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The adhesion of copper films deposited onto aluminum nitride

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Good adhesion between copper film and AlN substrate is obtained when the surface of AlN is laser-irradiated prior to copper film deposition and post deposition annealing is conducted. Surface chemistry of AlN substrates before and after laser irradiation and the interfacial reactions of copper film/AlN couples were studied with Auger Electron Spectroscopy (AES) to understand the adhesion mechanisms. The surface of as-received AlN substrates was covered with a thin sheath of Al_2O_3. Laser irradiation removed the surface Al_2O_3 layers, smoothened the surface, and decomposed AlN leaving metallic aluminum on the surface. The interfacial reactions in the copper film/AlN couple are affected by the amounts of oxygen and metallic aluminum available at the interface. The adhesion mechanism is the formation of a Cu-O-Al compound at the interface of copper film/AlN couple. Since copper does not react with AlN, laser induced decomposition of AlN seems to be the driving force for the formation of the compound. © *1999 Kluwer Academic Publishers*

1. Introduction

Due to its high thermal conductivity [1], interest in AlN has grown very rapidly in hybrid circuit applications that require a rapid dissipation of the heat generated during service in the conductive path of the circuit. The first step in the application of AlN in circuits is an achievement of good adhesion between a metallic line, i.e. copper, nickel, or gold, and the AlN substrate.

The surface structure and composition of metals and ceramics are usually different from those of the bulk. So, interfacial chemical reactions may occur in some systems even though the bulks are mutually non-reactive in a thermodynamic sense. However, copper and AlN are not expected to react with each other at the interface under thermodynamic equilibrium [2]. Therefore, the adhesion between copper and AlN is very poor. For this reason, prior to copper film deposition, the AlN surface was modified to augment the likelihood of interfacial reactions. Laser irradiation was employed for the surface modification in this work.

It has been reported [2] that aluminum nitride (AlN) can be thermally decomposed by laser irradiation and the decomposition products are liquid Al and gaseous N. The gaseous N is ejected into the atmosphere, leaving metallic aluminum layers on the surface of the substrate after re-solidification. In this work, the formation of metallic aluminum in AlN by laser irradiation was studied with AES and the analysis results were correlated with the adhesion between copper film and AlN substrate. AES was also used for the analysis of the interface between copper and AlN to understand adhesion mechanisms. The following were studied in this work:

(1) Characterization of AlN substrate using Scanning Electron Microscopy (SEM) and Auger Electron Spectroscopy (AES) before and after laser irradiation,
(2) Pull adhesion testing to measure the adhesion strength of copper film/AlN couples,
(3) AES interface analysis of strongly and weakly adhered Cu/AlN couples.

In order to study the film-substrate interface with AES, a relatively thick film was deposited and the deposited film was removed layer-by layer by sputter etching until the interface was revealed and then the substrate became exposed. In contrast with a method that uses AES (or XPS) analysis with gradual film deposition, with this technique the formation of film islands that possibly take place at the initial stage of film deposition can be prevented, and the sample charging that takes place during AES of insulators can also be circumvented. The main problem of this destructive method is the ion-beam induced damage. The damage could be mitigated by reducing the ion beam energy during the sputter etching.

2. Experimental procedure

High purity AlN substrates (99%+) with less than 0.4 μm surface roughness and average grain size of approx. 3 μm were irradiated with a pulsed XeCl excimer laser operating at 308 nm wavelength and pulse

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duration at FWHM of 41 ns. The irradiations were conducted in an oxidizing or a reducing (Ar-4%H_2) atmosphere at various energy densities, viz., 0.3, 0.5, 1, 1.5, 2, and 3 J/cm^2 with 10 sequential pulses. Copper film was then sputter-deposited onto these substrates to a thickness of about 800 Å by bombarding the target with Ar neutrals and ions at 7 keV beam energy and 1 mA current. A Paulus and Reverchon type ion gun was used for the sputter deposition [3, 4]. The beam incident on the target is largely composed of neutral Ar because most of the ions transfer their energy to gas atoms. Base and work pressures of the chamber were $\sim 2 \times 10^{-6}$ Torr and $\sim 10^{-4}$ Torr, respectively. Subsequently, the couples were annealed at 300 or 500 °C for 1 h in a vacuum pressure of 10^{-5} Torr. Pull adhesion testing was, then, conducted to measure the adhesion strength of the couples.

For pull adhesion testing an aluminum pin coated with epoxy resin was glued to the metallic film. The procedure to ensure a strong bonding of the epoxy to the metallic film has been described elsewhere [5]. Subsequently, the aluminum pin was firmly clamped and then the pin was pulled down at a speed of 3 μm/s by means of a stepping motor. The bonding strength of the glue that connects pin and copper film, ~70–75 MPa, set the upper limit of the adhesion testing. The samples were very accurately aligned in order to prevent undesirable shear stresses at the couples interface during the pull testing. In order to get rid of the contributions of the copper film plastic deformation during pulling to the adhesion strength, the test parameters were kept constant for all the samples so that only the interfacial adhesion strengths could be compared with each other. For each processing condition, five samples were pull-tested and the reported values are the average over the five measurements. After determining the adhesion strength, interfaces of the couples that showed either strong or weak adhesion were analyzed with AES.

Surface topography was observed with SEM. Scanning Auger microprobe (SAM) Phi model 660 combined with ion sputtering gun was used for the chemical analysis of the surfaces and the interfaces. The resolution of the SAM analyzer was 0.6% and the energy resolution during data acquisition was 0.5 eV/step. An accelerating voltage of 3 kV and electron beam current of 10 nA were used for AES analysis. These potential and current levels eliminated electron beam induced decomposition of AlN as checked during this study.

Auger mappings at a magnification of 10 kX were done for the substrate laser-irradiated at 1 J/cm^2 in Ar-4%H_2 to investigate the elemental distributions. The metallic aluminum formed by laser irradiation is reoxidized immediately upon exposing in air, therefore, the reoxidized layers were removed by sputtering before analysis. The exposed metallic aluminum after sputter etching was oxidized in about 10 min even at a 10^{-9} Torr pressure in the vacuum chamber. Therefore, this surface oxides that grew in the vacuum chamber (usually less than a mono layer) need to be gently sputtered away with 0.5 keV Ar for 10 s every 5 min during the data acquisition for metallic aluminum mapping.

