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Mechanical and thermal properties of Cu/Al_2O_3 systems; effects of substrate surface ion bombardment etching

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Abstract

Nominal-contact-area analysis is combined with x-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and measurements of the scratch test critical load (L_c) to study interfacial properties in thin-film adhesion and heat transfer. This work complements an earlier investigation of the enhancement of adhesion strength and thermal contact resistance (R_c) produced by ion bombardment of the substrate surface before deposition. In this study, we have investigated Cu films deposited by radio-frequency sputtering onto alumina substrates. Extended ion bombardment etching leads to three related effects: the nominal contact area is increased significantly; R_c and L_c are decreased and increased respectively; XPS shows a greater penetration of the film material into the substrate and the formation of a complex interface. These results are interpreted as confirmation that ion bombardment leads to the formation of microcavities in the interface layer and, consequently, to increased adhesion strength and heat transfer by allowing mechanical interlocking between the film and the substrate.

1. Introduction

The durability of coatings is of primary importance in many diverse technological areas. One of the principal factors affecting durability is the coating–substrate interfacial bond strength. Attention has recently been focused on thermophysical properties of solids on submicronic scales. Good adhesion of thin films to their substrates is essential in most applications but knowledge of this topic is extremely limited. In spite of difficulties in its modelling, the scratch test has become the most widely used method for characterizing adhesion failure of well-adhering thin films [1–3].

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Plasma treatment of the alumina substrate is currently used to enhance the adhesion strength and the heat transfer of the metal layer deposited onto the alumina substrates [4]. Depending on the nature of the alumina substrates and also on the nature of the gas used, several explanations can be yielded for the modification of the mechanical and thermal properties of the metal–alumina interface. The effects of substrate treatment before deposition were investigated by means of x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and nominal-contact-area analysis. The results are discussed in relation to the adhesion and thermal properties of the metal layer on the alumina substrates.

2. Experimental procedure

2.1. Surface treatment and coating deposition

The substrates studied in this work were of hardened Al_2O_3 ceramic (Vickers hardness 996 Hv). They were subjected to some initial preparation which consisted of an ethanol washing. After this common initial preparation, the samples were quickly introduced into the deposition chamber. Then, the chamber was pumped down to 10^{-4} Pa. Some of the samples were directly coated with Cu; others received an *in situ* ion bombardment before deposition. In that case, the etching treatment was performed at a frequency of 13.56 MHz in an Ar atmosphere. The pressure of the etching gas was 5 Pa and the applied r.f. power was about 200 W (power density 11.3×10^3 W m^{-2}). For all samples, the Cu films were deposited by r.f. planar sputtering of a Cu target, with a power of 250 W (power density 8×10^3 W m^{-2}) under an Ar pressure of 5×10^{-1} Pa.

To investigate the relationship between the coating thickness and the deposition time, the deposition rate was measured by an optical profilometer. In order to allow a direct comparison between the critical load and the thermal contact resistance values measured for the samples, a given deposition time (1 h) was used for all specimens. The corresponding Cu film thickness was about 0.23 μm.

2.2. Measurement of the mean critical load

All of the mean critical load measurements were performed with the scratching apparatus described in reference [4]. In this apparatus, a diamond stylus of tip radius 17 μm was mounted on a balanced beam, while the sample was fixed on an x–y table. Each scratch was obtained for a given value of the load, by moving the table in the x-direction with the help of a d.c. motor. A standard scratch speed of 3.7 mm min^{-1} was used, the scratches being about 5 mm long. The y-displacements and load were realized by a manually operated micrometer screw, allowing us to make a series of parallel scratches on the same sample. The shapes of the scratch channels were studied by optical and scanning electron microscopies. The adhesion failure probability was estimated for each load (Q) by optical inspection of the channels. In fact, for a given load, a series of at least three scratches were made and each channel was inspected at five or more different positions. Therefore the adhesion failure probability (P_f) used to plot the Weibull diagrams was the mean value of at least 15 different evaluations.

