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Enhanced metal-ceramic adhesion by sequential sputter deposition and pulsed laser melting of copper films on sapphire substrates

ANTHONY J. PEDRAZA, MUKUND J. GODBOLE
Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee 37996-2200, USA

DOUGLAS H. LOWNDES, JAMES R. THOMPSON Jr*
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056,
**and also Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200, USA*

A study is presented of the effect of pulsed XeCl (308 nm) laser treatment on the adhesion between sputter-deposited copper films and sapphire substrates. Laser treatment (LT) of individual 80 nm thick copper films results in adhesion enhancement, relative to the as-sputtered film for XeCl energy densities $> 0.35\,\mathrm{J\,cm^{-2}}$. Thicker ($\sim 1\,\mu$m), strongly adherent copper films can be built up by alternating discrete and sequential sputter deposition with pulsed laser irradiations carried out in air. This sequential process yields smooth films whose adherence, as measured by the scratch test, is a factor of more than two to three greater than for as-sputtered films. The only way to remove the copper layer after irradiation was by cutting through the sapphire. Although formation of a metal oxide is a common consequence of LT in air, adhesion tests reveal no significant effect of carrying out LT in oxidizing or reducing atmospheres. During the earliest stages of the sequential process, the laser-melted film tends to break into small clusters. It is concluded that this process is driven by a surface energy gradient generated by lateral thermal gradients in the melt. These gradients, in turn, are due to the early establishment of isolated regions of good bonding and thermal contact with the substrate. One of the characteristic features of the sequential process is that this good bonding, once established in a given region, is maintained throughout successive meltings of the region. Adhesion mechanisms under LT are discussed.

1. Introduction

The strength of the metal–ceramic interface is relevant to a number of applications that range from microelectronic components to tools. In particular, the metal on alumina (polycrystalline Al_2O_3) or sapphire (single-crystal Al_2O_3) compound system has been extensively studied in the past [1–12]. Karnowsky and Estill [1] used the scratch test to measure the adherence of thin metal films to quartz and to sapphire substrates. They reported that copper films were removed from sapphire, leaving a clean substrate, when a load between 50 and 100 g was applied. Their results showed, as had been previously shown by Benjamin and Weaver [2], that the adhesion of metals to oxides is related to the free energy of formation of the corresponding metal oxide.

Ritter and Burton [3] studied the adhesion of nickel and of nickel alloys to sapphire by melting small cylinders of the metals on sapphire plates under different atmospheres and in vacuum, with a minimum pressure of about 6×10^{-6} torr. Good adherence was obtained when nickel was melted in vacuum or in impure argon (5×10^{-3} % oxygen content). A substantial reduction in nickel/sapphire bonding was reported when the nickel was melted under purer argon or pure hydrogen. The authors suggested a mechanism of adhesion via the formation of a nickel oxide. Sutton [4] also analysed the bond-strength of a nickel/sapphire interface under vacuum using similar techniques. However, he obtained substantially higher bond strength values and, more remarkably, a strong dependence of adherence on changes in metal purity of only tens of p.p.m.

Nicholas and co-workers [5, 6] studied the strength of metal/alumina interfaces by the sessile drop technique in a furnace, in a vacuum better than 3×10^{-5} torr. The interfacial strength was calculated by measuring the load required to push the drop off the plate. They found that copper, gold, aluminium, nickel and iron were able to form a strong bond with alumina, despite the fact that those metals, when molten, do not wet sapphire.

It is clear from the preceding results that metals can strongly bond to alumina, if contact is established when the metal is in the molten state. On the other hand, this fact has little practical use for improving the

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adhesion of thin metallic films on sapphire, if conventional heating procedures are used, because the liquid metal will tend to cluster in small droplets on the alumina or sapphire.

The initial purposes of the work presented here were (1) to determine if pulsed laser melting could be used to improve the adhesion between thin metal films and oxide ceramics, (2) to study the effects of very short duration heating on the film morphology, and (3) to determine whether thicker adherent metal films could be built up by sequential deposition alternating with laser treatment (LT).

2. Experimental procedures

The film depositions were made in a sputtering module under an argon pressure of 5×10^{-3} mbar on substrates cooled to ~ 15° C. The applied d.c. voltage was set at 300 or 400 V and a deposition rate of 0.4 to 1.1 nm sec^{-1} was used. Sapphire substrates were sputter-cleaned for 120 sec before starting the copper deposition. Laser irradiations were carried out using an XeCl (308 nm) excimer laser (Lumonics model 292) equipped with electrodes designed to produce a highly uniform fluence. The pulse duration (full width at half maximum) was approximately 40 nsec. The laser energy density at the specimen was controlled by focusing the laser pulses with a 300 mm focal length lens. Pulse energies were measured prior to focusing, using a Gentec surface-absorbing detector which had been calibrated against a Scientech volume-absorbing calorimeter. Samples were held with a vacuum chuck on a microprocessor-controlled x–y translational stage that permitted a large surface area (~ cm^2) to be scanned under the laser beam with approximately micrometre resolution.

The scratch tester used for the adhesion tests has a balanced lever arm with a spherical diamond stylus of 0.2 mm radius and a load platform above the stylus. Tangential forces on the stylus were measured with a strain gauge rigidly attached to the load platform. The stage with the specimen was moved under the stylus at a constant speed of 27 μm sec^{-1}, provided by a gear ratio motor. The scratch profile was measured with a Tencor Alpha Step profilometer.