For the interface analysis of the copper film/AlN samples with AES, the metallic films were removed layer-by-layer with an Ar^+ ion gun. Auger signals were detected after each sputtering cycle. An ion beam energy of 500 eV and an ion current of 20 nA were used for the sputter etching. As calculated with the TRIM code [6], ion bombardment at 500 eV energy does not generate significant damage in the surface. The sputtering lasted 30 s per cycle and sputtering area in the vicinity of the interface was $200 \times 200\,\mu m^2$. A 10 Å thick surface layer, approximately, could be removed per cycle. Sample charging due to the insulating part of the couples could be eliminated by selecting the analysis area close to the metallic films since the metallic film is a conductive path. When the substrate became exposed, the analysis was ceased. Data were acquired in $E^*N(E)$, however, the display mode of Auger spectra in this work is in $d\{E^*N(E)\}/dE$ unless otherwise stated.

Prior to the analyses, studies were conducted for the reference Auger peak positions. Our standard O KLL peak positions from Al_2O_3, CuO, and Cu_2O are, respectively, 506 eV as obtained from as-received Al_2O_3 substrate, 509 eV, and 512 eV. The Cu LMM peak positions from elemental copper, CuO, and Cu_2O are 920, 919, and 918 eV, respectively. These values are the Auger electron kinetic energies at the minimum of the negative of the differentiated Auger spectra and were carefully determined by comparing with surface carbon peak as an internal standard. It may contain an error of ±0.5 eV. The reference peak positions for the copper oxides were determined from thermally grown copper oxides on elemental copper [7]. Al LVV and KLL Auger spectra from AlN were respectively 59 and 1388 eV, while those from metallic aluminum were 68 and 1396 eV, respectively.

In the analysis of insulators with rough surfaces with AES, the sample charging as well as the decomposition due to electron beam irradiation matters. In-depth studies on these topics were conducted previously and described in [8, 9]. Hence, AES analysis results shown in this paper contain none of these artifacts.

3. Experimental results

3.1. Surfaces of laser-irradiated AlN

The surface of as-received AlN (Fig. 1a) exhibits large cavities and sharp edged grains, as can be seen in Fig. 1a. The images in Figs 1a, d, and e are obtained at 60° tilting angle. Therefore, the surface topography can be compared more clearly in these images than in the planar observations shown in Figs 1b and c. The appearance of melt flowing can be observed on the surface laser irradiated at 0.7 J/cm^2 (Fig. 1c), but no evidence of melting occurrence is seen in samples irradiated at 0.5 J/cm^2 (Fig. 1b). Therefore, the threshold energy density for melting is approx. 0.7 J/cm^2. Significant surface smoothening takes place upon laser irradiation with 1 J/cm^2 (Fig. 1d), and the substrates become smoother when irradiated with higher energy densities (3 J/cm^2, Fig. 1e).

Figs 2a and b are, respectively, Auger mappings of metallic aluminum and nitrogen of an AlN substrate irradiated at 1 J/cm^2 in Ar-4%H_2 atmosphere. White

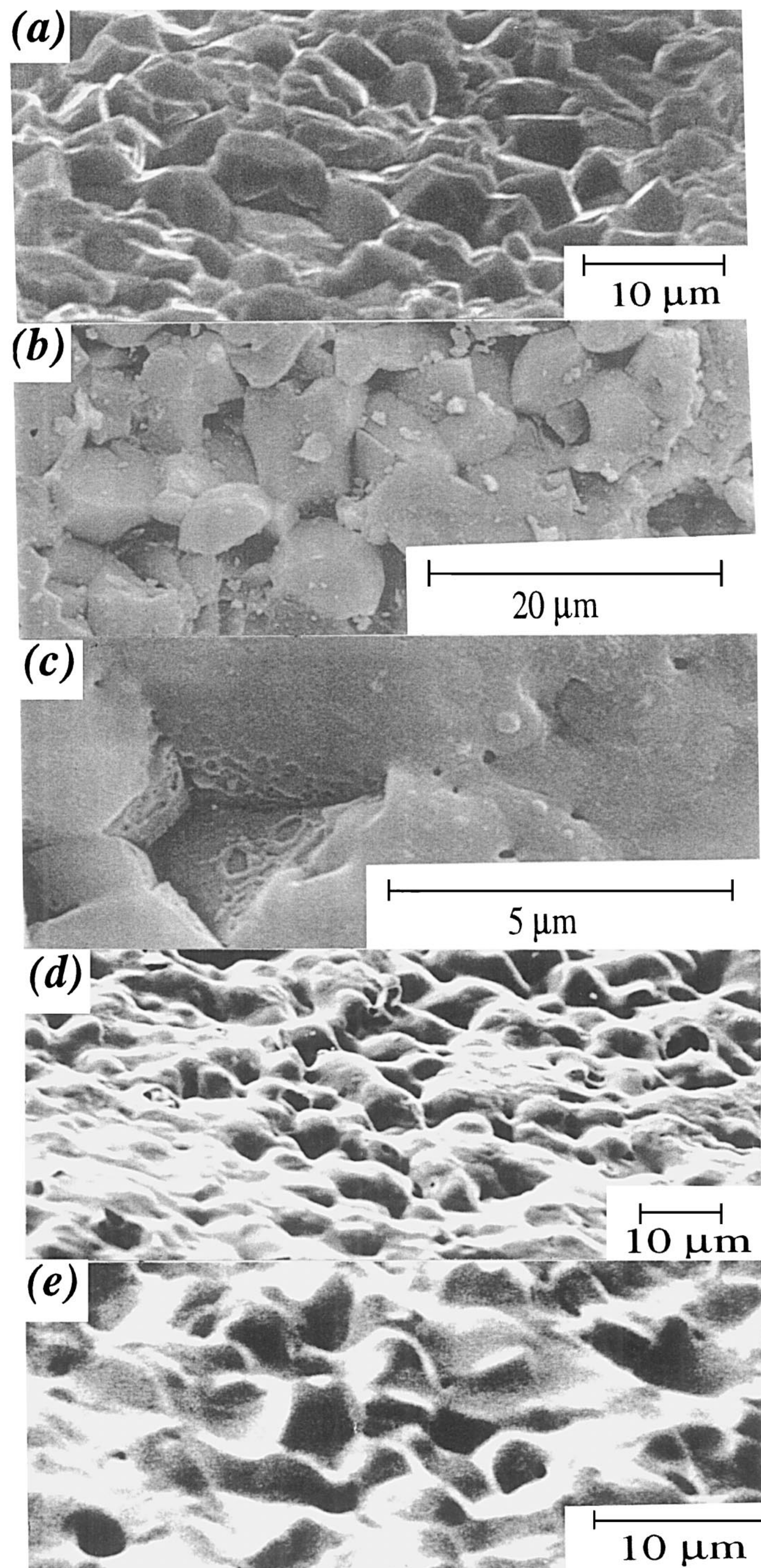


Figure 1 The surface of as-received AlN includes large cavities and exhibits sharp edges for each grain (a). However, significant surface smoothening takes place upon laser irradiation, and the substrates become smoother when they are irradiated with higher energy densities (c, d, and e). The appearance of melt flowing can be observed on the surface laser irradiated at 0.7 J/cm^2 (c), but no evidence of melting occurrence is seen in samples irradiated at 0.5 J/cm^2 (b). The images, (a), (d), and (e) are obtained at 60° tilting angle to observe the surface roughness more distinctively.

