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ON THE ORIGIN OF LASER-INDUCED SURFACE ACTIVATION OF CERAMICS

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ABSTRACT

The surfaces of Al_2O_3 and AlN are modified by pulsed-laser irradiation This modification promotes the deposition of copper when the irradiated substrates are immersed in an electroless bath. In this paper the nature of the surface modification is analyzed using results from Auger Emission Spectroscopy (AES) and Cross Sectional Transmission Electron Microscopy (XTEM). During irradiation AlN thermally decomposes leaving a discontinuous metallic film on the surface. A film of Al_2O_3 is detected at the surface of the irradiated AlN substrate, much thicker when the irradiation is performed in an oxidizing atmosphere than when done in a reducing one. Nanoparticles of metallic aluminum are generated during laser irradiation of Al_2O_3 in a reducing atmosphere. When the irradiation of Al_2O_3 is performed in an oxidizing atmosphere, regions containing aluminum or substoichiometric alumina are detected by AES. It is concluded that the presence of metallic aluminum is the main reason why electroless deposition can occur in both AlN and Al_2O_3. Deposition kinetics are completely consistent with this conclusion. It is very likely that also substoichiometric alumina helps to catalyze the electroless deposition.

INTRODUCTION

In the process known as laser-induced surface activation of dielectric materials a given pattern is imprinted on a substrate by laser irradiating its surface. The pattern can be produced by laser-scanning or by illuminating the substrate through a mask. When the substrate thus treated is immersed in an electroless solution, a metallic film is deposited in the laser-exposed area only. Surface activation can be conducted many weeks ahead of the electroless deposition. Excimer, argon ion, copper-vapor and CO_2 lasers have been used (1 - 7) to activate the surface of a variety of materials including ionic and covalent oxides, a nitride, a polymer and diamond films. All of the ceramic materials that have been laser activated for electroless metal deposition have a low absorption coefficient or are transparent to low power density ultraviolet radiation in their single-crystalline forms. In this work, careful surface characterization of irradiated substrates have led us to understand why electroless copper deposition takes place in the laser irradiated area.

CHARACTERIZATION OF LASER IRRADIATED Al_2O_3 AND AlN SUBSTRATES

The effects of 308 nm-wavelength laser irradiation on Al_2O_3 (8) and AlN under reducing and oxidizing atmospheres have been studied by transmission electron microscopy (TEM) (9), x-ray photoelectron spectroscopy (XPS) (10) and Auger emission spectroscopy (AES). AES is particularly well suited to analyze the chemical changes because it can resolve unambiguously the chemical state of aluminum, whether in a metallic, in an oxide or in a nitride environment. The Auger electron kinetic energy for the LVV transition of aluminum in AlN is 5 eV higher than the corresponding value for the oxide. The energy for the LVV transition of aluminum in a metallic state is 9 eV higher than the corresponding value for the nitride. Therefore it is relatively simple to resolve the chemical state changes of these materials with AES.

The surface of as-received AlN consists mostly of Al_2O_3 layers, as can be seen in Figure 1. This is consistent with Al_2O_3 being thermodynamically more stable than AlN (11). Thus, mechanical and/or thermal processing in air induces oxidation of the AlN surface. Spectra ii and

iii shown in figure 1 were taken at increasing depths. They demonstrate that as the distance to the surface increases the chemistry changes from Al_2O_3 to AlN, as expected.

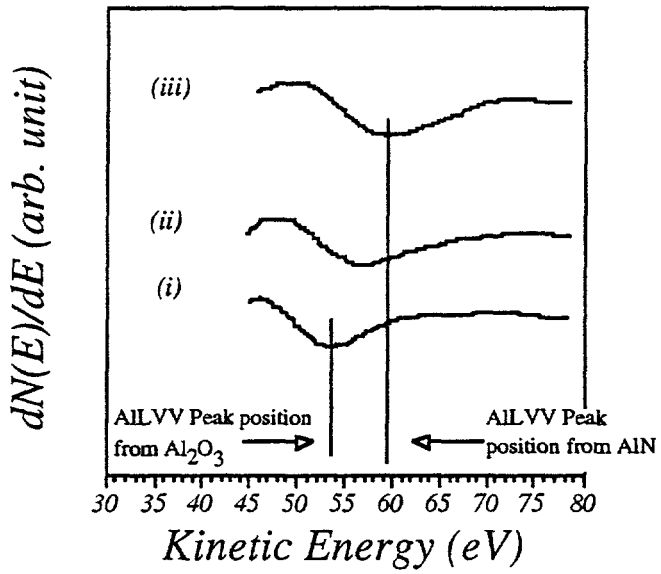

Figure 1. Al LVV peak spectra from the surface (i) and the subsurface (ii and iii, at increasing depth), of as-received AlN substrate. To obtain the subsurface AES peaks the surface was gently sputter-etched in situ. The spectrum from the surface is that of stoichiometric alumina (i). As sputter etching advances to deeper substrate layers, the surface chemistry changes from aluminum oxide to aluminum nitride.