3. Excimer laser processing

Visible and ultraviolet laser radiation is absorbed by solids mainly by electronic excitations, followed by conversion to heat (phonons). For metals the free (conduction) electron density is high and the laser energy is mostly absorbed by the conduction electrons within a penetration distance of the order of the electromagnetic skin depth, i.e. ~ 10 to 20 nm. Part of the incident energy is re-emitted (reflection) while the remainder is converted to phonons (lattice heating) in a very short time ($< 10^{-12}$ sec) [13]. The reflectance of metals depends strongly on the frequency of the incident light. In the case of copper irradiated with 308 nm photons, about 65% [14] of the energy of the incident beam is transformed into heat generated in a very thin (10 to 20 nm) surface layer. On the other hand, sapphire is almost transparent to 308 nm light. Therefore, during laser treatment of a copper/sapphire couple, the sapphire is heated only by conduction from the metallic surface layer, across the metal–ceramic interface.

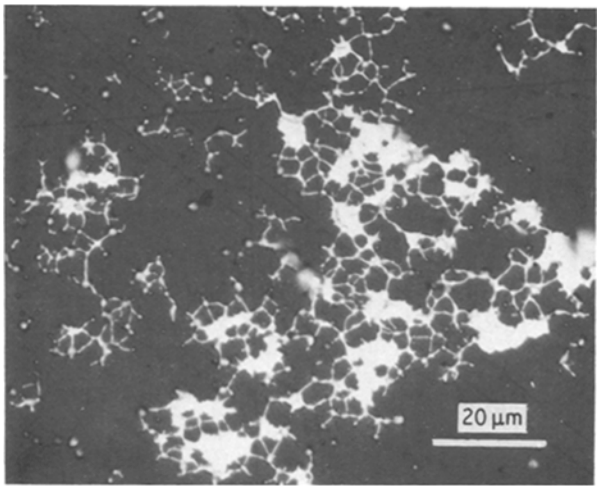

Figure 1 Micrograph of sapphire substrate where an 80 nm thick film had been sputtered and laser irradiated at 0.29 J cm^{-2}, after tape test. Note the islands of good contact between copper and sapphire.

4. Experimental results

4.1. Process and microstructure

In order to investigate the effect of a single laser pulse, 80 nm copper films were deposited on several sapphire crystals. The films were laser treated at energy densities (E_l) of 0.25 to 1.0 J cm^{-2}. The films irradiated at 0.25 and 0.29 J cm^{-2} were almost completely removed by tape-pulling tests. With these energy densities only small islands of copper remained strongly attached to the substrate, as is shown in Fig. 1. The film irradiated at 0.36 J cm^{-2} was only removed in a small region. Films irradiated at higher energy densities remained bonded to the substrate even after many pulling attempts. No cracks were detected anywhere in the irradiated films. Fig. 2 shows the film irradiated at 1.0 J cm^{-2} after the tape test. The tape pulled off only from the part of the as-deposited film that was not

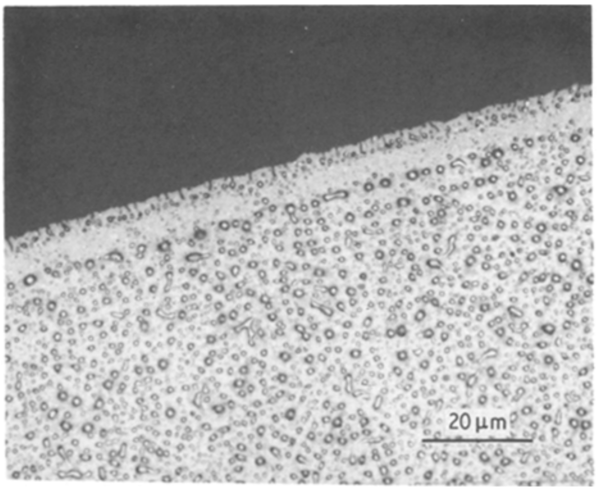

Figure 2 Micrograph of the border of an 80 nm thick sputtered copper film after 1.0 J cm^{-2} laser irradiation and tape test. Note perfect delineation of laser-treated region, and the untreated transparent sapphire (black region), where the film was stripped by the tape.

irradiated, exposing the substrate (black region in Fig. 2), whereas the laser-irradiated portion was unaffected.

Laser processing using $E_l \gtrsim 0.35\,\mathrm{J\,cm^{-2}}$ clearly improves the adhesion of these films. However, the originally flat surface of the as-deposited film became more irregular, and covered with adhering but protruding copper particles. In these regions, approximately 1 μm across and spaced 4 to 5 μm from each other, copper has been collected from surrounding regions, without exposing the substrate in most of the treated area.

The morphology shown in Fig. 2 can be understood by analysing the forces acting on the copper film under laser-treatment conditions. A surface tension analysis indicates that liquid copper under equilibrium conditions will break into small droplets with a contact angle larger than 100° [15]. However, during laser processing the copper remains liquid for an extremely short time (probably $\lesssim 100$ nsec) and equilibrium conditions are not achieved, as demonstrated by the fact that after melting the films preserve their integrity. One common observation in all the laser-treated samples is that there are smooth lines, free of copper particles, while the copper particles appear aligned alongside those lines (see Fig. 2). These lines are easily recognized as polishing scratches in the sapphire substrate; in the original as-sputtered surface these scratches are coated with copper, as illustrated in Fig. 3a. When the copper melts it detaches from the bottom of scratches (Fig. 3b), because of the high value of the copper/sapphire interface energy. As thermal contact with the substrate is lost the temperature of the film above the scratch increases relative to the surrounding film. This temperature increase may be large under LT conditions, because the energy input rate is extremely high. Fig. 3c is a schematic representation of the temperature and surface free energy variations across a scratch. However, if good thermal contact is established in some region along the scratch border, material will tend to accumulate in this colder place, driven by the surface free energy gradient. Possin *et al.* [16] treated this surface tension-driven convection mechanism by using an approximate solution to the Navier–Stokes equation. They concluded that significant lateral transport can occur on a time scale of 100 to 500 nsec if thermal gradients develop in a region of 10 μm or less. Both their calculated time interval and spatial dimensions are commensurate with our experimental values.