spots in each mapping reveal the distribution of the element under investigation. The holes that appear consistently in each figure are due to the surface roughness; that is, Auger electrons can not be emitted because they are blocked. In Fig. 2a, the size of the metallic aluminum clusters is $\leq\sim 3\ \mu$m. The white areas in Fig. 2b roughly correspond to the dark areas in Fig. 2a and vice versa, except for the regions where there are holes. This means that metallic aluminum and AlN coexist in the laser irradiated AlN surface. However, as will

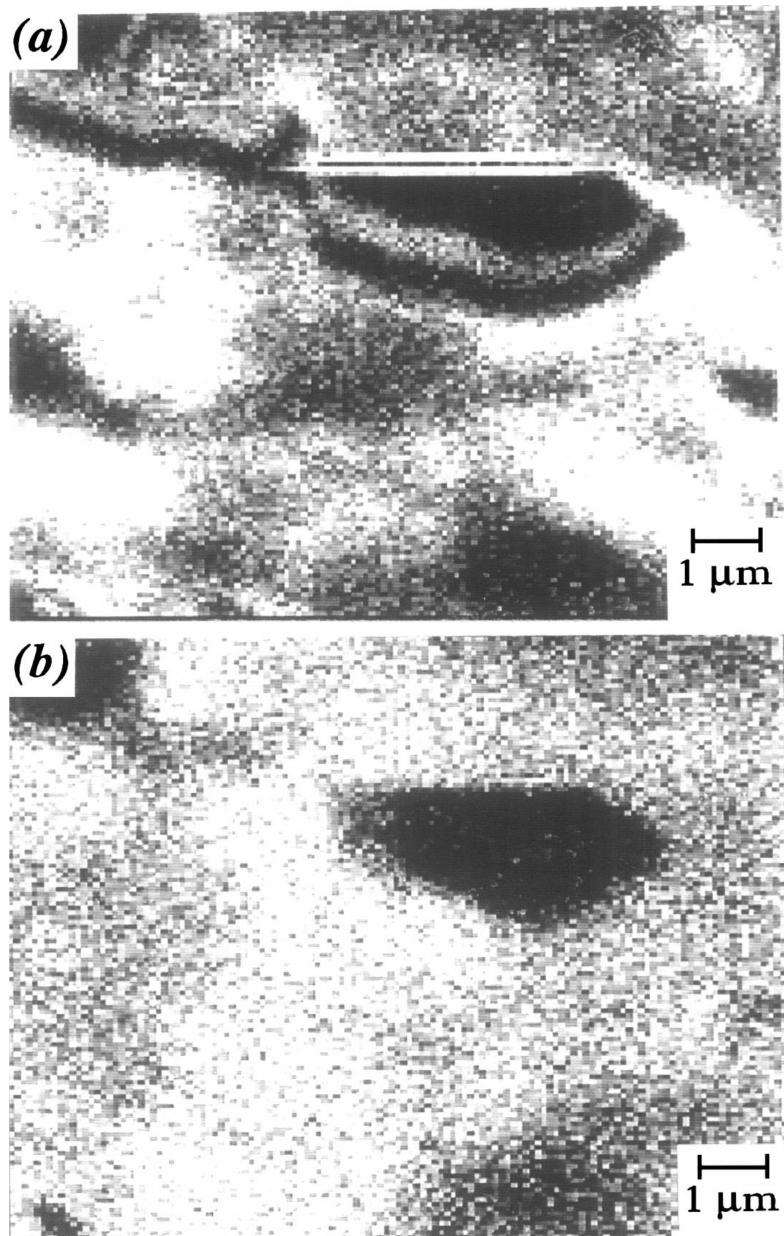


Figure 2 Auger mappings of metallic aluminum (a) and nitrogen (b). The holes that appear consistently in each figure are due to the surface roughness; Auger electrons can not be emitted. The size of the metallic aluminum clusters is $\leq\sim 3\ \mu m$ (a). The white areas in (b) roughly correspond to the dark areas in (a) and vice versa.

be shown in Fig. 4, a small amount of undecomposed AlN particles is always found in a metallic aluminum patch.

Fig. 3 shows Al LVV Auger peak spectra of as-received AlN as a function of depth from the surface. The Al LVV spectrum from the surface (Fig. 3i) is mostly from Al_2O_3. As subsurface layers of substrate are being exposed by sputter etching, the Al LVV peak is shifting toward the Al LVV from AlN (peaks ii in Fig. 3), as it is expected.

The surface of AlN substrate laser-irradiated at 2 J/cm^2 in a reducing atmosphere (Ar-4%H_2) consists of mostly Al_2O_3 (peak i in Fig. 4), however a slight shift of this peak by $\sim$1 eV to high kinetic energy direction implies that AlN also exists on the surface of the irradiated substrate. In consistence with this, small amount of N were also detected along with O. On the other hand the subsurface contains a mixture of metallic Al and AlN (peaks ii and iii in Fig. 4). The oxide layers on the substrate laser-irradiated in Ar-4%H_2 atmosphere were only one to two monolayers thick, whereas those on as-received AlN and the substrates irradiated in air were a few tens of monolayers as approximately measured by AES depth profiling.