Figure 2 shows the Al LVV peaks from the surface and from the interior of an AlN substrate laser-irradiated at 2 J/cm^2 in a reducing atmosphere (Ar-4%H2). The surface is mostly Al_2O_3 and,

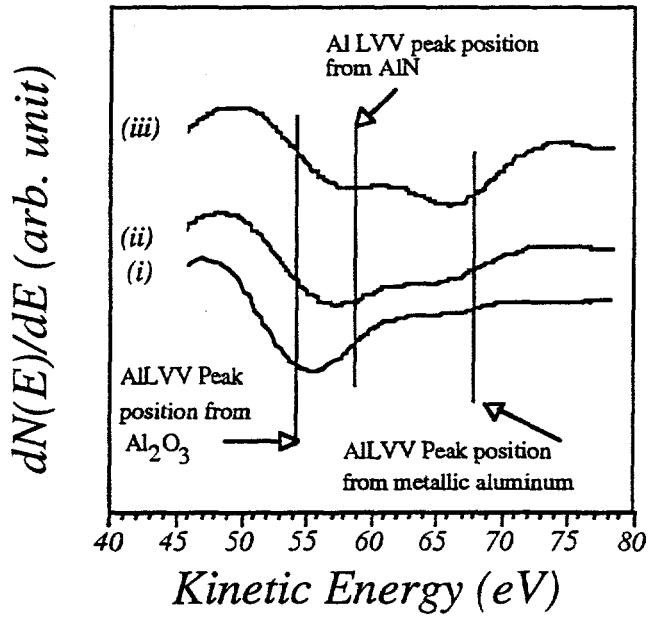

Figure 2. Al LVV peak spectra from the surface (i) and subsurface (ii and iii) of AlN laser-irradiated in Ar-4%H_2 at 4J/cm^2. Al LVV from the surface (i) is a superposition of peaks from Al_2O_3 and AlN, while sputter etching reveals that the subsurface peaks are from both AlN and metallic aluminum (ii and iii).

as the surface layers are removed, metallic aluminum appears together with Al_2O_3. Deeper inward the substrate consists of metallic aluminum and AlN. The amount of metallic aluminum at level iii) is larger that the amount of aluminum in AlN form (Figure 2). The oxide layer after laser irradiation is one to two monolayers thick, whereas that of as-received AlN was much thicker, but varied depending on the area. After laser irradiation in a reducing atmosphere AlN decomposes and a relatively thick layer of aluminum is formed. This implies that the laser irradiation increases the temperature above the decomposition value (12). When the specimen is exposed to air the aluminum is oxidized forming aluminum oxide. The decomposition of AlN is thermally induced and, hence, it takes place even if the irradiation is performed in air or in pure oxygen. When the irradiation is performed in an oxygen-rich atmosphere, however, the oxide layer is significantly thicker. This is not surprising because the aluminum layer that results from the decomposition is exposed to oxygen at high temperatures.

Auger mapping (13) and cross sectional TEM (9) revealed that metallic aluminum produced by laser -induced decomposition clustered in the AlN matrix.

An AES study was conducted in alumina in a similar manner to the study in aluminum nitride. Alumina substrates were irradiated in oxygen and in Ar-4%H_2 at 2 J/cm^2. The surface chemical composition of the specimen irradiated in oxygen corresponds to Al_2O_3, while in the subsurface regions metallic aluminum and/or substoichiometric aluminum oxide is observed (Figure 3).

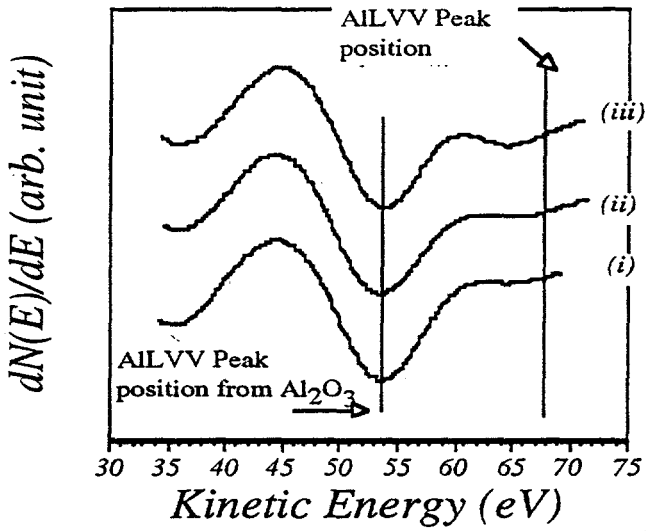

Figure 3. Al LVV peaks from the surface (i) and subsurface (ii and iii) of alumina laser irradiated in air at 2 J/cm^2. Metallic and/or substoichiometric aluminum oxide is detected in the subsurface region.

