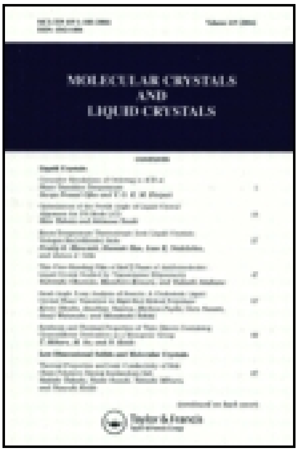

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Evidence for a Charge Transfer Mechanism in Laser Induced Chemical Vapor Deposition

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EVIDENCE FOR A CHARGE TRANSFER MECHANISM IN LASER INDUCED CHEMICAL VAPOR DEPOSITION

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Abstract Photodecomposition of triisobutylaluminum (TIBA) adsorbed on an aluminum surface by pulsed ultraviolet laser irradiation is studied by observing the photoproducts with time-of-flight mass spectroscopy. The fragmentation pattern at different laser wavelengths (193, 248, and 351nm) is very similar and the intensity of fragments at these three wavelengths is 1:0.6:0.05 even though in the gas phase, absorption drops off rapidly for wavelengths above 193nm. In addition, the translational energy of the fragments is considerably less than the photon energy. These findings support a mechanism whereby absorption of light by the surface creates hot electrons which induce desorption of the TIBA molecules, rupture isobutyl groups to create methyl radicals, and induce β-hydride elimination reactions that create isobutylene molecules which desorb from the surface.

Keywords: Chemical vapor deposition, photodecomposition, laser processing, paterned growth, triisobutylaluminum (TIBA) photodesorption

INTRODUCTION

Considerable effort has been invested in the general area of laser induced film deposition[1]. In electronics applications thin film growth and particularly patterned growth are being pursued. Patterned growth is most often used for customizing or repairing circuits because direct laser writing, though it has tremendous flexibility for quick reprogramming of whatever pattern is to be generated, is usually too slow to equal the complex pattern generation obtainable with lithographic processing. It has been possible to use laser deposition by direct projection through a mask for pattern generation[2]. The lack of speed in the laser processing is overcome by using a two step growth technique[3]. The initial step is to deposit a thin layer of metal using the laser followed by a second step in which the laser is turned off and the film is selectively grown only in the places in which the growth was prenucleated with the laser. In this technique the bulk of the film growth is at rates comparable to standard chemical vapor deposition rates. We have already investigated the surface chemical mechanism responsible for this selective deposition[4-6]. The thin film that is deposited consists of small metal clusters that act as nucleation sites for chemical vapor deposition. Away from the laser prenucleated region the inhibition of film growth depends on surface oxygen such as is present in a native oxide of silicon (or water). The oxygen reacts with the organometallic (in this case it is triisobutylaluminum--TIBA) and prevents the completion of the decomposition of the molecule. Surface adsorption sites are all tied up by these partially decomposed species and further adsorption and film growth are inhibited. Without the presence of oxygen, TIBA decomposes through a process known as β-hydride elimination in which a hydrogen on the second carbon away from the aluminum is inserted in place of the first carbon-aluminum bond allowing an isobutylene molecule to leave the surface intact[7]. This process is extremely desirable because clean aluminum deposition without carbon contamination is possible. In the presence of oxygen this β-hydride elimination is suppressed[4-6,8] but only for the last isobutyl group[9].

We turn our attention in this paper to the mechanism of laser induced decomposition. Various decomposition mechanisms have been utilized in laser deposition processes: thermal decomposition, gas phase photodecomposition, and photodecomposition of species bound on the surface[1]. Recent results have shown that light absorption by the surface can cause desorption[10-11] or decomposition[12-13] of model compounds adsorbed on the surface. In these cases, before the hot electrons generated by the laser pulse are thermalized, they induce desorption and dissociation. In fact cross sections for such charge transfer processes more than two orders of magnitude higher than gas phase photodecomposition cross sections have been observed[13]. In this paper we present evidence that adsorption by the surface followed by hot electron transfer (and not thermal or direct photodecomposition) is the dominant mechanism for the deposition of aluminum films from the decomposition of adsorbed TIBA using low power ultra-violet laser irradiation.