3.2. Pull adhesion testing results

Adhesion strengths are plotted as a function of laser energy density in Fig. 5. The adhesion strength of Cu/as-received AlN couple is relatively weak without annealing ($\sim$25 MPa). Laser irradiation with low energy densities ($\leq$1 J/cm^2) both in air and in Ar-4%H_2 increases the adhesion strength to $\sim$40 MPa. As the laser energy density increases, the adhesion strength decreases and becomes even lower than the strength of the couple with as-received substrate. The couple irradiated in air shows higher adhesion strength than the couple irradiated in Ar-4%H_2. The difference of the

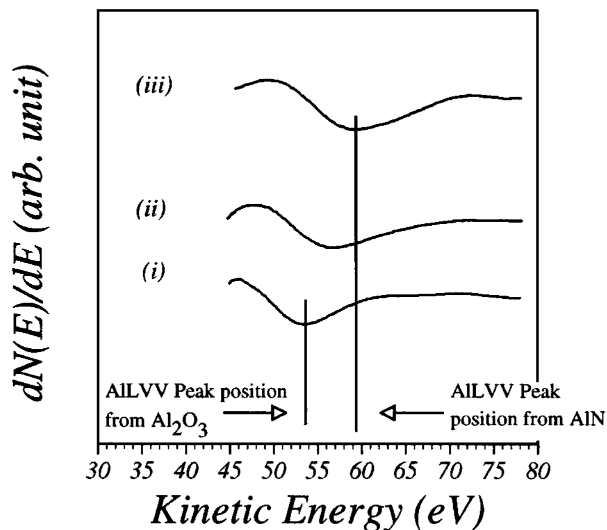


Figure 3 Al LVV peak spectrum from the surface (i) and the subsurface (ii and iii) of as-received AlN substrate. The spectra from the surface is that of stoichiometric alumina (i). As progressing the sputter etching, the surface chemistry changes from alumina to aluminum nitride.

adhesion strength between the couples irradiated in air and Ar-4% H_2 becomes larger as increasing the laser energy density. When the couples are annealed at 300 °C, the couples laser-irradiated with low energy density ($\leq$1 J/cm^2) show the maximum strength. However, the adhesion of the couples laser-irradiated with $\geq$1 J/cm^2 in both oxygen and Ar-4% H_2 atmosphere is increased to only about 1.5 times after 300 °C annealing, which is below the maximum strength. The couples irradiated in air show slightly higher adhesion strength than the couples irradiated in Ar-4% H_2. With 500 °C annealing, all the specimens laser-irradiated with $\geq$1 J/cm^2 energy density in both oxygen and Ar-4% H_2 atmospheres show the maximum adhesion strength.

3.3. Interface analysis of Cu/AlN couples

The interfaces of couples with substrates irradiated at laser energy densities of 0.3 and 3 J/cm^2 in air and of 1 and 1.5 J/cm^2 in Ar-4% H_2 were analyzed with AES. The first two couples were annealed at 300 °C

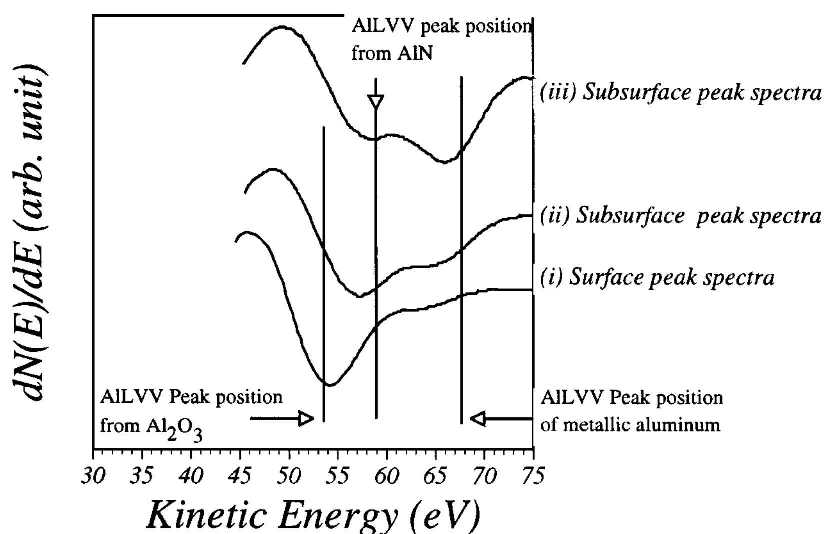


Figure 4 Al LVV peak spectrum from the surface (i) and the subsurface (ii and iii) of AlN laser-irradiated in air with 4 J/cm^2 energy density. Most of the surface is covered with Al_2O_3 layers, while aluminum in the subsurface exists in both AlN and metallic aluminum.

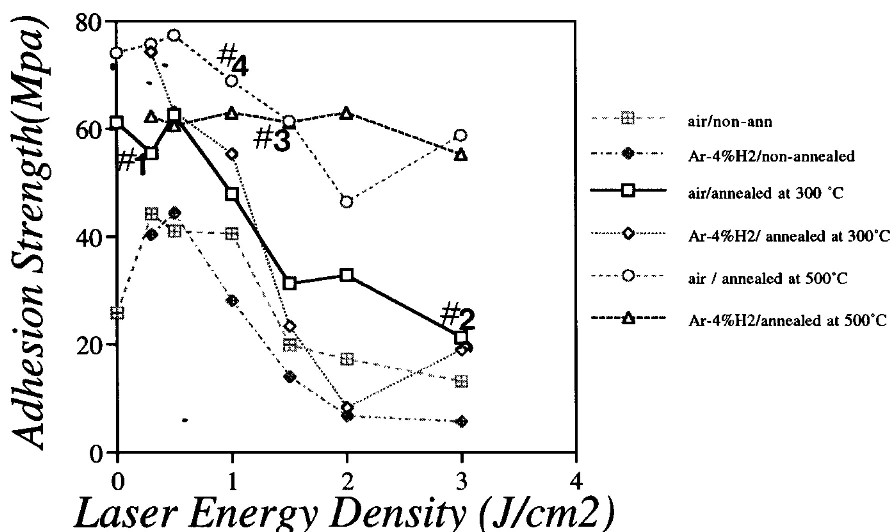
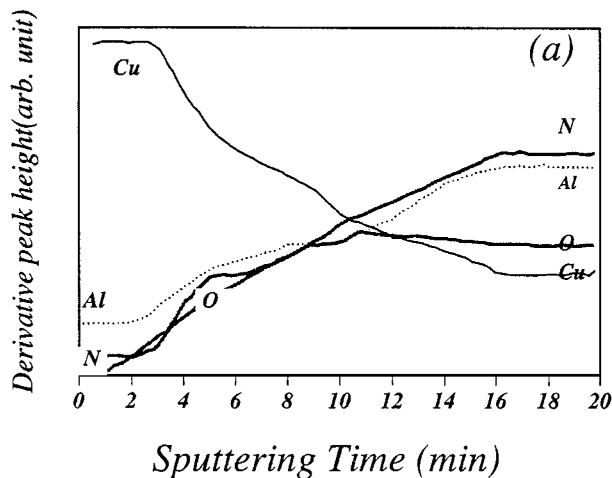


Figure 5 Adhesion strength of the copper films deposited onto AlN substrates laser-irradiated in air and Ar-4% H_2 atmospheres as a function of laser energy density. Annealing was done at 300 °C and at 500 °C for 1 h in the vacuum pressure of 10^{-5} Torr. (The zero laser energy density stands for as-received condition.)