The specimen irradiated in Ar-4%H_2 shows much more aluminum in the subsurface than the specimen irradiated in oxygen (figure 4). However, the amount of metallic aluminum in the Ar-4%H_2 irradiated alumina is much less than that formed in the aluminum nitride, as can be seen by comparison of the peak-to-peak heights of Al LVV peaks from metallic aluminum, Al_2O_3 and AlN (Figures 2 and 6). Substoichiometric alumina and/or metallic aluminum are detected in the irradiated sample even if the irradiation was done in an oxidizing atmosphere. These results thus demonstrate that during laser processing thermal decomposition of alumina takes place, independent of the irradiation atmosphere. Remarkably, XPS spectra (9) reveal that the amount of oxygen present in alumina laser irradiated in air is higher that in unirradiated substrates. EDS analyses confirmed that the oxygen content is higher in substrates irradiated in air that in as-received ones. It seems that a significant amount of oxygen is trapped into positions other than lattice sites. This rationale is supported by the observation that, after irradiation, the samples acquire a strong yellow-brownish color, characteristic of F centers.

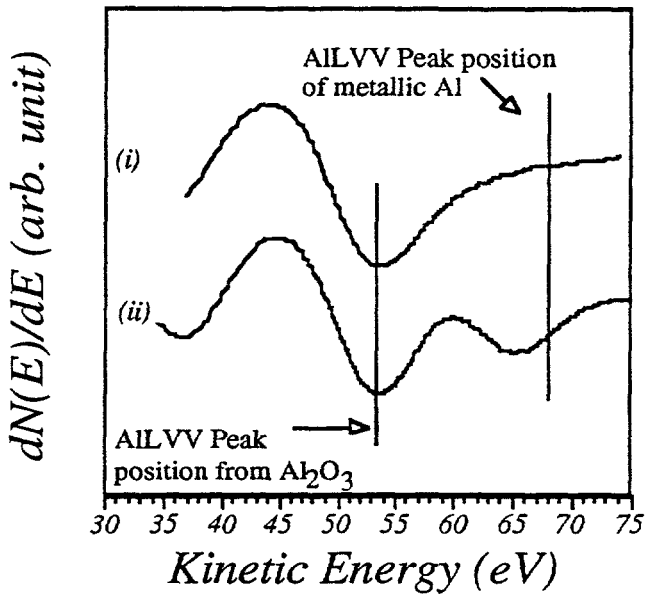

Figure 4. Al LVV peaks from the surface (i) and subsurface (ii) of alumina laser-irradiated in Ar-4%H_2 at 2J/cm_2. More metallic aluminum is left after irradiation in a reducing atmosphere than in an oxidizing atmosphere (shown in Fig. 3).

Figure 5 is a cross sectional transmission electron micrograph of an Al_2O_3 substrate irradiated in Ar-4% H_2. A 0.5 μm-thick layer of Al_2O_3 has been melted and it resolidified with a cellular structure also including a high density of small particles in a 0.34 μm-thick layer (figure 5a). In figure 5b the sample has been rotated to offer a better view of the particles. The spacing between lattice fringes observed when some of these small particles were imaged with high resolution corresponds to the spacing of aluminum (111) planes. The distribution of the aluminum particles suggests that their formation is related to gas evolution during solidification. Thus, it can be reasoned that atmospheric hydrogen dissolved in the liquid alumina is pushed away during solidification increasing its concentration ahead of the advancing interface. When the hydrogen concentration at the interface reaches a value high enough to start reducing Al_2O_3, liquid metallic aluminum should form by reduction of Al_2O_3 in front of the interface. When these pockets of liquid aluminum solidify they become the particles observed by TEM.