From this analysis and our experiments we can conclude that during laser irradiation localized regions of the film establish good bonding and thermal contact, producing cooler regions that accumulate material from the surrounding area by a surface tension-driven convection mechanism. The reason why initial bonding is localized in a particular region may depend on understanding details of the atomistic process of attachment, but clustering is clearly enhanced by the presence of surface defects such as scratches.

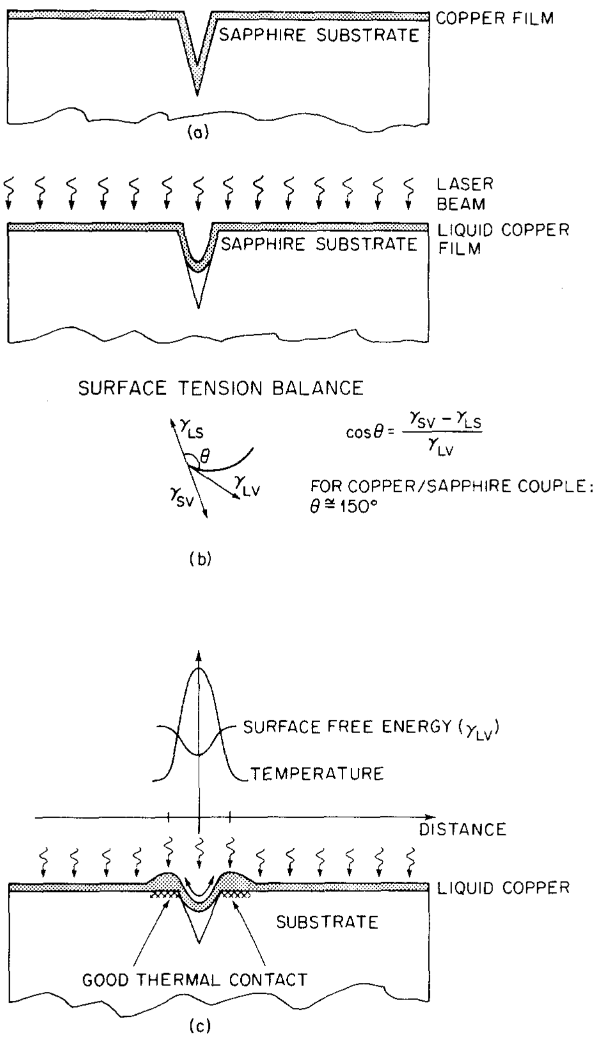

Figure 3 (a) Schematic illustration of copper deposition on a polishing scratch in the sapphire substrate. (b) Detachment of the liquid copper film from the bottom of the scratch, driven by surface tension. (c) Copper accumulation on both sides of the scratch, driven by the gradient of surface free energy associated with the thermal gradient across the scratch.

During the course of these experiments we also found that nonuniform deposition of laser energy, on a microscopic length scale, can also assist the process of copper bonding and accumulation of copper from surrounding areas. This was demonstrated by irradiating some specimens through a metal mask containing a 3 mm diameter circular aperture that was located just in front of each specimen. Because of the coherence of the laser radiation, the aperture edge produces a diffraction pattern with alternating maxima and minima in the light intensity near the aperture edge. As can be seen in Fig. 2, and more markedly in Fig. 4, copper clustering takes place adjacent to these extrema. The mechanism for copper clustering is again surface tension-driven convection, that is produced by the large local temperature gradients associated with the diffractive maxima and minima of the local laser energy density.

From the above results it follows that if clustering generally occurs in laser-melted copper-on-sapphire, then irradiation of very thin films should generate a more finely dispersed structure, because the clustering process, in the liquid state, will be quickly interrupted as the film becomes discontinuous in an earlier stage of the process. Thus if pulsed laser melting is done periodically during sputter deposition, a large density of good contact sites should be generated to cover the

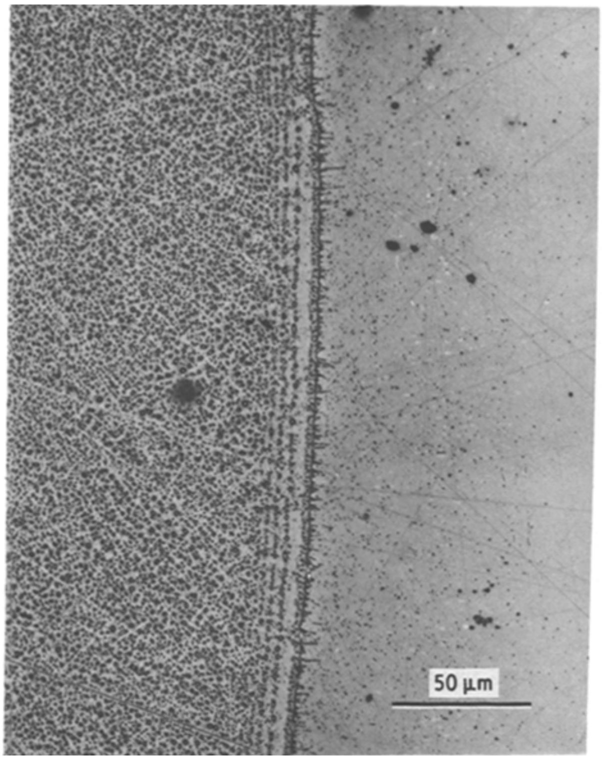

Figure 4 Micrograph of an 80 nm thick film after 1.0 J cm^{-2} laser irradiation through an aperture. Copper clustering produced by the local maxima and minima in the light intensity can be observed at the border of the irradiated region.

whole surface. Eventually a uniform and highly adherent film should cover the sapphire substrate.

