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ADHESION STUDIES OF MAGNETRON-SPUTTERED COPPER FILMS ON INCONEL SUBSTRATES

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Abstract

The adhesion strength of sputtered copper films to Inconel substrates has been studied using the scratch test. The effects of substrate treatments before deposition such as chemical or ion bombardment etching were investigated by means of a mean critical load derived from a Weibull-like statistical analysis. It was found that the mean critical load was very weak unless the amorphous layer produced by mechanical polishing on the substrate surface was eliminated. Chemical etching in a nitric-hydrochloric acid bath was shown to have practically no effect on the enhancement of the adhesion. In contrast, the addition in this bath of nickel and copper sulphates allowed removal of the amorphous layer and an increase in the values of the mean critical load. However, it was observed that excessive chemical etching could cancel out the mean critical load enhancement. The results obtained in the case of ion bombardment etching pretreatments could be far higher than those obtained with chemical etching. Moreover, for a sufficiently long period of ion bombardment etching, the adhesion strength was so high that it was impossible to observe evidence of an adhesion failure.

1. Introduction

Good adhesion of thin films to their substrates is essential in most applications but knowledge of this topic is extremely limited. A major reason for this is the difficulty of measuring adhesion. In the past, many measurements have been made using a variety of techniques, but these different methods were shown to be of limited use. One of the most reliable techniques is the scratch test method which is being increasingly used to evaluate the adhesion of strongly adhering films. The principle of the method consists in moving a charged stylus along the studied sample and in measuring the load applied on the stylus at which the adhesion loss occurs. This is the critical load[1]. However, there is often a large spread in the critical load values as a result of local inhomogeneities in the adhesion strength. In such cases, it is still possible to obtain reliable information by introducing a statistical method derived from the Weibull[2] analysis. This is the mean critical load which was recently used by Cailler and coauthors[3] to study the effects of surface pretreatments on the adhesion of copper coatings to aluminium and nickel substrates.

In the present paper, we report the results obtained for Inconel substrates covered with copper films. The effects of substrate treatments before deposition such as chemical or ion bombardment etchings were investigated and it was found that the mean critical load was very weak unless the amorphous layer produced by mechanical polishing on the substrate surface was eliminated. Chemical etching in a nitric-hydrochloric acid bath was shown to have practically no effect on the enhancement of the adhesion. In contrast, the addition in this bath of nickel and copper sulphates allowed removal of the amorphous layer and an increase in the values of the mean critical load. However, it was observed that excessive chemical etching could cancel out the mean critical load enhancement. The results obtained in the case of ion bombardment etching could be far higher than those obtained by chemical etching. Moreover, for a sufficiently long period of ion bombardment etching, the adhesion strength was so high that it was impossible to observe evidence of an adhesion failure.

2. Experimental procedure

2. 1 Surface treatment

The substrates of the samples studied in this work were made of Inconel 600 (hardness, 180HV). After mechanical polishing, some samples were chemically etched and quickly introduced into the deposition chamber. A detailed description of the different etching treatments is given in Table 1. In most cases, the substrates were promptly covered after etching; however, the samples etched by ion bombardment were kept in situ for 3min of latency time between the end of the ion etching and the beginning of the deposition.

2. 2 Coating deposition and measurement of the critical load

The pure copper films were deposited by d.c. magnetron sputtering with a power of 580W. In such circumstances, the deposition rate was constant and equal to 1.7nms^{-1}. A fixed deposition time was used for all samples, giving a coating thickness of about 180nm and allowing a direct

Table 1. The experimental conditions of substrate pretreatments

Process	Experimental conditions	Etching time
Chemical etching	Solution of 46% HNO_3 (3volumes) +HCl (1volume) at 20℃	10, 20, 30, 40, 50, 60, 90 and 120s
	Solution of 46% HNO_3 (3volumes) +HCl (1volume) +sulphates at 20℃	0.5, 1, 1.5, 2, 2.5, 3, 4 and 5min
Ion bombardment etching	Working pressure, 5.0Pa, Cathodic voltage, 620V	3, 6, 7, 8, 9, 10, 11 and 12min

comparison of the mean critical load valves.

All the present tests were performed with the scratching apparatus described in ref.20. Each scratch was made for a given value of the load. A standard scratch speed of 3.7mm min^{-1} was used, the scratches being about 5mm long.

Most of the scratches were performed with a diamond stylus of tip radius 17㎛, but in some cases, i.e. when the adhesion strength was very weak, we were compelled to use a tungsten carbide stylus with a tip radius of 350㎛ in order to demonstrate critical load variations.

