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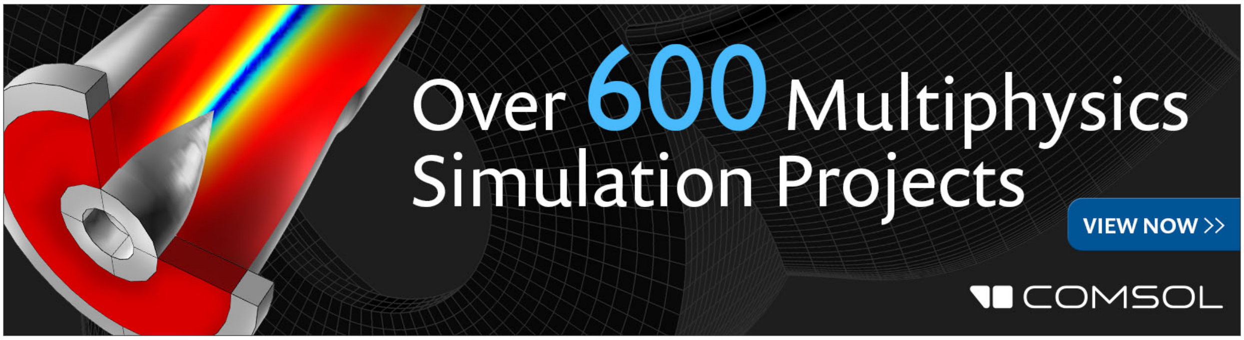

Laser-induced deposition of alumina from condensed layers of organoaluminum compounds and water

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The photoassisted deposition of thin aluminum oxide films from layers of trimethylaluminum (TMA), dimethylaluminum hydride, and aluminum hexafluoroacetylacetonate condensed with water on a cold substrate has been investigated. Laser energies of 4.6 or 2.3 eV were used to drive the reactions which led to film growth. Experiments show that clean aluminum oxide films can be synthesized at 80 K by irradiating co-condensed TMA and H_2O with 4.6 eV light. Techniques used to characterize the films include Auger electron spectroscopy and scanning electron microscopy.

Deposition of Al_2O_3 thin films is of significant interest in microelectronic, optical, and magnetic packaging applications.[1] Difficulties with past techniques for forming thin films of alumina have spurred work on alternative methods, such as plasma- or laser-assisted chemical vapor deposition (PACVD or LACVD).[2] We have recently shown that it is possible to grow Al_2O_3 by exposure of condensed layers of trimethylaluminum (TMA) and water to synchrotron radiation (SR).[3] In the current study, we demonstrate the application of this condensed layer technique to the deposition of Al_2O_3 on various substrates using an ultraviolet laser as the excitation source.

There are several potential advantages of this procedure over current methods. First, films are grown at far lower temperatures than are normally required for PACVD or LACVD techniques (80 K compared to 480 K or higher),[2] which is important when substrates are thermally sensitive. Also, since the vapor pressure of the condensed layer is less than 10^{-9} Torr, concentrations of reactants can be carefully controlled and monitored with surface science techniques. Finally, the film can be patterned without subsequent processing, since areas of the reactant layers which are not exposed will simply desorb when the substrate is warmed to ambient temperature. This last feature makes the method particularly attractive for resistless processing.

A few constraints on the application of the method should be noted. Obviously, the desired product should be formed from the reactant layers on excitation. Reaction or decomposition should be avoided in the absence of light. Undesirable side products should desorb either during irradiation or when the substrate is warmed. Most importantly, the reactants should be volatile below the minimum processing temperature (which is room temperature, in these studies).

Previous studies have been done which demonstrate deposition of numerous materials from layers of condensed gases under vacuum, including Fe and $Fe(CO)_5$ using a Hg lamp[4] and SR,[5] Cu from $Cu(acac)_2$ using KrF excimer laser light,[6] W from WF_6 using an electron beam,[7] and epitaxial CdTe from dimethyl cadmium and dimethyl tellurium using ArF excimer laser light.[8] However, none of this past research demonstrates the deposition of a dielectric film, which generally requires two reacting species to be intimately mixed. It was observed in earlier studies of dielectric film deposition[3,9] that a weak interaction (e.g., dative bond formation) between the reactants occurred before film growth was initiated. Indeed, this interaction may even be necessary for growth to occur.

The proximity of the condensed molecules to the surface implies the possibility of energetic electrons initiating reactions between the species. This may be the dominant effect in the SR studies, where the quantum yield of electrons is significantly greater than one. However, there is also the chance of direct photoexcitation and decomposition of TMA, which is the important pathway to deposition in LACVD. Finally, contributions from pyrolytic decomposition cannot be ruled out. The discussion below will address these concerns.