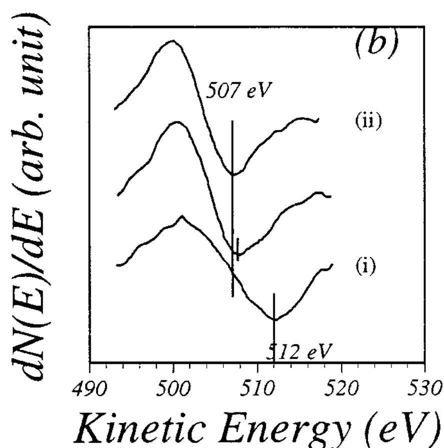


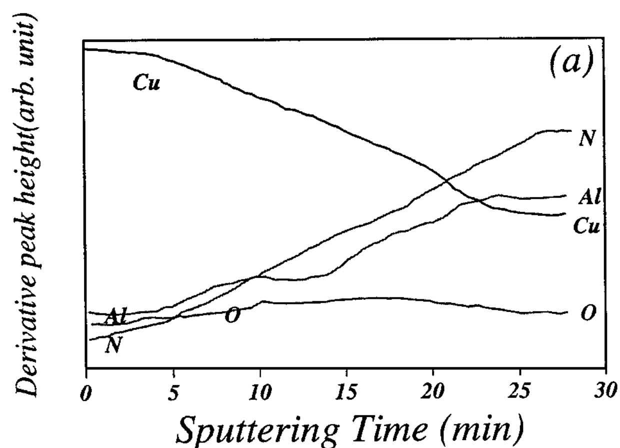
Figure 6 Elemental depth profile at the interface of a 300 °C annealed copper/AlN couple with the substrate laser-irradiated in air at 0.3 J/cm^2. As the interface is approached, the concentration of oxygen increases along with those of Al and N (a). As the interface is crossed, O KLL is detected first at ~512 eV which is from Cu_2O and then shifts to 507 eV which is closer to O KLL from Al_2O_3 (b).

and the next two were annealed at 500 °C. As shown in previous sections, the surface of aluminum nitride used here exhibited a mixture of Al_2O_3 and AlN. Therefore, the analysis was focused on the elemental profiles as well as chemical states at the interface.

Fig. 6a is a depth profile at the interface of a 300 °C annealed copper/AlN couple, the substrate was laser-irradiated in air at 0.3 J/cm^2 prior to deposition. This couple showed a strong adhesion as marked in Fig. 5 with #1. As the interface is approached, the concentration of oxygen increases along with those of Al and N. This implies that the surface oxide layers were not completely eliminated by laser irradiation. Similar to the strongly adherent copper/alumina couples [7], copper oxides were detected at the interface. As shown in Fig. 6b, as the interface is crossed O KLL is detected first at ~512 eV which is from Cu_2O and then shifts to 507 eV which is closer to O KLL from Al_2O_3.

Fig. 7 presents elemental depth profiles across the interface of a Cu/AlN couple with the substrate laser-irradiated in air at 3 J/cm^2, annealed at 300 °C. This couple exhibited very weak adhesion as shown in Fig. 5 with #2. In contrast with the couple irradiated in air at 0.3 J/cm^2, the amount of oxygen at the interface is relatively very small (Fig. 7a). O KLL was firstly detected at 510 eV and shifted to ~508.5 eV as approaching the interface (Fig. 7b). Encompassing the interface, Al was mostly from metallic aluminum as evidenced by the Al KLL peak at ~1393 eV. This implies that this substrate region, originally AlN, had mostly been decomposed by the laser. Nitrogen was also detected along with metallic aluminum, indicating that undecomposed AlN particles remained, buried in the metallic aluminum patch. Reoxidized surface Al_2O_3 was not detected in this depth profile. This may be due to the high sputtering rate relative to the oxide layer thickness.

Depth profiling of Cu/AlN with substrate laser-irradiated in Ar-4%H_2 at 1.5 J/cm^2, annealed at 500 °C, is shown in Fig. 8a. This couple showed very weak adhesion upon annealing at 300 °C but became very strong after a 500 °C anneal as shown in Fig. 5 marked with #3. A considerable amount of oxygen exists in the vicinity of the interface, the concentration increasing very steeply as the interface is approached. The oxygen concentration decreases as the copper concentration decreases, indicating that most of the oxygen is from the copper oxides. The O KLL kinetic energy is 512 eV (Cu_2O) in the film, while, as the interface is



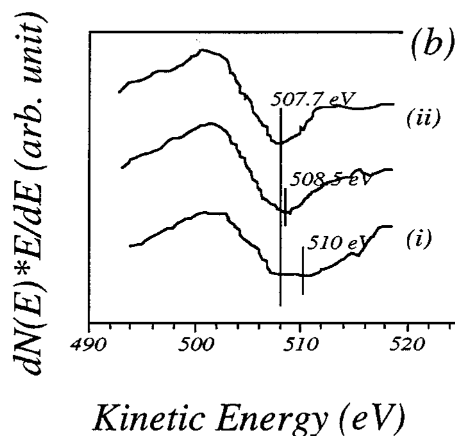


Figure 7 Elemental depth profiles across the interface of a Cu/AlN couple annealed at 300 °C with the substrate laser-irradiated in air at 3 J/cm^2. In contrast with the couple irradiated in air at 0.3 J/cm^2, the amount of oxygen at the interface is relatively very small (a). Most of the oxygen is from CuO as evidenced by O KLL intensity peak position at ~508.5 eV (b).