In order to test and demonstrate our ideas, a 1.08 μm copper film was grown on a sapphire substrate by alternating discrete, sequential sputter deposition with laser irradiations performed in air. Table I indicates each deposition step and the energy density used in the subsequent laser irradiation. Samples were taken for analysis after each successive step. The 30 nm as-sputtered copper layer exhibited an electrical resistivity close to that of bulk copper, but after laser treatment (stage II) electrical continuity was lost. The 80 nm-thick irradiated copper layer (stage III) showed an electrical resistivity 50% higher than that of the non-irradiated film. For total film thicknesses of 180 nm and higher (stage IV and above in Table I), all of the laser-treated copper layers had an electrical resistivity close to that of bulk material. After laser irradiation of the 30 nm film an unconnected network of copper islands developed, the sapphire substrate being exposed in the neighbourhood of the copper particles. Laser treatment of the 80 nm film also resulted in copper islands, but forming an interconnected network. From stage IV on, the copper films completely covered the surface, consistent with the resistivity measurements. Fig. 5 shows the surface of the 1.08 μm thick copper layer after the sequence was completed.

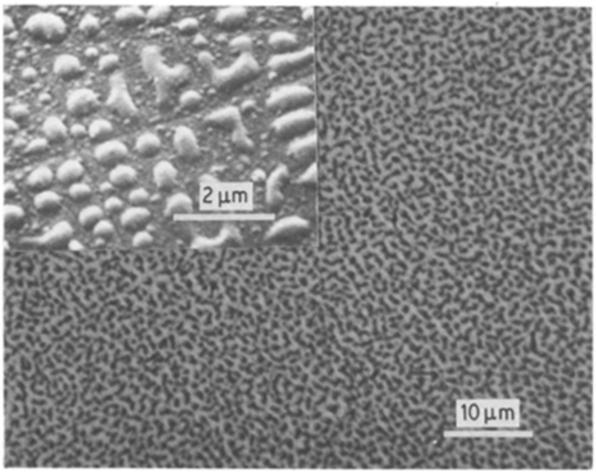

Figure 5 Nomarski phase contrast optical micrograph of a 1.08 μm film after stage VII was completed. (See Table I.)

Copper islands that developed in the 30 nm thick film after laser irradiation had a diameter of 0.5 μm, and were separated by ~ 1 μm, shown in Fig. 6. The 80 nm thick film produced by sequential deposition appeared to be generated from the island structure of the 30 nm film, with islands growing side by side and coalescing as more material was deposited and laser irradiated. Fig. 7 shows a region of the 80 nm thick film where the coalescence of small islands can be observed. The distance between the finest cells in the structure of Fig. 5 is also of the order of 1 μm.

TABLE I

Film thickness* (nm)	Stage	Thickness of the added layer* (nm)	Energy density (J cm^{-2})
1080			
	I	10	0.5
	II	20	0.5
	III	50	0.5
	IV	100	0.75
	V	300	1.10
	VI	300	1.50
	VII	300	1.50
300			
	I	10	0.5
	II	20	0.5
	III	70	0.7
	IV	200	1.0

*Thickness was measured with a thin film monitor. Copper loss by evaporation during LT has not been included.

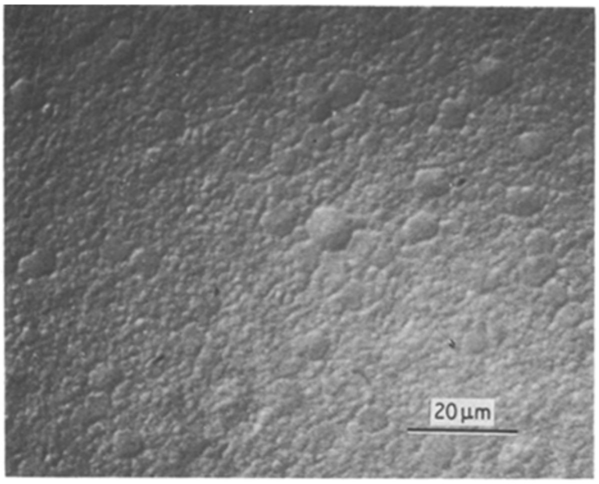

Figure 6 Micrograph of a 30 nm thick film corresponding to stage II of the sequential process for building a 1.08 μm thick film. (See Table I.) The initially continuous film is broken into 0.5 to 0.7 μm diameter islands separated centre-to-centre by approximately 1 μm.