All experiments were carried out in a turbomolecular and titanium sublimation pumped ultrahigh vacuum chamber, which attained a base pressure of $\sim 1\times 10^9$ Torr after bakeout. Surface characterization was by Auger electron spectroscopy (AES), using a Perkin–Elmer single-pass cylindrical mirror analyzer with a coaxial electron gun. The substrates were silver or nickel films of 0.3 or 0.7 μm thickness which had been evaporated onto a silicon wafer [of nominally (100) orientation] at 10^{-6} Torr in a preparation chamber. The wafer was clamped to a copper support which was in contact with a liquid nitrogen reservoir. Cleaning was accomplished by room temperature argon-ion sputtering for approximately 10 min, repeated until carbon and oxygen levels fell below 5 at. % as determined by AES. Additional sputtering after cooling to 80 K was necessary in some cases to restore surface purity. It should be noted that the silicon surface was not expected to represent a single-crystal face.

The TMA and dimethylaluminum hydride (DMAH) were obtained from Alfa Chemicals (electronic grade). Each was purified daily before use by repeated vacuum distillation

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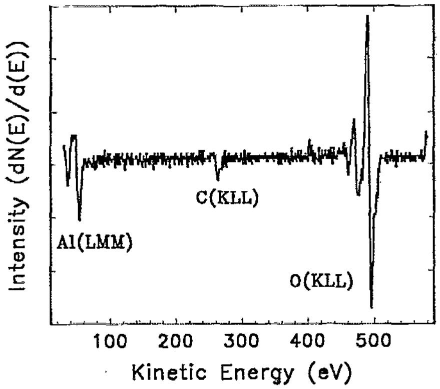

FIG. 1. Auger spectrum (AES) of Al_2O_3 deposited on silver from condensed TMA and H_2O, irradiated at 4.6 eV for 30 s and warmed to room temperature. The carbon level in the film is less than 10%.

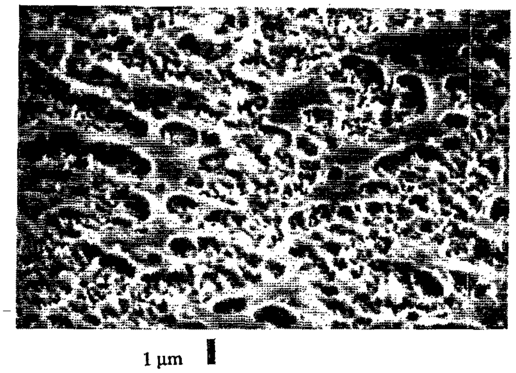

FIG. 2. Scanning electron micrograph of typical alumina deposit from TMA and H_2O over silver, Scale bar is 1 μm.

cycles at 150 K, until the m/e 57 [$(CH_3)_2Al^+$] peak was the highest intensity in the mass spectrum. The aluminum hexafluoroacetylacetonate [$Al(hfa)_3$] solid was heated while in the gas manifold to about 50 °C for dosing. In each experiment the sample was dosed simultaneously with one of the organoaluminum compounds and water for several minutes through separate needles aimed at the surface (partial pressures as measured by an ionization gauge were generally 2×10^{-8} and 2×10^{-7} Torr for the organoaluminum and water, respectively). Analysis of the resulting condensed films by AES was not possible because of charging effects, but it is expected that water was the principal component based on the high sticking coefficient and larger partial pressure. In previous experiments,[3] these conditions resulted in layers determined by photoelectron spectroscopy to be ~100 Å thick. The samples were then irradiated with the fourth harmonic of a Nd:YAG laser (continuum) at ~1.3 mJ/cm ^{2} pulse (10 Hz repetition) through a quartz window onto the sample. After exposure,the sample mounting was warmed to room temperature using a nichrome wire heater mounted behind the support, desorbing all volatile material, and the sample was characterized with AES. Scanning electron micrographs were taken after exposure of the samples to air.

Figure 1 shows an AES spectrum for condensed TMA/H_2O layers after exposure to 4.6 eV photons (~1.3 mJ/cm^2 at 10 Hz repetition) for 30 s. The carbon level is much lower than expected for stoichiometric TMA (estimated by using sensitivity factors to be about 10 at. %). This spectrum (Fig. 1) compares well with a standard spectrum of alumina.[10] An analysis based on attenuation of the silver *LMM* Auger electron signal (by a factor of at least 200) gives a lower limit of ~40 Å for the film thickness of a pinhole-free film.[11] We emphasize that warming the sample to room temperature without first irradiating results in the desorption of the condensed layer leaving the silver surface with submonolayer levels of carbon contamination.