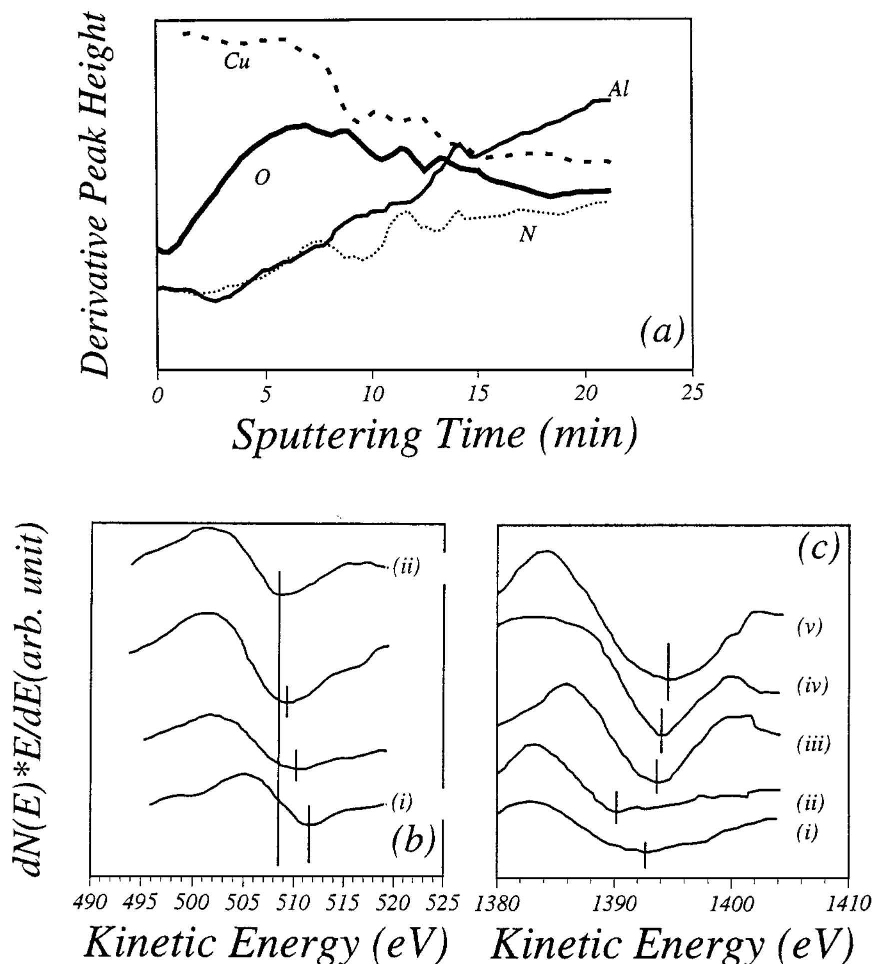


Figure 8 Depth profiling of Cu/AlN annealed at 500 °C with substrate laser-irradiated in Ar-4% H_2 at 1.5 J/cm^2 (a). A considerable amount of oxygen exists in the vicinity of the interface, the concentration increasing very steeply as the interface is approached. The oxygen concentration decreases as the copper concentration decreases, indicating that most of the oxygen is from the copper oxides. The O KLL kinetic energy is 512 eV (Cu_2O) in the film, while, as the interface is approached, the oxygen peak was detected at 509 eV (b).

approached, the oxygen peak was detected at 509 eV (Fig. 8b). Oxygen was detected all through the film. However, the concentration of the copper oxide is very small, because Cu LMM peaks acquired during depth profiling are mostly from elemental copper in the film. In this respect, this couple is different from other couples such as Cu/AlN couples annealed at 300 °C and all the Cu/Al_2O_3 couples [7] that showed the formation of copper oxide at the very interfacial region. Al KLL peaks at the interface are located at 1391 eV, implying that the aluminum is not from stoichiometric alumina (Fig. 8c, i). After removing the interfacial layers, most of the Al KLL signals are from metallic aluminum since the kinetic energies are around 1395 eV (Fig. 8c, ii). However, nitrogen which is from AlN was also detected, implying that AlN was not fully decomposed to metallic alluminum upon laser irradiation.

Cu film/AlN couple with the substrate laser-irradiated in air at 1 J/cm^2, after a 500 °C anneal exhibited very strong adhesion (marked with #4) while annealing at 300 °C resulted in very weak adhesion (Fig. 5). Depth profiling conducted at several areas of a strongly bonded sample is described next. Two different trends were found (Figs 9a and b). In Fig. 9a the aluminum concentration increases along with the oxygen concentration as the interface is approached, while in the other analysis area the aluminum content increases with the increase of nitrogen (Fig. 9b). However, the latter was more representative, because only one out of four analyzed areas showed the former profile. These profiles reveal that copper film is in contact with AlN as well as Al_2O_3 at the interface. In both cases, however, the oxygen concentrations abruptly change as the interface is approached (Figs 9a and b), implying that the oxygen source is in the interface. O KLL and Al KLL peaks were analyzed for the two areas. Figs 10 and 11 are, respectively, from the interfaces with enriched Al_2O_3 and AlN. In both cases, various oxidation states of copper were detected across the interface. O KLL kinetic energies are from ~512 to 506 eV (Figs 10a and 11a). In both cases Al_2O_3 was detected at the interface although the concentrations are different. Fig. 10b shows Al KLL spectra across the interface with enriched Al_2O_3. The peak position at the interface is ~1391 eV and then changes to ~1388 which corresponds to Al KLL from AlN after passing the interface by further sputtering.

No shift was ever detected for the N KLL peaks, implying that AlN did not react with copper.

4. Discussion and conclusions

Since Al_2O_3 is thermodynamically more stable than AlN [9], mechanical and thermal processing of AlN in air may have produced the oxidation of AlN in the