LASER-INDUCED SURFACE ACTIVATION OF AlN AND Al_2O_3

Laser-induced decomposition of AlN irradiated at or above 2 J/cm^2 leaves on the surface enough aluminum to form an interconnected network of islands, as verified by the much lower electrical resistance of specimens irradiated at 2 and 3 J/cm^2 compared to that of specimens irradiated at 1 J/cm^2 (14). Moreover, the electrical resistance decreases as the laser density increases indicating that the amount of metallic aluminum increases as the applied laser energy density increases. After immersion in an electroless bath, the electrical resistances of the 2 and 3 J/cm^2-irradiated specimens rapidly increase, while that of the 1 J/cm^2 specimen rapidly decreases. After a short period of immersion time the three specimens reach the same electrical resistance value. This value of electrical resistance is that of the measuring cell in the electroless solution (14). The metallic aluminum is mostly dissolved because the electroless bath contains NaOH which is well known to dissolve aluminum. We have observed by TEM that as the dissolution of aluminum progresses copper islands start forming at the same location (9). Thus, the partly dissolved aluminum film formed by the AlN decomposition acts as a catalyst for electroless deposition. Copper metallization is induced in the irradiated areas upon immersion of laser-treated substrates in a copper electroless bath. We have shown previously using TEM that

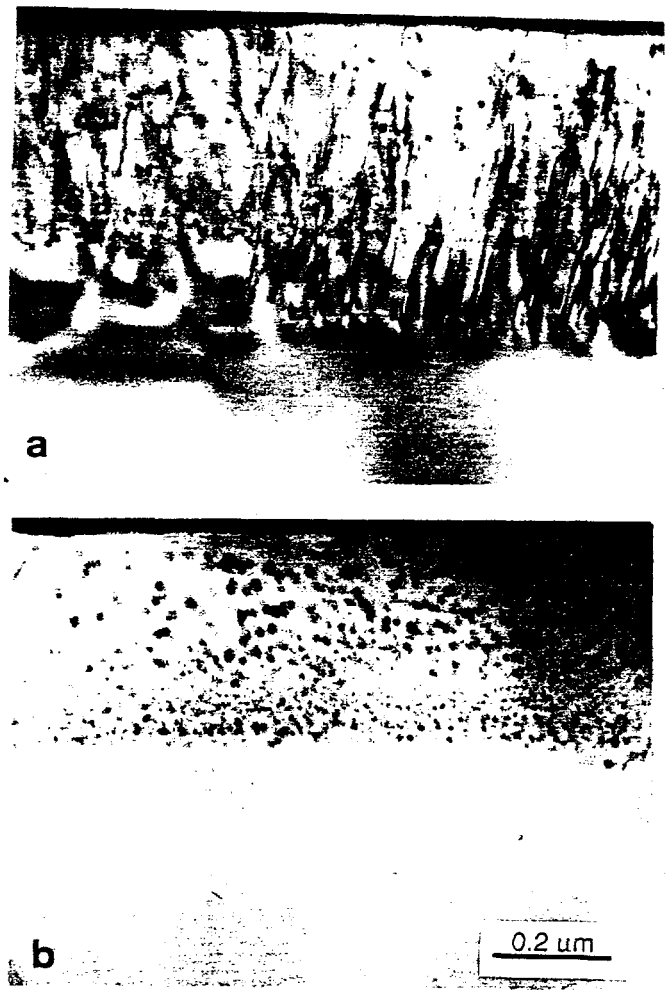

Figure 5. Cross sectional transmission electron micrograph of an Al_2O_3 substrate irradiated in Ar-4% H_2 at 1.6 J/cm^2. a) A 0.5 μm-thick layer of Al_2O_3 has been melted and it resolidified with a cellular structure including a high density of small aluminum particles in a 0.34 μm-thick layer. b) Specimen was slightly rotated to show only the metallic particles.

copper island appeared in the crevices and interfaces left by the dissolved aluminum islands (9). A galvanic displacement reaction in which aluminum is dissolved and copper is deposited is the most likely process start-up reaction (15). We deduce that, similar to what happens with AlN, the metallic aluminum detected by AES (Fig .3 and 4) and shown in XTEM (Fig.5) during laser irradiation of Al_2O_3 must promote the deposition of electroless copper.

DeSilva et al. (15) measured the time required to initiate and complete the electroless deposition in AlN and Al_2O_3 substrates irradiated in oxidizing and reducing atmospheres. Reducing irradiation atmospheres promote much faster electroless deposition rates because it takes a shorter time to dissolve a thinner oxide layer once the substrate is immersed in the electroless solution containing NaOH. At a given atmosphere and for a given laser energy density used for activation, the deposition of copper is much faster in AlN than in Al_2O_3. As described in the previous section, for given irradiation conditions more aluminum is produced by irradiation of AlN than by irradiation of Al_2O_3. Also the oxide layer produced in AlN during irradiation in an oxidizing atmosphere is much thinner than that produced during irradiation in an oxidizing atmosphere. The Auger results strongly suggest that substoichiometric alumina is also present when Al_2O_3 is irradiated in an oxidizing atmosphere. Deposition kinetics are in

complete agreement with the premise that metallic aluminum is the main cause of the electroless deposition in AlN and Al_2O_3. It is very likely that also substoichiometric alumina will help to catalyze the electroless deposition.

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