Similar plots, exhibiting standard deviations for each load, have already been reported for the case of aluminium coatings on XC 70 steel substrates [3]. The Weibull expression for the probability of failure is a function of two parameters which can be deduced from the Weibull diagrams and from which the mean critical load was determined [3].

2.3. Measurement of the thermal contact resistance

The method is illustrated in figure 1 and described in detail elsewhere [4, 5]. Briefly, the metallic thin film (figure 1), initially at a temperature T_i, is irradiated by a laser pulse of 20 ns duration with a high energy less than 0.5 J cm^{-2}. After a peak of temperature, T_{max}, the transient temperature decrease of the film (cooling phase) is analysed. The temperature measurement is deduced from the electrical resistivity variation of the metallic film. R_c is identified simultaneously with the effusivity by fitting theoretical and experimental (figure 2) normalized thermograms over a temporal sequence ranging from about 10^{-7} to 10^{-6} s.

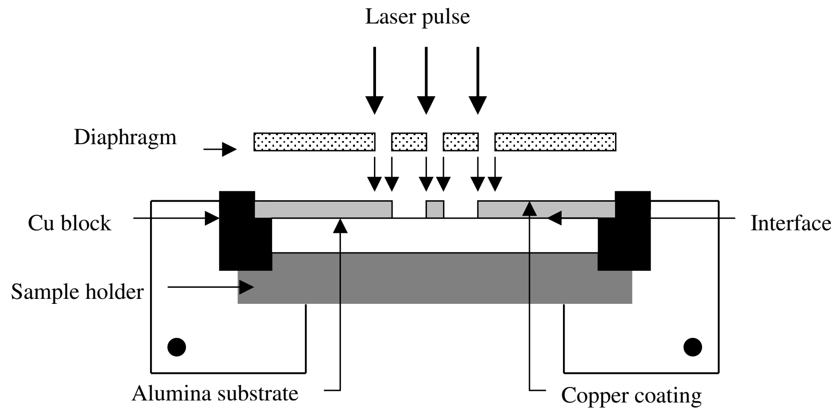


Figure 1. The test sample and its holder.

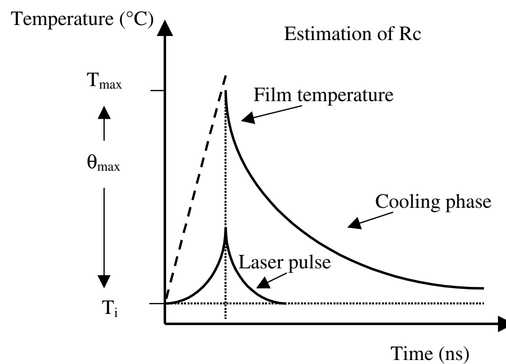


Figure 2. The principle of the thermal contact resistance measurement.

2.4. X-ray photoelectron spectroscopy

XPS experiments were performed on ceramic substrates covered with 100 nm thick copper layers. The spectra were recorded on an ESCA Leybold LH 12, using Mg Kα excitation (1253.6 eV). The base pressure of the chamber was maintained at 10^{-9} mbar during the experiments. The resolution of the analysis was 0.5 eV with a pass energy of 50 eV. No charging effect was observed in the spectra and the binding energy (BE) was checked for Cu $2p_{3/2}$ (932.4 eV) from the copper layer. The substrate is characterized principally by the

aluminium and oxygen lines for Al 2p (75 eV) and O 1s (532 eV), respectively. The Cu/Al_2O_3 interface was examined by successive removals of the Cu layers by 1 kV argon-ion etching. A separate test of the ion bombardment performed on reference ceramic substrates using identical conditions indicated that there is an important change in line shape and peak positions for both aluminium and oxygen. The interfacial layers correspond to the simultaneous appearance of copper, aluminium and oxygen spectra.

The deposition conditions were identical with those used to measure the mean critical load and thermal contact resistance.

3. Results and discussion

3.1. Critical load data

In the first series of experiments we evaluated the mechanical properties of the Cu/Al_2O_3 using the scratch adhesion test. Figure 3 presents the results obtained for the variation of the mean critical load (L_c) measured in units of the force exerted by 1 g of mass (gf) as a function of the ion etching time. It was found that L_c remained as low as 4 gf when the etching time was less than 5 min. After this time, L_c began to increase rather quickly and finally tended to be constant at about 25 gf for an etching time greater than 1 h.