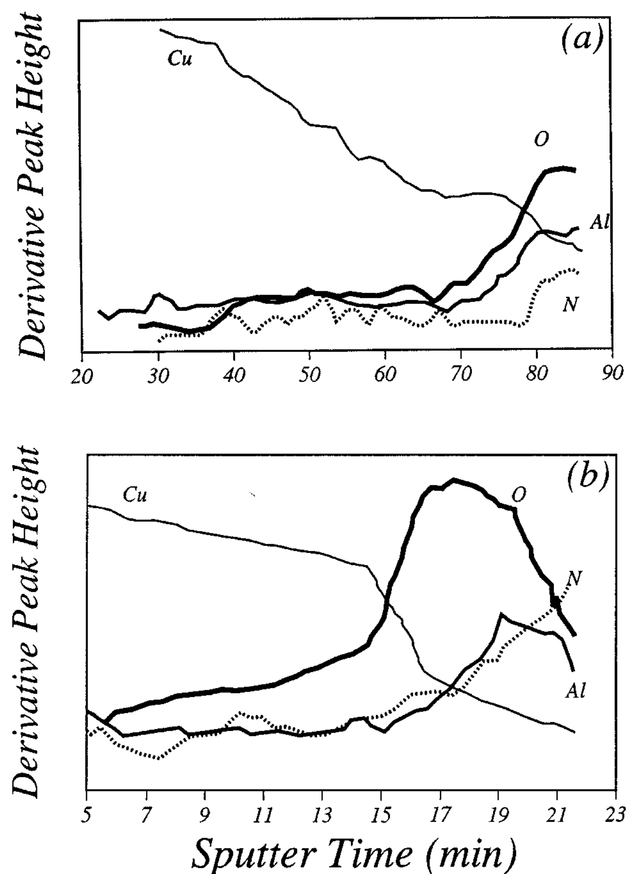


Figure 9 Two different depth profiles of Cu film/AlN couple with the substrate laser-irradiated in air at 1 J/cm^2, after a 500 °C anneal. In one analysis area, the aluminum concentration increases along with the oxygen concentration as the interface is approached (a), while in the other analysis area the aluminum content increases with the increase of nitrogen (b). However, the latter was more representative, because only one out of four analyzed areas showed the former profile. These profiles reveal that copper film is in contact with AlN as well as Al_2O_3 at the interface. In both cases, however, the oxygen concentration changes abruptly as the interface is approached.

surface. As shown in Fig. 3, the surface of as-received AlN was mostly covered with Al_2O_3. Along with the decrease in the surface roughness of as-received AlN substrate by laser-irradiation, the surface chemical composition is also changed. After laser-irradiation in Ar-4%H_2 at 2 J/cm^2, the Al LVV peak position shifts to a higher kinetic energy (Fig. 4). However, the surface Al LVV peak is not from AlN alone, instead the irradiated surface is found to consist of AlN and Al_2O_3. Subsequent sputtering changes the chemical composition from a mixture of AlN and Al_2O_3 to a composite of Al and AlN (peak iii in Fig. 4). Since the analysis area for these Auger spectra was much smaller than the size of metallic aluminum patch (approx. 3 μm) determined by Auger mapping (Fig. 2a), Fig. 4 implies that undecomposed AlN particles are embedded in the metallic aluminum patch. The chemistry changes from the surface to the subsurface region can be explained by the formation of metallic aluminum in both regions as AlN is decomposed by laser irradiation. However, the surface is subsequently reoxidized upon exposure to the atmosphere.

Electrical resistivity measurements of the laser irradiated AlN showed that the resistivity decreased as the laser energy density was increased [10]. This indicates that the amount of metallic aluminum in AlN increases with increasing the laser energy density, which contrasts with the result obtained in alumina laser irradiated in Ar-4%H_2 that is electrically insulating [11]. These results tell us that AlN is easily decomposed by laser irradiation, forming an interconnected network of aluminum islands.

In the 300 °C annealed Cu/AlN couple with the substrate laser irradiated in air at 0.3 J/cm^2 energy density, oxygen from the copper oxide as well as from aluminum oxide is detected at the interface (Fig. 5). The existence of Al_2O_3 indicates that the laser irradiation did not ablate the aluminum oxide layer that existed on the as-received AlN substrate because the threshold energy density for the melting of the alumina and of aluminum nitride (approx. 0.7 J/cm^2) is much higher than the energy density employed, it would appear unlikely that any chemistry change occurred on the ceramic surface laser-irradiated at 0.3 J/cm^2. However, the detection of O KLL peaks at other kinetic energies in the interfacial region (Fig. 6b) implies that a chemical reaction took place in this couple during the 300 °C anneal. Surface cleaning and preferential ablation are possible changes

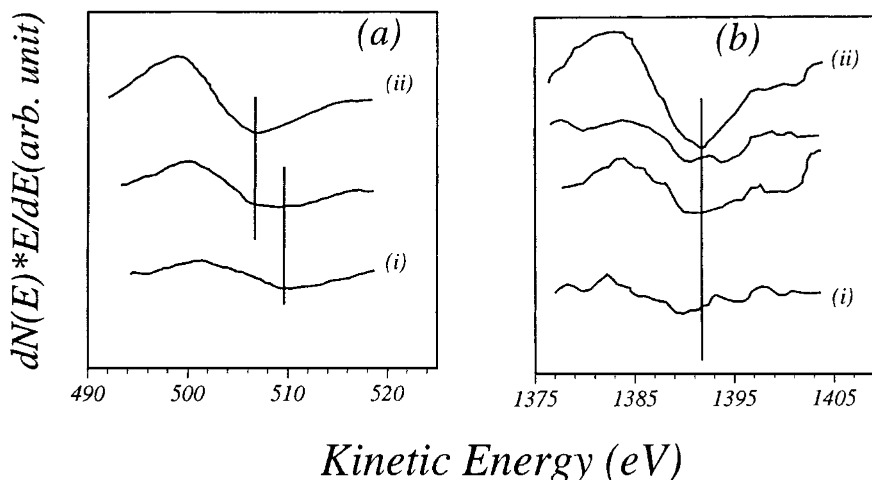


Figure 10 O KLL (a) and Al KLL (b) at the interface with enriched Al_2O_3 of Cu film/AlN couple with substrate laser-irradiated in air at 1 J/cm^2, after a 500 °C annealing.

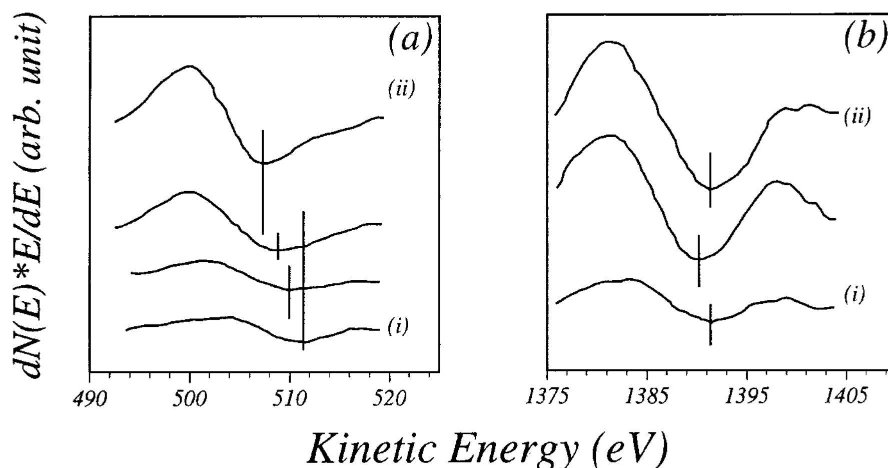


Figure 11 O KLL (a) and Al KLL (b) at the interface with enriched AlN of Cu film/AlN couple with substrate laser-irradiated in air at 1 J/cm^2, after a 500 °C annealing.

in the substrate irradiated at 0.3 J/cm^2. It is suggested that these changes in the alumina layer on the surface of AlN may have played a role in compound formation at the interface. This rationale also applies to understanding why a relatively strong bonding also was obtained when the substrate was irradiated in Ar-4%H_2 atmosphere (Fig. 5).

