, a, b, and c, respectively. For each species, a small shift in the TOF maximum to shorter times was observed, indicating an increase in the photofragment velocity as mass flow to the surface was increased from 1.5 to 3.0 sccm. A summary of the translational temperatures for CH$_3$, InCH$_3$, and In(CH$_3$)$_2$ is presented in Table I. At very high surface coverage (>3 sccm for a 1% TMI in He mixture) the TOF profiles for CH$_3$ were much narrower than would be calculated for a Maxwell–Boltzmann distribution.

Product kinetic energies were not sensitive to laser power over the range 5–20 mJ/pulse. The effect of increasing laser power was observed to increase the intensity of the TOF profile without changing the kinetic energy. Although at 5 mJ/pulse the laser intensity at the center of the beam was enough to photolyze all the adsorbed TMI in that region, the weaker laser intensity at the edge of the beam was not. As the total energy per pulse was increased, there was an increase in the signal as a result of an increase in the laser intensity at the beam edge. All measurements were made under conditions that kept surface coverage of TMI to a minimum and as a result photon flux was always a factor of 100–1000 times greater than the average concentration of TMI on the surface.

Discussion

The strong dependence of the fragment translational temperature as a function of dosing rate can be rationalized by examining what is known about the spectroscopy of adsorbed TMI and by examining the structure of photolytically grown films. The spectroscopy of the adsorbed organometallics has been studied as a function of surface coverage by Osgood.[15,29] There were two distinct differences between the spectrum observed in the gas phase and the adsorbed state. These changes were seen in the resonant feature and in a region to the red of the strong absorption. The electronic spectrum of the adsorbed species is similar to what was observed in the gas phase, indicating that the electronic properties of the adsorbed species were similar to the gas-phase species. However, in the red,[15] the absorption intensity increases nonlinearly with surface coverage. For Cd(CH$_3$)$_2$ Osgood[29] concluded that the absorption at the red end of the spectrum resulted from Raleigh scattering caused by nonuniform molecular coverage, organometallic clusters which were formed at high surface coverage.

Osgood[13,30] has also shown that the UV irradiation of surface adsorbed organometallics results in the formation of small metal clusters on the surface. As irradiation time increases, the photodissociation occurs preferentially at the cluster. This is presumably due to a higher sticking coefficient of the gas-phase species with the metal cluster compared to the quartz substrate. In other words, metal clusters act as nucleation sites for the formation of organometallic aggregates during surface dosing. In addition, it is possible that there is enhanced photochemistry at the metal cluster as a result of the interaction of the laser electric field with the metal.[30]

Our results suggest that surface photochemical behavior is caused by these two types of aggregates that are formed on the surface. Initially as TMI is adsorbed on the surface, organo-

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metallic clusters are formed even when the average concentration of TMI on the surface is low. Irradiation resulted in the photochemical decomposition of the organometallic clusters, leaving behind small metallic clusters on the quartz surface. As the metal cluster size increases, more TMI is adsorbed which increases the rate at which metal is deposited on the surface. In our measurements, these processes were manifest by an induction period for the generation of a strong TOF signal for the photofragments observed when starting with a clean quartz surface. The appearance of an indium film on the surface was accompanied by the increase in the TOF intensity for all species detected.

As the organometallic cluster size increases, it is very likely that there is a change in the interaction potential between the aggregate and the surface resulting in an overall weakening of the intermolecular bonds due to increased electron delocalization within the aggregate. This could be the source of the observed red shift in electronic spectra in going from the gas to the liquid phase. (For $Cd(CH_3)_2$, a comparison of the vapor- and liquid-phase spectra showed a red shift of about 1200 cm^{-1} for the onset of the strong electronic transition seen in the UV[29].) Osgood has shown that there is a weakening of the intramolecular interactions in $Cd(CH_3)_2$ as a function of surface coverage by as much as several hundred wavenumbers.[29]

In TMI, product translational energies increased ca. 300 cm^{-1} over the range of coverages studied. It is reasonable to assume that to a first approximation the photofragment translational energy is determined by the total photon energy less the fragment binding energy. Since aggregation gives rise to a decrease in the energy difference between the ground state and the dissociative state, this would in turn would leave more of the photolysis photon energy available for translational excitation. Since it is also observed that organometallic binding energy to the surface is decreased as a function of coverage, this could also yield fragments with increasing translational kinetic energy. Either of these possible mechanisms would result in the observed variation in photofragment translational energy as a function of surface coverage and rely on the fact that even at a low average surface coverage, the adsorbed organometallic has strong lateral interactions due to cluster formation.