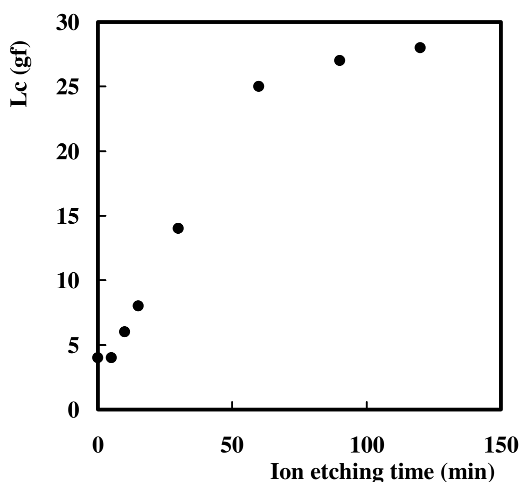
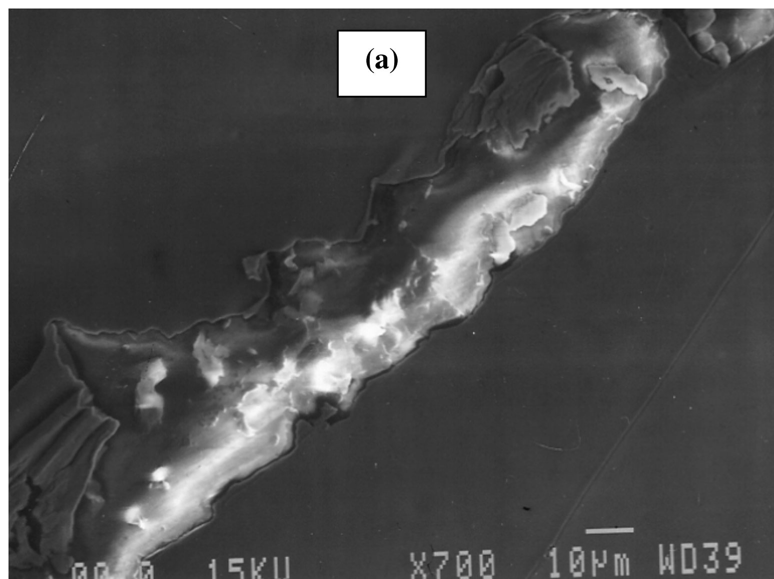


Figure 3. Scratch adhesion test data showing the mean critical load as a function of the ion etching time for Cu films deposited onto alumina substrates.

Figure 4 exhibits scanning electron micrographs of the scratch channels for the Cu/alumina samples. In figure 4(a), obtained without a treatment and for a stylus load of 4 gf, the film was mostly stripped from its substrate. Some scales were broken and ejected far from the scratch channel, leaving the substrate bare. After ion bombardment etching, higher values of the stylus load were needed to separate the film from its substrate. For a load of 35 gf, there was an adhesion failure which was characterized by the formation of small scales along the edges of the scratch channel. In these zones, the film was detached from its substrate and the substrate became visible in the adhesion-loss zones. In contrast, in the central part of the track there was no evidence of adhesion loss between the film and its substrate (figure 4(b)).