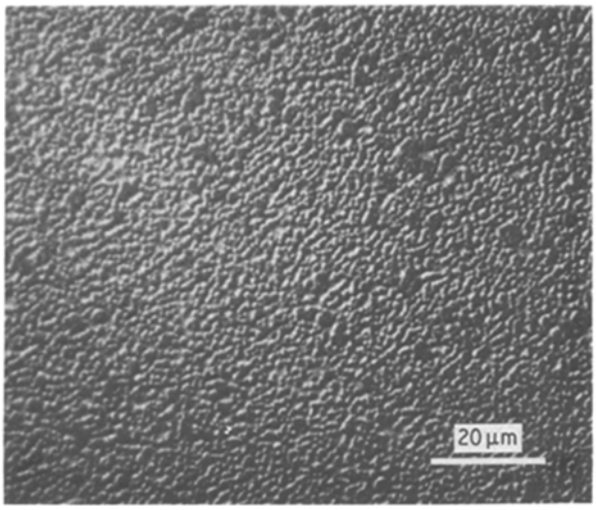

Figure 7 Micrograph of 80 nm thick copper film corresponding to stage III of the sequential process. (See Table I.)

However, some large cells can also be observed, probably due to a process of coalescence of the small cells. We note that each successive irradiation had enough energy to melt the film and then to reconstruct completely the original copper island configuration.

The cumulative effect of several sequential depositions and laser irradiations is to produce a much smaller particle size together with some exposed sapphire region, as can be seen by comparing Figs 2 and 7.

From these microstructural observations some characteristics of the process can be elucidated. Nucleation sites for island formation are established at the earliest stages of the sequential process. Subsequent sputter depositions and laser irradiations produce growth and coalescence of the original copper islands. Good bonding and thermal contact are established when copper is still in the liquid state. Places in the sapphire where good contact is established presumably remain as the clustering sites for liquid copper particles in subsequent melting events. With this mechanism, the cellular structure of thick films can be understood as developing from the copper particles formed at the early stages of the sequential process. These particles collect copper from their surroundings at successive stages; the copper-depleted regions between particles thus form the cell walls. As the film thickness increases, several adjacent regions in good thermal contact will act as a unit in extracting heat and collecting liquid copper, thus merging and allowing the cells to grow.

In order to study the possible influence of ambient air on this process, a 300 nm thick copper film was grown in a reducing atmosphere of 96% and 4% hydrogen. The sequential growth process for this film is detailed in Table I. The 300 nm film was very uniform and presented a cellular structure of regular size throughout the treated region, as can be seen in Fig. 8a. Fig. 8b shows the particle structure of a 30 nm film (also treated in 96% Ar/4% H_2) in which the sequential process has been stopped after the second stage had been completed as indicated in Table I. There are no apparent differences in microstructure as a result of LT in a reducing atmosphere.

4.2. Adhesion tests

A microhardness tester with a Vickers stylus under a 10 g load was used to produce grooves on the thin films. Samples were mounted on a manually operated translational stage. Fig. 9a shows a scratch performed on a 300 nm thick as-sputtered copper film. The "centipede" features observed in the micrograph are due to detachment of the film from the substrate. The film was completely removed when the stylus crossed a pronounced scratch on the sapphire substrate. This photograph was taken with a microscope using both reflection and transmission light letting the places where the film has been removed appear very bright. Fig. 9b shows another scratch performed in the way just described, but on a 480 nm film sequentially laser treated up to stage V in Table I. In this case the groove is sharp and there is no indication of peeling or clearing away of copper anywhere.

In order to measure the adhesion, standard scratch tests were performed in the apparatus described earlier. The laser-treated film remained adhered to the substrate even after being scratched with a load of

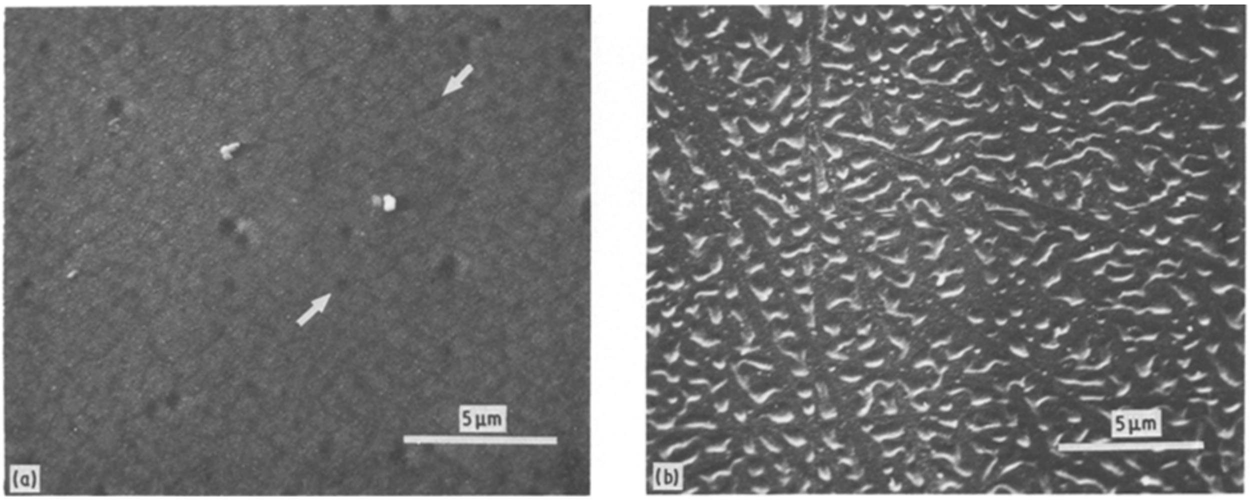

Figure 8 (a) Scanning electron micrograph of a 300 nm thick film built by sequential deposition as indicated in Table I. (b) Scanning electron micrograph of a 30 nm thick film in which the sequential process was stopped after stage II. (See Table I.)