3. Experimental results

Fig. 1 presents the results obtained for the variation in the mean critical load as a function of the chemical etching time or as a function of the ion bombardment etching time, in the case of Inconel substrates. As can be seen from this figure, the mean critical load remains very weak in the case where the chemical etching is performed in

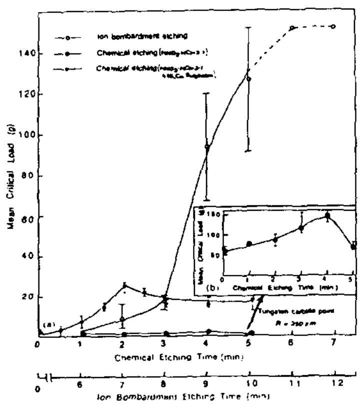

Fig. 1 Scratch adhesion test data of Cu/Inconel samples showing the mean critical load as a function of the chemical etching time or as a function of the ion bombardment etching time.

a nitric-hydrochloric acid bath, whatever the etching time is. In fact, it is so weak that it was quite impossible to demonstrate significant changes. To overcome this difficulty, we replaced the diamond point by a tungsten carbide stylus of tip radius 350㎛ which requires much higher applied loads to produce the adhesion failure and, as a consequence, allows the effects of the etching to be observed more easily. The results obtained with this latter point are shown in Fig. 1(b). They show that the mean critical load increases up to an etching time of 4min and decreases afterwards. This indicates that an excessive etching time can reduce the adhesion strength of a coating to its substrate.

A slower but more satisfactory chemical etching can be obtained by adding some quantities of nickel and copper sulphates into the nitric-hydrochloric acid bath. The best results for the mean critical load were obtained by addition of 20g of each sulphate per litre of solution. In such circumstances, the mean critical load is increased from 1gf after mechanical polishing up to a maximum value of 24.3gf for an etching time of 2min. Above this value of the etching time, the mean critical load is slightly decreasing and reaches a value of about 18gf after 5min of etching. While these conditions were those giving the best results among those we experimented with, we cannot consider that they were completely optimized. Because of its importance, we shall return to this problem in a future paper.

In the case of ion bombardment, the mean critical load increase very rapidly with increasing etching time but only if the latter is longer than about 8min. Again, beyond this value of the etching time, the shape of the scratch channel does not produce any evidence of adhesion failure.

4. Discussion

The experimental results presented above can be interpreted as resulting from modifications of the substrate surface roughness and of the chemical nature of the coating-substrate interface.

4. 1 Effect of the surface roughness

It has already been determined that surface roughness has an effect on the critical load. Pulker and Perry have suggested in their review paper that the adhesion is greatly influenced by the physical and chemical structures of the substrate surface and of the neighbouring areas as well as by the morphology of the surface. Valli and Makela showed that the surface roughness is one of the factors affecting the critical load. In addition, Oh showed in his thesis that the critical load was increased by changing the surface roughness with a mechanical brushing. Recently, Cailler and Lee provided evidence that, for copper films deposited on aluminium substrate, the mean critical load was highly modified by changing the roughness of the substrate surface by either chemical or ion bombardment etching.

Fig. 2 shows the surface morphologies of Inconel specimens chemically etched in a nitric-hydrochloric acid bath. Again, the presence of an amorphous layer after the mechanical polishing of the surface gives the mean critical load a very low value. Its elimination is very difficult in such a solution as can be seen from Fig. 2. However, for a longer etching time, the roughness of the surface is slightly increased. As a consequence, the mean critical load remains very low. Moreover, it decreases when the etching time exceeds 4min. A better attack is obtained by adding nickel and copper sulphates in the nitric-hydrochloric acid solution.

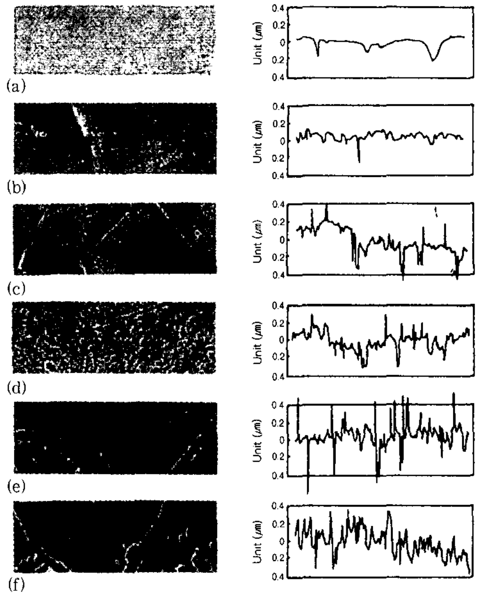

Fig. 2 Roughness profiles of the surface and related and scanning electron micrographs. (a) After mechanical polishing and for etching times of (b) 30s, (c) 40s, (d) 1min, (e) 2.5min (f) 5min.