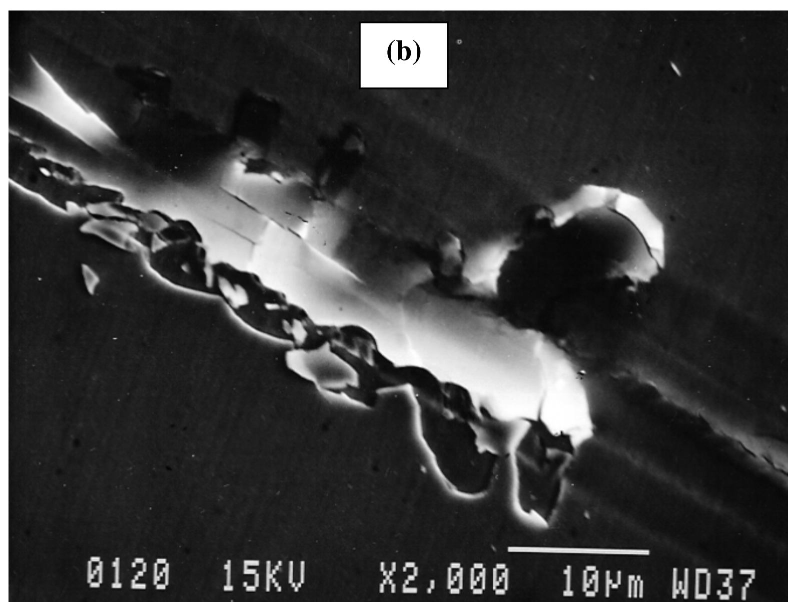


Figure 4. Scanning electron micrographs of scratch tracks obtained by scribing a Cu film on an alumina substrate. Untreated (a) and Ar-treated (b) samples. The stylus loads were of 4 gf in (a) and of 35 gf in (b).

3.2. Thermal contact resistance

In the second series of experiments, we determined R_c by an original method using the electrical resistivity variation of the copper film [5]. Figure 5 shows R_c for the Cu/Al_2O_3 system as a function of the ion etching time. The number of measurements for each sample was two to three. As the ion etching time increases, the heat transfer is enhanced and the measured R_c decreases. R_c ranges from approximately 1.38×10^{-7} to 0.61×10^{-7} m^2 K W^{-1} for an ion etching time of 0–120 min. This is in good agreement with the R_c-measurement results [4]. The low value of R_c was obtained for strong adhesion by ion etching the substrate before deposition.

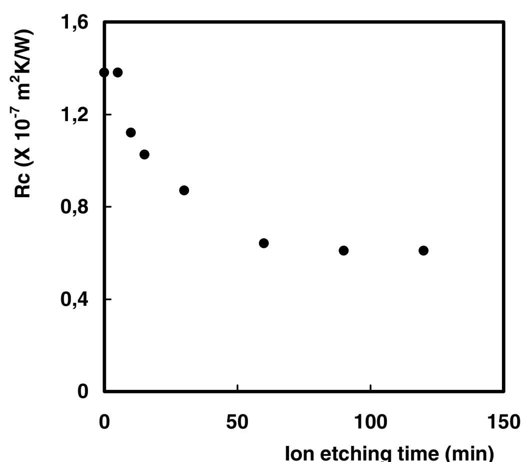


Figure 5. Heat-transfer experimental data showing the thermal contact resistance as a function of the ion etching time for Cu films deposited onto alumina substrates.

However, for ion etching time greater than 5 min, the substrate surface (figure 6) presents an aspect that is much more regular and compact than that of the untreated substrate. A particularly remarkable feature of the surface roughness is its cellular form. This form of the cavities allows a good anchoring of the coating to its substrate, so a high stylus load is needed to produce adhesion loss. The replacement of a columnar discontinuous surface by a large collection of cavities seems to play an important role in the adhesion and heat-transfer enhancement.

XPS was employed to study the effect of ion bombardment etching on the interfacial domain. Indeed, ion etching can remove some or all of the native contamination on the substrate surface prior to deposition. Moreover, the energetic ions can create defects on the surface which are shown, in this and previous studies [6–10], to enhance the adhesion strength.

A series of XPS spectra were taken at different values of the ion milling time in the ESCA spectrometer. They have already been presented elsewhere [4] and will not be reproduced here. The new features observed in both aluminium and oxygen spectra together with the 932.17 eV component of the copper line strongly suggest that a metal–oxygen–alumina complex is formed in the interface on the treated substrate. We consider that the increase in the L_c-values is due to the formation of a complex in the interface allowing a very good adhesion. This phenomenon seems to be responsible for the R_c-enhancement (decrease) in Ar-treated substrates.