EXPERIMENTAL

The vacuum system was pumped by a 170 l/sec turbo pump with bearing purge. The quadrupole mass spectrometer was differentially pumped by a 20 l/sec ion pump. A skimmer with a 0.5mm aperature a few millimeters from the surface separated the two chambers. Fragments from laser decomposition desorbing normal to the surface could pass through the aperature and travel the 9 cm flight path to the ionizer of the quadrupole. The delay time was measured between the laser pulse and the fragment detection at the quadrupole. The delay time is the sum of three quantities: the time the fragment spends on the surface, the time-of-flight (TOF) to the ionizer, and the time delay in the quadrupole. The quadrupole delay is know and is subtracted from the data and the time spent on the surface is assumed to be short so the remaining time is the TOF. One great advantage of time-of-flight detection is that fragments created at the surface can be distinguished from further fragmentation that occurs in the ionizer. If two fragments have the same TOF then it can be expected that they have a common parent that left the surface. Furthermore the TOF of the parent is an important indication of the dynamics of the photodecomposition process at the surface.

The TIBA gas was prepared as was described previously[4]. At the beginning of each day a fresh aluminum layer was deposited by chemical vapor deposition on the surface at 300°C and a pressure of 10^{-6} torr of TIBA (as measured with an ion gauge without any sensitivity correction) for five minutes. During the laser desorption experiments, the background pressure was maintained at $2\text{x}10^{-7}$ torr; however, the gas was introduced through a gas doser so the effective pressure at the surface was approximately one order of magnitude higher.

A pulsed excimer laser was alternately operated as ArF, KrF, and XeF (wavelengths 193, 248, and 351nm respectively). The laser was reflected from the surface (incident angle of 75° relative to the surface normal) with the fluence kept low to minimize thermal effects. The repetition rate was kept at 2 Hz so that there would be sufficient surface dosing between laser pulses for the surface nominally to be at full coverage for each laser shot. Depending on the mass peak being observed, data from 500 to 10,000 laser pulses were collected.

RESULTS

The most intense peak in the TOF mass spectra occurs with the quadrupole tuned to mass 39. Peaks with the same TOF also occur at masses 27, 55, and 56. These peaks all come from isobutylene (mass 56) desorbing from the surface (a more complete description of the all the peaks appears elsewhere[14]).

Figure 1a shows the TOF of mass 39 for 25mj/cm^2 ArF laser irradiation. One peak and a long tail appear in the TOF spectrum, the peak is the true TOF for fragments leaving the surface and are characterized by a temperature of 283°K. The temperature T is simply calculated from the equation:

$$\frac{1}{2} m(x/t_p)^2 = 2KT \tag{1}$$

where x is the distance from the surface to the ionizer (9cm), K is the Boltzmann constant, t_p is the time for the peak of a Boltzmann fit to the TOF distribution[15] (in this case the distribution is slightly broader than a Boltzmann function), and m is the mass of the parent fragment that is traveling from the surface to the ionizer and not necessarily the mass that the quadrupole is tuned to. The long tail is due to molecules that are scattered, probably within the ionizer, before being detected.