During irradiation, a pressure rise of about 4×10^{-8} Torr was observed, which we attribute to methane desorption. Irradiation of condensed TMA/H_2O layers[3] with broadband synchrotron light leads to a similar pressure increase, which was identified by mass spectrometry to be primarily methane. It follows that methane desorption is the most probable mechanism by which carbon is removed from the reacting mixture in the laser experiment.

Scanning electron microscopy (SEM) was used to characterize the morphology of thick aluminum oxide films formed by irradiating TMA and H_2O layers which were greater than 100 Å. The SEM pictures of the deposit showed a porous film which uniformly covered both silver and silicon (Fig. 2). The structures formed may be due to gaseous methane formation during the growth, or desorption of unreacted volatile species (such as water) during warmup. It may be possible to improve the morphology by changing the conditions (e.g., growing more slowly with lower flux). Future studies will address these questions, and compare these images with films grown by SR.

To test the hypothesis that photolysis is the dominant process in these reactions, film growth was attempted on several substrates. However, no effects outside experimental error could be determined when the substrate type was varied, and TMA and H_2O were the reactants. It is expected that changing the work function of the substrate will effect the quantum yield of photoelectrons, and hence change the rate of any reaction mediated by photoelectrons. Although most studies were based on silver, a clean silicon wafer, nickel films, and silver films with 10% potassium coverage were also used. The work functions of these substrates vary from ~3.2 eV for K/Ag to 5.15 eV for Ni with corresponding quantum yields of ~10^{-2} (electrons/photon) to less than 10^{-6}, at 4.6 eV.[12] Since the irraditions were for the same length of time in each case, and the resulting films are roughly the same thickness, we can conclude that other mechanisms may be more important in this study.

Finally, rough estimates of surface heating suggest that there is little pyrolytic component to the reaction mechanism. The absorbance of the condensed layers can be neglected, since the cross section for TMA is low and H_2O is negligible.[13] For a laser pulse of 4 ns, the energy is thermally dissipated into the substrate, and the temperature rise over the pulse at the surface would be not more than 50 K.[14] Also, in experiments done with 2.3 eV photons (frequency doubled Nd:YAG), no observable reaction above background occurred, even at up to 300 mW/cm^2 power.

Experiments using DMAH or $Al(hfa)_3$ as the aluminum

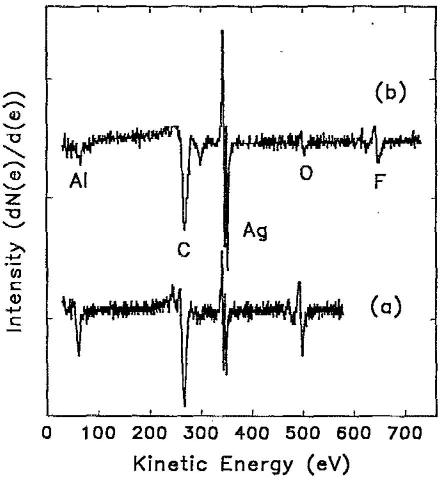

FIG. 3. AES of alumina deposited from (a) DMAH and H_2O and (b) $Al(hfa)_3$ and H_2O. Considerable carbon contamination is present, and incomplete coverage of the silver is indicated.

source succeeded in producing films, but impurity levels were significantly higher (Fig. 3). Although CVD of clean Al_2O_3 has been demonstrated by passing $Al(hfa)_3$ over a heated substrate,[1] the less volatile fragments in our case may become trapped in the growing film. This illustrates a striking difference in the criteria for the precursors in this method compared to surface-mediated processes such as CVD. Based on the intensity of the silver Auger features in Fig. 3, we note that the resulting films in both of these cases were not as thick (in a pinhole-free approximation) as those grown with TMA and water.

These observations suggest that the primary mechanism of film deposition is by direct TMA photodissociation for the following reasons. (1) Substrate photoelectrons are limited by relatively low mean-free paths from contributing to the visible (thick) growth, suggesting that they do not have a major effect on film growth. (2) The electronic states generated by the metal-centered orbitals in TMA have the highest cross section for absorption at 4.6 eV.[13,15] (3) No variation in film growth is observed when changing the photoelectric quantum yield of the substrate by four orders of magnitude. (4) The effects of heating at the interface are minimal compared to what should initiate pyrolytic decomposition of TMA.

In summary, we have deposited relatively pure alumina on a variety of substrates by using UV laser irradiation at 4.6 eV to initiate reactions from a condensed mixture of TMA and water, held at 80 K. Growth is obtained with DMAH and $Al(hfa)_3$ as the aluminum containing precursors, but with substantial contamination in the resulting films. The nature of the experiments suggests a direct photoexcitation mechanism in the condensed layer, contrasting with a previous SR study where the mechanism is believed to be due mainly to energetic secondary electrons from the substrate.

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