For an untreated sample, it is worth noting that the interfacial domain is identified by the simultaneous presence of 532 eV oxygen and 284 eV carbon lines. However, its clear from the present study and also from previous work [3] that after mechanical polishing of the

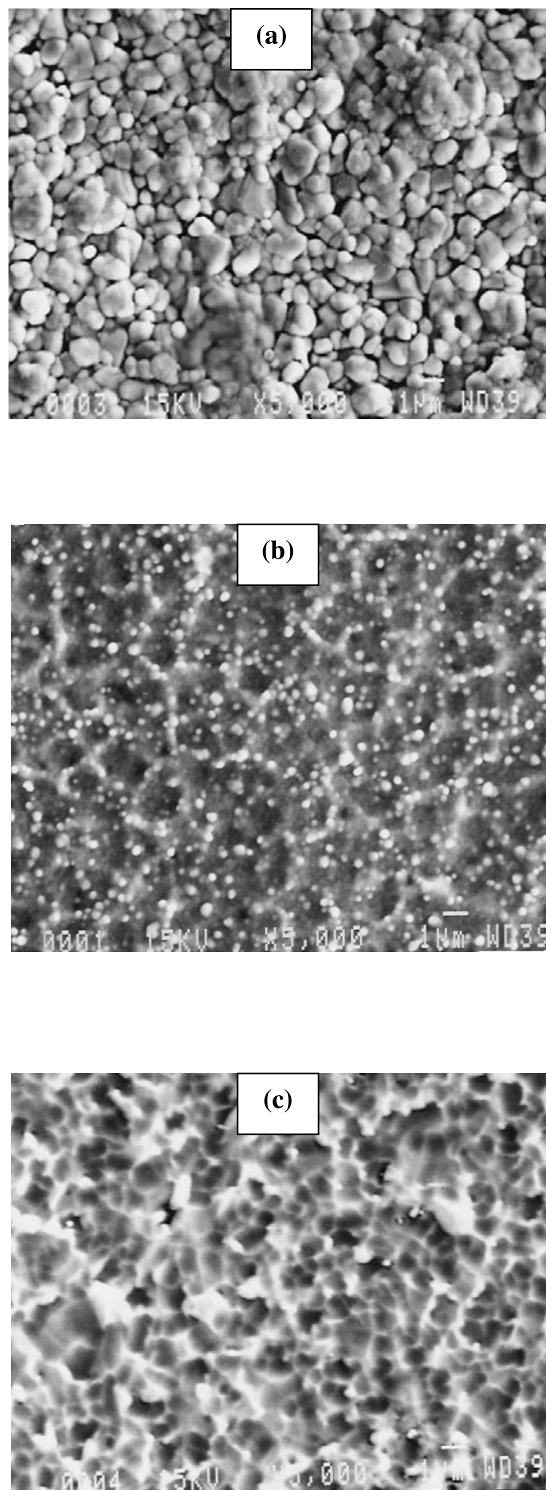


Figure 6. Scanning electron micrographs showing the morphology of three ceramic substrates: untreated (a), Ar treated for 30 min (b) and Ar treated for 60 min (c).

substrate the adhesion strength of a coating is always weak. A second important observation can be made, namely that the interface domain is revealed by the abrupt appearance of the aluminium line.

For the Ar-treated substrate, the interface domain is characterized by the absence of the carbon line. Again, the intensity of the oxygen line seems to be lower than previously. However, there is a wide interfacial region between the copper film and the alumina substrate in the case of the treated sample.

A complementary illustration of this observation is shown in table 1, which represents the evolution of the contact area and the interface thickness as a function of the ion etching time.

Table 1. Experimental data showing the evolution of the contact area and the interface thickness as functions of the ion etching time.

Ion etching time (min)	Contact area (%)	Interfacial layer (nm)
0	0.6	6
5	0.6	6
10	0.65	19
15	0.75	25
30	0.88	32
60	1.2	54
90	1.3	55
120	1.32	55

The present observation that *in situ* ion etching leads to a wider interface domain than *ex situ* mechanical polishing is consistent with previous reports. For instance, AES investigations of SiO_2 layers on titanium, nickel and Inconel substrates [11] revealed wider interface regions following ion etching. SIMS measurements of copper penetration into nickel and Inconel substrates [10] also clearly indicated enhanced penetration for the ion-etched substrates relative to the mechanically polished substrates. In all of these cases, the adhesion strength was largest in the layers with the broadened interfacial domains.