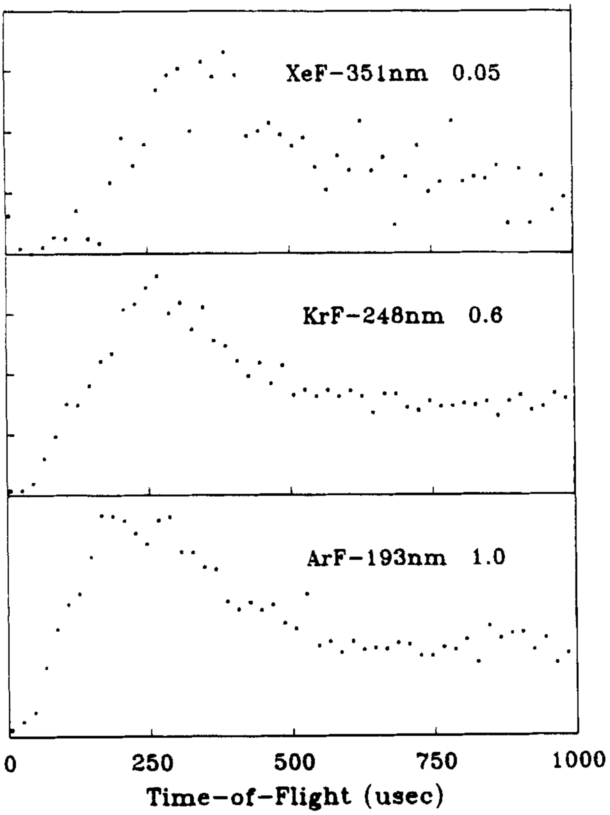

FIGURE 1: Mass 39 time of flight spectra for different laser wavelengths.

Similar TOF spectra are shown in figures 1b and 1c for laser wavelengths 248nm-KrF and 351nm-XeF (incident laser pulse fluence was 40mj/cm^2 and 12mj/cm^2 respectively). In these cases the best fit temperatures are 196°K and 125°K respectively. Translational temperatures lower than the surface temperature have previously been seen for photodissociation of trimethylaluminum on hydroxylated silicon surfaces[16]. The relative signals normalized to the photon flux and the average velocity of the TOF distribution are 1:0.6:0.05 for ArF:KrF:XeF. There is no correction for angular distributions since they are not measured in these experiments. In order to extract relative cross sections such a correction is essential.

The differences in temperature cannot be related to a difference in surface heating or gas phase collisions as seen from figure 2 showing the temperature of and integral of the TOF distribution versus laser fluence for 248nm-KrF radiation (Similar data is seen for 193nm-ArF[14]). If laser fluence were the determining factor then there should be a far stronger increase in temperature as a function of laser fluence in figure 2. The relative independence of the temperature versus fluence as well as the linear increase in the intensity versus fluence are indications that these fragments are created by a photochemical process.

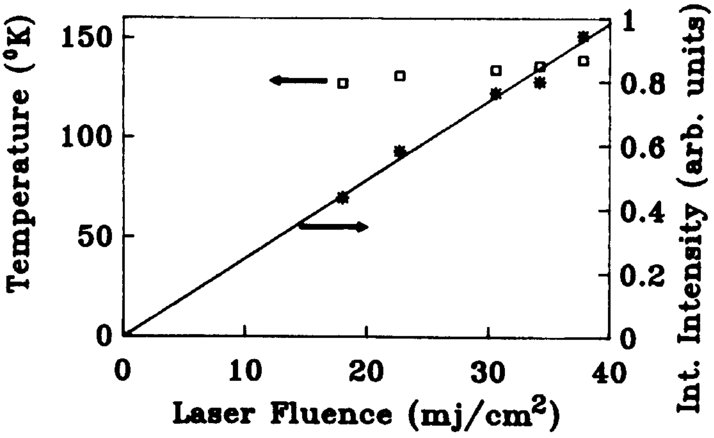

FIGURE 2: Translational temperature (squares) and normalized integrated intensity (asterisks) as a function of laser fluence for isobutylene desorption (as measured by mass 39) caused by KrF 248nm light.

TOF spectra were also measured at mass 15, mass 27, and mass 85. Since no peak appears at mass 16 the peak at mass 15 is due to methyl radicals and not methane. For 193nm and 248nm radiation and conditions identical to those for mass 39 the temperatures are 338°K and 214°K respectively and the intensity ratio was 1:0.4. Due to the large background at mass 15 it was not possible to extract a signal for 351nm radiation. A peak at mass 85 appears with the same TOF as the peak at mass 141. Both 85 and 141 may be fragments of the TIBA molecule which is not observed directly at mass 198 due to the propensity of the molecule to crack in the ionizer of the quadrupole (mass 198 is seen when large quantities of TIBA condensed on a liquid nitrogen cooled surface are desorbed). The translational temperatures (assuming that it is mass 198 leaving the surface) are 505°K, 224°K, and 268°K for 193, 248, and 351nm radiation respectively. The relative normalized intensities are 1:0.7:0.4. For mass 27 no peaks other than those that correspond to higher masses fragmented by the ionizer appear for 248 and 351nm radiation though an extra peak does appear with many eVs of translational energy for 193nm radiation. Details of this fragment are presented elsewhere[14].