4. 2 Physical-chemical analyses

Auger electron spectroscopy has been employed to study the ion bombardment etching effects on the nature of the interface prior to the deposition. By means of this etching technique, it is possible to remove contamination layers and surface oxides and then to modify the adhesion strength. For instance, Chapman pointed out in his review paper that etching can remove tenacious materials such as surface oxides. Jacobsson and Krusefound that, for ZnS films deposited on glass, the critical load in their pull-off test was nearly double by ion bombardment etching of the glass surface before deposition of the coating. Also, Butler found an improved adhesion of copper films evaporated on glass, if the substrate was submitted previously to glow discharge cleaning. In addition, Helmersson et al. suggested that changes in the nature of the oxide layer present on the surface of the substrate can increase adhesion strength. By using Auger electron spectroscopy, they found that a sputtering treatment of the substrate surface prior to deposition improved the film adhesion, even though complete removal of the oxide layer was not achieved.

The peak-to-peak heights of the principal Auger lines have been plotted against the ion milling time. To make clearer the conclusions, the variations in the oxygen and carbon Auger lines in the interfacial domain are presented on a larger scale in Fig. 3. As clearly shown in this figure, the interfacial region after ion bombardment exhibits no important enrichment in oxygen. Consequently, we can consider that the major part of the oxides of the substrate surface produced during or after the mechanical polishing was eliminated by the ion bombardment. The marked enhancement of the mean critical load resulting from ion bombardment should be principally due to the elimination of this layer. However, the 510eV oxygen line remains perceptible on the Auger spectra obtained after ion bombardment etching for 12min, suggesting that there is not a complete removal of the oxide layer.

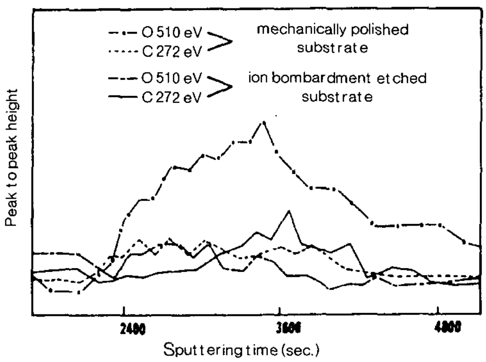

Fig. 3 Auger electron spectroscopy depth profile across the interface of Cu/Inconel samples.

Therefore, we could consider that the mean critical load values depend on the presence of oxygen at the interface. When it is present, oxygen prevents a good adhesion. Its elimination by ion bombardment allows good adhesion between the substrate and its coating.

5. Conclusion

Mean critical loads for copper films deposited on Inconel 600 substrates were measured by the scratch test. It was found that they were highly dependent on the substrate pretreatment. Using scanning electron microscopy and Auger electron spectroscopy we were led to the following conclusions.

Different surface roughness were obtained by chemical etching. However, an efficient attack of the substrates was only possible by adding copper and nickel sulphates into a nitric-hydrochloric acid bath. The mean critical load, reported as being less than 1gf for a mechanically polished specimen, increased up to 24.3gf after chemical etching for 2min. When the etching time exceeds 2min the mean critical load decreases to reach about 18gf at 5min. In the absence of sulphates, the mean critical load remains very low.

This value increased up to about 130gf when the substrate was etched by ion bombardment for 10min. Above this, it was not possible to measure the mean critical load exactly because of the absence of adhesion failure evidence.

In the case of chemical etching, the enhancement of the mean critical load was attributed to an increasing roughness of the substrate surface. On the contrary, in the case if ion bombardment etching the high values of the mean critical load cannot be explained in terms of roughness, because the latter remains very low. In that case, Auger electron spectroscopy analyses performed across the interface between the coating and its substrate suggest strongly that the adhesion enhancement should be due to cleaning of the substrate surface before deposition. However, the mechanism might be complex because of the possibility that the ion beam creates vacancies and microcavities.

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