It is interesting to note that the translational temperature of the CH_3 radical measured in this study is less than that of the indium-containing fragments. This result is contrary to what we would expect for the gas-phase photodissociation of TMI where the lighter fragment (CH_3) carries away more of the translational energy than the heavier fragment ($InCH_3$, $In(CH_3)_2$). Harrison et al.[1] observed a similar phenomena in the photodissociation of adsorbed CH_3Br. Their results were explained in terms of the geometry of the adsorbed molecule. When a CH_3 group was trapped between the Br atom and the surface, photodissociation resulted in collisional excitation of the heavier Br atom and scattering of the trapped CH_3 group. In their study,[1] a significant fraction of Br atoms produced photolytically on the surface had more translational energy than Br atoms produced in the gas-phase photolysis of CH_3Br. The photofragment translational energies observed by Harrison et al.[1] were ~1 eV and the TOF profiles for CH_3 were multicomponent, with broad distributions.

In our measurements on TMI, the CH_3 radical TOF profile did not exhibit similar long tails in the velocity distribution and seemed well described by single-component Maxwell–Boltzmann distributions with fragments kinetic energies on the order of 0.1 eV. This indicates that the collisional model is probably not operative in TMI. However, we believe that the translational energy dependence of the photofragments as a function of the fragment mass may be related to the geometry of the adsorbed species.

The CH_3 kinetic energy is determined by both its interaction with the central atom and with the surface. Strong methyl–surface interactions have been observed by Higashi[31] in the 193-nm photolysis of adsorbed trimethylaluminum on Al_2O_3 and SiO_2 at room temperature. In that study,[31] TOF profiles for CH_3 were characterized by translational temperatures of 150 K, far below the substrate temperature of 300 K. At 193 nm, there is about 3.5 eV of excess energy after the Al–C bond has been broken yet very little of this energy appears as translational excitation of CH_3. Higashi[31] discussed the photodissociation mechanism in terms of an excited-state potential energy surface which has both strongly and weakly bound states as a function of motion along the various reaction coordinates.

In TMI, the variation in the fragment translational energy with mass suggests a stepwise removal of CH_3 groups from the adsorbed TMI. This mechanism is supported by recent studies on the photodissociation of adsorbed trimethylaluminum (TMA) on a SiO_2/Si surface.[19] In that study, the laser pulse energy threshold dependence for the formation of successively smaller fragments led the authors to conclude that these species were produced in a sequential manner from the adsorbed parent molecule. Similarly in TMI, photodissociation on the surface involves the ejection of a CH_3 which is strongly interacting with the surface and the central indium atom which is followed by the reorientation of the remaining fragment on the surface. Following desorption of the surface-bonded CH_3 group, the neutral adsorbed $In(CH_3)_2$ will continue to interact with the surface and the radiation field. It could photodesorb to yield the neutral $In(CH_3)_2$ species in the gas phase or reorient on the surface. This type of motion could easily take place on the time scale of the photolysis laser. Continued interaction of the adsorbed fragment with the radiation field results in the ejection of a second CH_3 radical but with nearly the same translational energy as the first desorbed methyl group. This assumes that the total $In–CH_3$ and the CH_3–surface interactions are of similar strengths in each case. This mechanism is consistent with a number of our experimental observations: CH_3 radical TOF profiles are best described by a single Maxwell–Boltzmann velocity distribution with translational temperatures that are lower than the other fragments; and it accounts for the formation of all the TMI fragments observed and the variation in translational kinetic energy with fragment mass.

Conclusions

The photochemical decompositional of TMI on a quartz surface at 150 K has been investigated at 222 nm. Irradiation of TMI produced a film of indium metal on the surface. Surface-desorbed products were detected by time of flight mass spectrometry using REMPI and EI ionization. The combination of these techniques allowed the identification of photoproducts formed on the surface. These photoproducts were identified as the neutral species CH_3, In, $InCH_3$, and $In(CH_3)_2$ in addition to the ions CH_3^+, In^+, and $InCH_3^+$. The velocity distributions of the neutral photofragments were found to be Maxwell–Boltzmann and yielded different translational temperatures for each species identified. The surface photochemistry was different from the gas-phase photochemistry reported for similar molecules, $M(CH_3)_3$ (M = Al, Ga),[20,22] in that the neutral fragment, $In(CH_3)_2$, was observed.

At submonolayer coverages, the translational temperatures of the surface-desorbed neutral species increased as a function of surface coverage. The gradual increase in translational energy could have resulted from the formation of TMI aggregates of increasing size which weakened the intermolecular and molecule–surface bonds. The translational temperature for the CH_3 radical was lower than those of the neutral $InCH_3$ and $In(CH_3)_2$ species. This may be explained in terms of the geometry of adsorbed species and the degree to which the methyl groups interact with both the central indium atom and the surface.

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