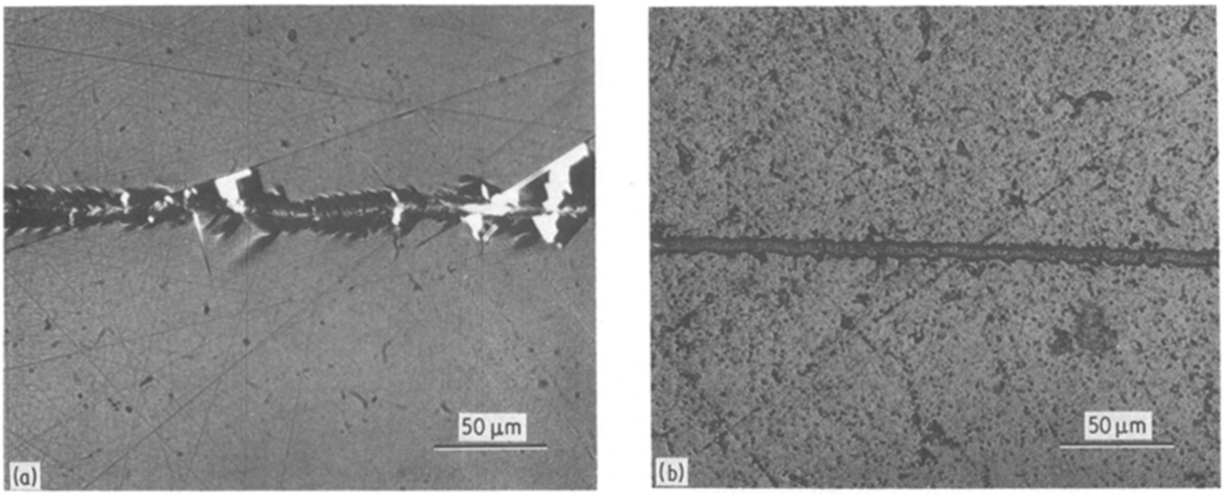

Figure 9 (a) Optical micrograph of a scratch on a 300 nm thick film, produced with a Vickers stylus under a 10 g load. The micrograph was made using both reflected and transmitted light so that places where the film is completely removed appear bright. (b) Optical micrograph of a scratch on a 480 nm thick laser-treated copper film. No indication of peeling or transmitted light can be observed anywhere.

400 g, which is the maximum load that can be used in this apparatus. Fig. 10 shows a 100 g scratch performed on a 1.08 μm thick film across the boundary between a fully laser-treated region (lighter) and a portion in which the last deposited layer (300 nm) was not laser irradiated (darker). Ripples are seen on the side of the groove in the unirradiated portion where the film has peeled off, while a smooth groove with no indication of detachment can be seen on the fully irradiated side. This last experiment indicates that copper does not adhere well to the thin oxide surface layer formed during the previous laser treatment. The last irradiation improves the adhesion of copper/copper oxide couples because it melts and either dissolves or disperses the former oxide film. Other scratch tests, using the Vickers diamond pyramid indentor with 75 to 100 g loads, showed that the only way to remove the copper layer after irradiation was by cutting through the sapphire. Thus, very strongly adherent films are built up in this way. Even in this case, the groove remained sharp with no indication of peeling from the sides.

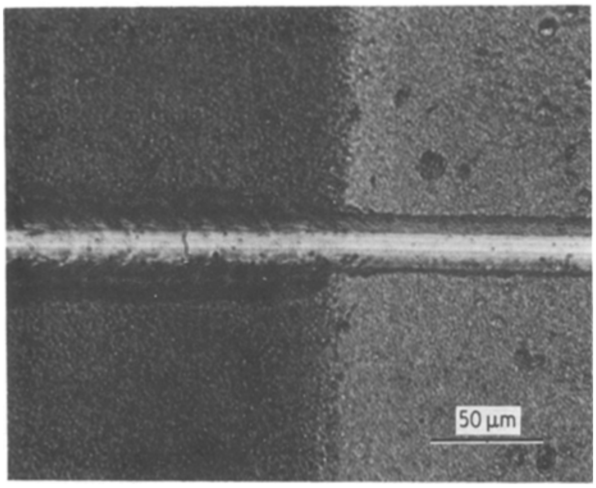

Figure 10 Optical micrograph (reflection illumination) of a groove generated by a spherical diamond tip with a load of 100 g in a 1.08 μm thick film. Note that the scratch contains ripples on the side of the film that was not exposed to the laser in the last stage (dark region), while no indication of peeling can be seen on the fully irradiated side (lighter region).

Figure 11 shows a profile across the scratch; extensive plastic deformation has occurred on both sides of the groove, as should be expected because copper is very ductile. Another good indication that no peeling takes place is that the surface at the sides of the groove is raised above the average level only in the region very close to the groove itself. When peeling occurs, the above-average level surface area is considerably larger than the groove area, due to the formation of cavities.

The model developed by Benjamin and Weaver [17] was used to quantify the results obtained in the scratch tests. This model assumes full plasticity in the material around the indentor. The shear stress, F, at the lip of the stylus indentation is computed as

$$F = P[a/(r^2 - a^2)^{1/2}] \quad (1)$$

where a is the radius of the circle of contact, r is the radius of the stylus and P is the mean pressure. This mean pressure can be calculated by using the measured value of a as

$$P = (\pi a^2)/(Wg) \quad (2)$$

where W is the applied load. The penetration depth, b, can be more accurately measured than a, and can also be used to calculate a as

$$a = [(2r - b)b]^{1/2} \quad (3)$$

Although the shear force of Equation 1 may not be an accurate absolute measure of adhesion, as has been recognized [18], it is useful for comparison purposes.