DISCUSSION

The gas phase absorption of TIBA rapidly cuts off above 193nm and goes almost completely to zero by 210nm[17]. Gas phase photodissociation has been observed at 248nm though it is considerably smaller than at 193nm[18]. Neither study found any evidence of absorption in the gas phase at 351nm[17,18]. Small red shifts in the absorption spectra of other organometallics adsorbed on surfaces have been seen but too small to account for the relative intensities measured at the wavelengths in this study[19]. This might account for photodissociation at KrF-5.1eV being half that at 193nm but not at the significant amount of dissociation at XeF-3.6eV unless the structure of the TIBA molecules changes radically on adsorption. There is no evidence for such radical changes on adsorption from the vibrational spectra of the first monolayer (as compared to multilayers of TIBA) from EELS measurements of the vibrational modes [7] or from XPS measurements of Al 2p binding energies (on oxide-free silicon surfaces)[6]. Yet the linear dependence on laser fluence and the minimal temperature rise of the surface clearly indicates a photoprocess and not a thermal process.

A mechanism other than direct photodecomposition is implicated. Previous studies of photodissociation of model compounds on surfaces have been shown to be caused by light absorption by the surface followed by charge transfer to the adsorbed species[12-13]. There is other evidence from this work that this is the case for TIBA also. The translational temperature of the fragments is extremely low considering that the photon energy is many electron volts. In fact all the fragments that are seen have relatively small translational energies relative to the photon energy except for Al atoms which desorb with many eVs but are only generated with 193nm radiation and increase in intensity as the fluence is increased in a nonlinear manner[9]. Another interesting point to note is that the species leaving the surface is isobutylene (mass 56) and not the isobutyl radical (mass 57). A peak at mass 57 is measured but this peak appears later in time than the mass 39 peak. Mass 57 is correlated in time with other peaks at masses 85 and 141 so it originates from a larger fragment that leaves the surface. The TOF of mass 39 does match that of mass 56 which is evidently its parent. This is significant because it indicates that the mechanism for removal of isobutyl radicals is (photoinduced) β-hydride elimination.

The appearance of methyl radicals (mass 15) indicates that the decomposition of isobutyl groups is also occurring. This reaction is undesirable because carbon fragments are left behind in the deposited film[4]. It also indicates that the hot electron induced chemistry in this system is not as selective as the thermal reaction which below 600°K produces only clean aluminum deposition[7]. Another undesirable reaction is TIBA desorption because desorption competes with dissociation to reduce the reaction rate. The appearance of desorption at all is interesting because on thermal heating of adsorbed layers, such as those that should exist on the surface at low pressures and at room temperature, only decomposition is observed[7]. Desorption does not seem to decrease as rapidly with photon energy as the decomposition channels do, with 351nm the intensity measured here is still a third of that measured with 193nm. So, lowering the photon energy is not analogous to lowering the surface temperature. The selectivity does not seem to improve and in the end deposition will be limited at low photon energy by photoinduced desorption.

CONCLUSION

A linear dependence of the product formation on laser fluence, as is seen here for fragments created by pulsed uv-laser irradiation of TIBA on CVD deposited aluminum surfaces, is a clear indication that the mechanism of formation is photochemical in nature. Despite the reduced direct absorption by TIBA at 248nm and the lack of absorption at 351nm there is still a significant probability of photoinduced dissociation of molecules at these wavelengths. The translational energy of fragments is considerably lower than the photon energy at all wavelengths studied particularly at 193nm where direct adsorption is possible. This supports a mechanism in which the chemistry is driven by hot electrons created by light absorption at the surface. These hot electrons drive chemistry similar to thermal reactions in the same system. The primary mechanism of decomposition is still β-hydride elimination. A significant side reaction is methyl removal which has the unwanted effect of leaving carbon in the deposited film. On the other hand molecular desorption is not seen thermally but is observed here. It is surprising that the translational temperatures are so low--considerably lower than the surface temperature in a number of the cases especially at the longer wavelengths. Any mechanism in which the fragment is assumed to be promoted to a state on a repulsive barrier and then is repelled off the surface must be ruled out.

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