In fact, it can be thought that the ion bombardment etching, in addition to the elimination of the carbon and oxygen contamination, has formed microcavities in the Al_2O_3 substrate into which the Cu coating could enter. This form of the cavities produces an important contact area and allows a good anchoring of the coating to its substrate, with the result that a high stylus load is needed to produce adhesion loss.

In conclusion, the enhancement of L_c (or decrease of R_c) can hardly be attributed to the nature and chemical composition of the interface domain. Moreover, it could be attributed to a subsequent mechanical interlocking between the copper coating and the substrate surface resulting from the formation of microcavities and compact structure at the substrate surface during the ion bombardment etching. This latter explanation is supported by the fact that there is a larger penetration of the coating into the substrate (table 1).

The correlation between the heat transfer and the adhesion is made easier to see in figure 7, which presents the variation of the ratio $1/R_c$ as a function of the L_c-value. As can be seen from this figure, the adhesion influences considerably the quality of the heat transfer in the interfacial domain, the best results being obtained for 28 gf. At this mean critical load a contact area of 1.32% is reached for an etching time of about 2 h.

A very noticeable alteration generated by the increase in the contact area is the growth in the interface region width. This widening itself results at least partially from the increase in the

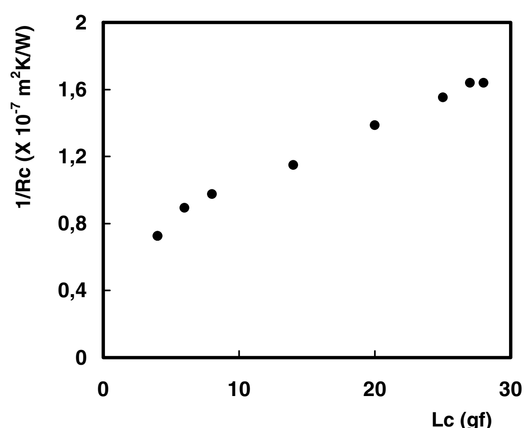


Figure 7. The correlation between the heat transfer and the adhesion: variation of the ratio $1/R_c$ as a function of the L_c-values.

roughness of the substrate surface but is probably due also to an enhanced diffusion of copper into the substrate, which in the range of ion etching time should be significant (above 1 h). It can also result from an increase in the elemental resputtering rate of the growing film with increasing substrate temperature, as emphasized by Green and Pestes [12]. All of these mechanisms lead to an increase in the width of the chemically graded junction between the coating and its substrate and consequently ensure a better anchoring of the coating on its substrate. Details of these interactions between coating and substrate are explained elsewhere [13].

Further investigation is needed to explore the correlation between the deposition temperature, internal stress, thermal contact resistance and scratch adhesion.

4. Conclusions

We have studied the thermophysical and mechanical properties of Cu/Al_2O_3 systems, including the influence of plasma treatment. The mean critical load (L_c) and thermal contact resistance (R_c) for these systems were measured by scratch adhesion testing and an original method, respectively. The effects of an ion bombardment etching on the values of L_c and R_c were studied. These measurements were complemented by observations by SEM, XPS and by contact-area analysis. From a comparison between the L_c-, R_c-, physical–chemical and contact-area observations, we were led to the following conclusions:

(1) There is an important correlation between the heat transfer and adhesion.
(2) A higher value of the ratio $1/R_c$ was obtained for strong adhesion caused by ion etching of the substrate before deposition.
(3) The increase in the heat transfer and the scratch test critical load is caused by a better hooking of the film to its substrate resulting from an important contact area of the interfacial domain.

Both the morphology change of the alumina surface and the growth in the interface region width seem to be responsible for the enhancement of the heat transfer and adhesion in Ar-treated samples.

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