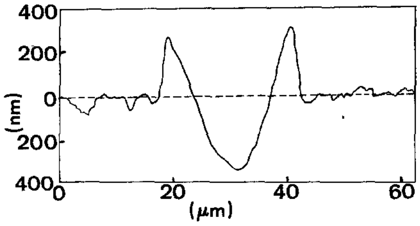

Figure 11 Profile across a scratch on the irradiated side. Notice extensive plastic deformation on both sides of the groove.

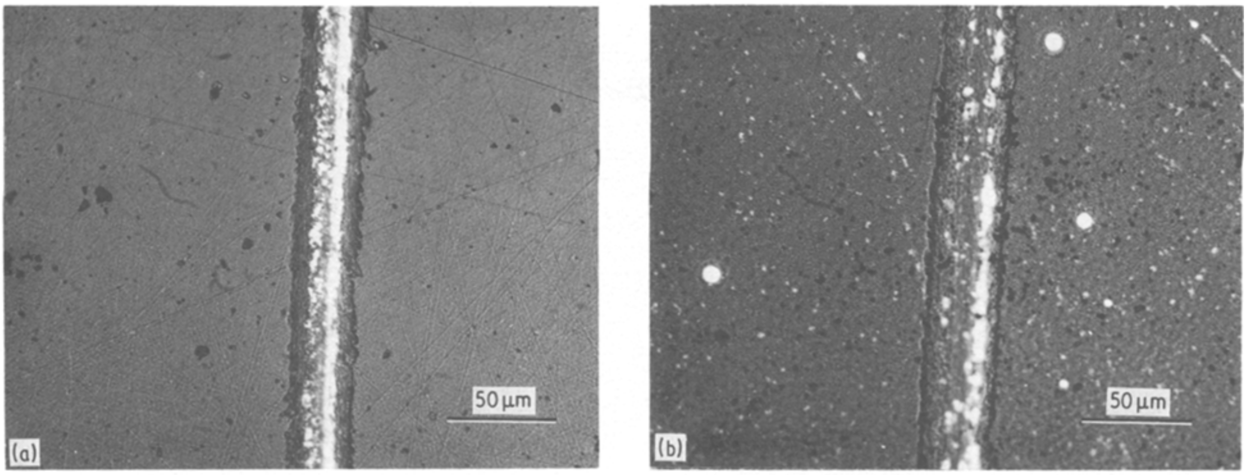

Figure 12 Optical micrograph of (a) a 200 g scratch on a 300 nm thick untreated copper film, and (b) a 400 g scratch on a LT 300 nm thick film. A combination of transmitted and reflected light were used for both micrographs.

Scratch tests for measuring adhesion were performed on the LT 1.08 μm thick under air and on the LT 300 nm thick films under an argon–4% hydrogen atmosphere. Shear stresses were calculated using Equations 1 to 3. Table II gives the measured and calculated model parameters together with the shear forces calculated for the maximum load that could be applied without any film removal (for the 1.08 μm thick films) or clearing of copper (for the 300 nm thick films) from the scratch as detected by transmitted light with a microscope. Laugier's model [19] was used to check that the total radial stress acting at the leading edge of the moving indentor was compressive in nature. This indicates that the film will be detached from the substrate if a sufficient force is applied, and will be detected by light microscopy. Table II compares results obtained for 300 nm and 1.08 μm thick LT films and for a 300 nm thick as-sputtered film.

As is discussed in more detail elsewhere [20], the magnitude of incident laser energy density is critical to this process. The laser energy densities utilized in the last two stages of building up the 300 nm (nominal thickness) films were probably excessive so that considerable evaporation took place. When scratch tests were performed in these LT films some film removal took place at the higher loads. In many places the removal was clearly associated with surface damage produced by the final laser shots. For this reason, these films were considered to have failed the scratch test following the "cleared path" criterion. Fig. 12a shows a 200 g scratch performed on a 300 nm untreated copper film, where the cleared path (bright region) seen in the film was taken as an indication of adhesion failure. Fig. 12b shows a 400 g scratch in a 300 nm (nominal thickness) laser-treated film; although there are some spots where the film was removed, a cleared path cannot be seen and no adhesion failure was recorded. The micrographs of Fig. 12 were taken with a combination of transmitted and reflected light. The bright spots observed to both sides of the scratch in Fig. 12b are holes produced during the laser-irradiation process and are clearly associated with damage produced during LT.

5. Discussion and conclusions

5.1. Process analysis

The results presented in this paper demonstrate that the adhesion of copper films to sapphire substrates can be remarkably improved if the films are pulsed laser treated. All the different tests performed showed a clear enhancement of adhesion. We have also shown that the sequential process of copper deposition, alternating with LT, produces films that are fairly smooth. There is more than a two-fold improvement of adhesion if the shear force calculated by the Benjamin and Weaver model is considered, or over three-fold if the adhesion is simply measured by the applied load in the scratch test. (In fact, the latter test was limited by the 400 g load limit of the tester.)