High adhesion strength can also be obtained for the couple with an as-received AlN substrate after 500 °C annealing. In this case, there might have been excess oxygen in Al_2O_3 layers as well as less surface contaminant by chance. The couples with AlN substrate irradiated at lower laser energy density may not be so practical, because low energy laser irradiation does not smoothen the rough AlN surface. For this reason, the substrates irradiated in higher laser energy density should be considered in this study.

Cu/AlN couple with the substrate irradiated in air at 3 J/cm^2 shows weak bonding at 300 °C annealing but very strong bonding at 500 °C annealing. Although the energy densities are different, the couple irradiated in Ar-4%H_2 at 1.5 J/cm^2 also shows similar trend (Fig. 5). By comparing the depth profiles across the interface of these two couples, a large difference is observed in the gradient of oxygen concentrations. In the couple annealed at 300 °C, the variation of the oxygen concentration at the interface is almost negligible as compared to the changes of Al and N concentrations (Fig. 7a). This means that the film mostly contacts the AlN substrate. On the other hand, in the couple annealed at 500 °C the concentration gradient of oxygen increases steeply as the interface is approached (Fig. 8a). The oxygen seems to be mostly from copper oxides because the oxygen concentration decreases with decrease of the copper concentration. The thickness of the oxide layers is about 200–300 Å. It may be questioned how the oxygen was introduced at the interface when the annealing was conducted at 500 °C. The followings may be considered as possible oxygen sources: (i) oxygen dissolved in the film may have diffused to the surfaces of the film, followed by the oxidation, (ii) the oxygen may have become trapped on the substrate surface before deposition due to the rough surface characteristic of the AlN substrate (Fig. 1), and (iii) oxygen may have diffused from atmosphere into film with formation of oxide at the interface. The captured oxygen may have diffused out during annealing and the amount of the diffused oxygen is proportional to the annealing temperature. If case (i) is true, oxygen concentrations both on the surface of the film and at the interface should be the same. However, in the couple annealed at 500 °C the concentration at the interface is much higher than that on the surface of the film. Therefore, the oxygen may be argued to have come from the interface as explained in case (ii) or to have diffused from the atmosphere thru the film (iii). As the interface with substrate irradiated in Ar-4%H_2 at 1.5 J/cm^2 annealed at 500 °C is traversed by the sputtering, the O KLL peaks change from 512 to 507.5 eV and the Al KLL peaks from ~1392 to 1395 eV. As previously discussed, O KLL at 507.5 eV and Al KLL at 1392 eV are probably from a Cu-Al-O compound formed at the interface of this couple. In this respect, the strong bonding mechanism of the copper deposited on AlN substrate is similar to the copper on alumina substrate [7]. As indicated by the 1395 eV Al KLL, metallic aluminum is formed in both of the substrates by the laser induced decomposition of AlN. That metallic aluminum may have been reoxidized before the film deposition, but the thin reoxidized layer may become unstable during annealing at higher temperature. Thus, Cu-O-Al interfacial compound may have been produced by the increased concentration of oxygen at the interface during annealing at 500 °C, leading to the strong bonding. In the couple with the substrate irradiated in air at 3 J/cm^2 and annealed at 300 °C, O KLL and Al KLL showed similar behavior to the case of the irradiation in Ar-4%H_2 at 1.5 J/cm^2, but the low concentration of the oxygen may have produced poor linking between the copper film and AlN substrate, resulting in the weak bonding. 3 J/cm^2 laser energy density should produce metallic aluminum by thermal decomposition and thick re-oxidized layers may be expected because the irradiation was conducted in oxidizing atmosphere. However, the oxidized layer in this sample was so thin that it could not be detected in the depth profiling. This may be due to the balancing effects among the ablation, decomposition, and reoxidation. That is, the surface oxide is mostly ablated by the laser irradiation and the

subsurface of the as-received substrate are decomposed and reoxidized forming new surface after laser irradiation. In turn, high concentration of the oxygen was detected at the interface of this couple after annealing at 500 °C.

When the substrate was irradiated in air at 1 J/cm^2, Cu/AlN couple showed strong bonding when annealed at 500 °C (Fig. 5). At the interface the copper was in touch with Al_2O_3 and AlN enriched areas. In both areas, copper oxides were detected (Figs 9a and b), while the concentrations are different. In both cases, after removing the film O KLL peak positions are ∼507 eV closer to O KLL from Al_2O_3. Therefore, interfacial reactions take place in both areas. It should be noted that metallic aluminum exists in AlN enriched area, whereas undecomposed AlN also exists in the metallic aluminum patch (Fig. 4). Therefore, copper contacts metallic aluminum (reoxidized) even in AlN enriched area. The amount of the reaction products depends on the contacting area in this couple.

As shown in Fig. 5, in this experiment the good adhesion between copper film/AlN is also obtained without the surface modification of AlN prior to film deposition. As discussed above, this may be attributed to the aluminum oxides formed on AlN substrate. In this respect it can be questioned why the laser should be used for the adhesion enhancement of copper/AlN couple. The advantages could be as follows: (i) the formation of aluminum oxides on AlN can not be a standard condition of AlN substrates and rough characteristic of as-received AlN surface is impractical in the circuit applications. (ii) Laser irradiation which is able to ablate the surface oxides and smoothen the surface produces a standard surface condition of AlN substrate.

5. Summary

(1) Surface smoothening and decomposition take place in laser irradiated AlN. The decomposed metallic aluminum reoxidized at the utmost surface upon exposure to air, leaving buried metallic aluminum patches. Therefore, Al_2O_3 and AlN coexist on the laser irradiated AlN surface.

(2) AlN does not react with deposited copper. Therefore, the adhesion is affected by the relative amount of metallic aluminum which is combined with oxygen.

(3)The mechanism leading to strong bonding of the Cu/AlN couple with substrate laser-irradiated is the formation of a Cu-Al-O compound at the interface of the couple.

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