Our microstructural observations support the hypothesis that regions of good thermal contact are developed at the earliest stages of sequential

TABLE II

Film	Thickness (nm)	Normal force (N)	Tangential force (N)	Coefficient of friction	Shear stress (GPa)	Comment
LT	1080	3.92*	0.67	0.170	0.38	no de-adhesion detected
LT	300	3.92*	0.35	0.088	0.65	no de-adhesion detected
As-sputtered	300	0.98	0.098	0.100	0.21	no de-adhesion detected
		1.96	0.19	0.097	0.38	de-adhesion detected

*Higher loads are beyond the limits of the tester.

processing. The average power input during typical laser shots is 1 to 4 MW cm^{-2}. A simple heat balance calculation shows that if most of this energy is not quickly transferred to the substrate then the copper will reach temperatures far higher than its boiling point. One-dimensional heat conduction models have been applied to the case of metals irradiated by nanosecond laser pulses and yield temperature gradients normal to the surface of the order to 10^7 K cm^{-1} [13]. If we assume, as a rough approximation, that only lateral heat conduction toward the cooler regions develops in thermally isolated regions, then these lateral gradients would also be very large. The high lateral thermal gradients then will generate a lateral gradient of surface free energy that drives the clustering of copper, in times compatible with the process duration [16]. The cell structure in the 1.08 μm film was related to the mechanism of surface free energy gradient. However, not all the cells had dimensions commensurate with the size of the particles formed at the early stages of the sequential process. As the thickness of the film increases, lateral thermal gradients would be expected to decrease and become negligible. This process may randomly generate larger cells. Fig. 8a shows that for a 300 nm thick film the cell structure is uniform, whereas larger cells are seen in the 1.08 μm thick film shown in Fig. 5. Moreover, the cell spacing in the thinner film is similar to the particle spacing at the beginning of the process, as can be seen by comparing Figs 8a and b. A clear indication that copper has been drained from the walls toward the cells is that exposed sapphire can be seen in junctions, as indicated by arrows in Fig. 8a.

Two drawbacks of this process are copper evaporation and the formation of holes. Copper evaporation may be eliminated by adjusting the energy density of the laser shots. At the beginning of the sequential process the laser will vaporize atoms that are not well attached to the substrate; this is beneficial for enhancing adhesion in later steps. However, when all the surface has been covered by a uniform and well-adhered copper film, the only reason for continued laser treatment is that subsequentially deposited copper layers do not adhere well to the oxide film that has formed, in the absence of laser treatment (see Fig. 10).

Two main causes of hole formation during LT have been identified: (1) substrate imperfections such as scratches; and (2) junction points or cell/walls. The holes due to scratches are easy to identify because they are aligned in the scratch direction. The triple point or cell wall holes have already been explained, and can be detected by SEM inspection. Both defect types can be observed in Fig. 12a, together with some sparsely distributed larger holes. Those holes are much larger than cells and may have a different origin, probably hot spots in the laser beam. In general, the sequential process tends to heal the film and as it grows thicker most holes disappear.

The formation of all the holes is thus related to the generation of hot spots in the liquid during irradiation. Those due to the lack of good thermal contact with the substrate can be eliminated in thinner films if the number of regions with good bonding is increased. In order to increase the number of sites with good thermal contact it is necessary to decrease the thickness of layers while increasing the number of layers and of laser shots in the sequential process, until the surface is covered with a uniform copper film.

As can be seen in Table II, adhesion strength shows no significant dependence on whether LT is performed under an oxidizing or a reducing atmosphere. This seems to indicate that the formation of copper oxide, which takes place in the oxidizing atmosphere, does not affect the adherence of subsequent layers deposited and melted in this sequential process.

5.2. Mechanisms of adhesion

Poor adhesion is obtained when epitaxial thin films of copper are grown on sapphire heated up to 775 K [12]. (This epitaxial relation is possible because a lattice parameter difference of only 3% exists between the two lattices [21].) However, a remarkable increase in the bonding of the copper/alumina couple takes place if copper is allowed to remain liquid (1773 K) on an alumina substrate for 1800 sec under a pressure less than 3×10^{-5} torr [5]. Copper atoms in the liquid state are not constrained and may easily attain favourable positions to establish a bond with oxygen atoms of the alumina. Moreover, the higher temperature of liquid copper aids this reaction. Johnson and Pepper [22] have suggested the formation of an ionic bond between the copper 3d and the oxygen 2p orbital electrons on the alumina surface. Also Ohuchi *et al.* [23] and Baglin *et al.* [12] found experimental evidence of this bonding by X-ray photoelectron and ultraviolet photoemission spectroscopies.

Our experimental results suggest that good thermal contact and good bonding with the substrate are produced while copper is in the liquid state. One of the benefits of the sequential process is that good bonding, once established, tends to be maintained throughout successive meltings. The persistence of good bonding is probably due to both the short duration of the melting cycle and to the much lower temperature, during LT, in the regions where such bonding exists than in other areas. The formation of an intermediate compound could also contribute to maintaining the regions of good bonding through successive meltings.

Two factors seem to be mainly responsible for the enhancement of adhesion: (1) liquid copper contacts the sapphire, and (2) the extremely high temperatures that are attained during LT. Whether the bonding established during LT is due to an interfacial reaction or to the formation of an intermediate compound between copper and sapphire remains to be established.

Our conclusions may be summarized as follows.

1. The sequential sputter deposition of copper on sapphire substrates alternating with pulsed laser irradiation produces smooth films whose adherence, as measured by the scratch test, is two to three times higher than the adherence of as-sputtered films.

2. During the early stages of the sequential process the laser-melted film tends to break into small clusters. This phenomenon is driven by a surface energy gradient which is generated by lateral thermal gradients in the melt.

3. Microstructural observations support the hypothesis that regions of good thermal contact are established during the earliest stages of the sequential process and maintained through successive meltings.

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