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The Adhesion of Electroless Ni(P) on Alumina Ceramic Using a Vacuum-Deposited Ti-Pd Activator Layer

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ABSTRACT

The adhesion of electrolessly deposited nickel on Al_2O_3 ceramic substrates using sputtered and evaporated Ti-Pd activator films was studied. The adhesion was measured using the direct pull-off test and the 90° peel test. The morphology and the chemical composition of the fracture surfaces of the samples with evaporated Ti-Pd activator film were studied with scanning electron microscopy/energy dispersive x-ray, and static secondary ion mass spectroscopy. Failure did not occur along the metal-ceramic interface, but mainly in the alumina, and therefore the strength of the system is determined primarily by the substrate material. Cross-sectional transmission electron microscopy and high-resolution transmission electron microscopy were used to study the interface structure before failure. The oxidation state of Ti at the interface was measured with x-ray photoelectron spectroscopy. This was carried out in the (sub)monolayer range by using a Ti wedge deposited on alumina with a maximum thickness of 0.35 nm. It is concluded that the strong adhesion at the metal-ceramic interface is caused by chemical bonding of the first Ti monolayer with substrate oxygen atoms.

Generally, the adhesion between electrolessly deposited Ni layers and nonconducting substrates is weak. Often this can be improved by increasing substrate surface roughness, thus making use of mechanical interlocking.¹ In some cases, however, this is not possible or not sufficient. In this work a procedure is described to improve the adhesion of electroless Ni(P) layers on smooth substrates.

Usually Pd, required as a catalyst for the initiation of the electroless deposition, is deposited on the substrate surface as nuclei from aqueous solutions, *e.g.*, by immersion in SnCl_2 and PdCl_2 solutions.^{2,3} However, a vacuum-deposited Pd layer can also act as a catalyst for the initiation of this process.^{3,4} Unfortunately, adhesion properties deteriorate with increasing nobility of the metal. The stronger adhesion of base metals like Ti, Al, and Cr, compared to semimetal and noble metals like Ni, Cu, Ag, and Pd is ascribed to the tendency of the former group to form chemical bonds with oxygen atoms of the substrate surface.⁵ For a number of metals, a proportionality relationship has been established between oxidation potential and adhesion strength.⁶ The adhesion of noble metals is often improved by alloying with base metals or by applying a thin interlayer of such a metal.^{5,7} Furthermore, the adhesion of electroless Ni is stronger on metal substrates than on nonmetallic substrates.⁸ A combination of these observations leads to the idea of using stacks of metal layers, for instance the stack shown in Fig. 1. The relatively thick electrodeposited Ni layer was applied on top of the electroless Ni(P) layer in order to increase the strength and the stiffness of the metal layer which was necessary for the adhesion measurements. For the deposition of Ti and Pd films several techniques are in use. The two common techniques applied here are magnetron sputtering and evaporation.

In order to obtain information on the nature of the chemical interaction at the metal-ceramic interface, the Ti layer has been investigated with x-ray photoelectron spectroscopy (XPS) during the initial stages of deposition. Similar investigations to interpret adhesion phenomena have been reported for Ti on silica and sapphire,⁹ Al on silica,¹⁰ and Al on polymers.¹¹

At first sight it may not seem useful to combine a relatively expensive vacuum-deposition technique for the activator layer with the simple wet-chemical deposition of the nickel layer. However, for a number of applications electroless Ni(P) has to be used because of specific properties required, such as high strength and hardness, good wear resistance, oxidation and corrosion stability, and resistance

to various chemicals.¹² In such cases, where high specifications have to be met, a vacuum-deposition technique for the activator layer can be a suitable solution for obtaining strong adhesion.

Experimental Procedures

Metal layers were deposited on two types of substrates; on relatively rough 96% alumina (HCT, Hoechst Rubalit 708), with an R_a value of 0.3 μm and on relatively smooth 99.5% alumina (MRC 996), with an R_a value of 0.06 μm . The substrates were cleaned with a fluorinated alkylsulfonate detergent solution and etched for 4 min in a 2.5% HF solution. The changes in chemical composition of the surface due to these treatments is reported elsewhere.¹³

The magnetron-sputtered Ti and Pd films were deposited under the following conditions: *ca.* 20 nm Ti was sputtered at a rate of 0.1 nm/s for 200 s, immediately followed by the deposition of *ca.* 20 nm Pd at a rate of 0.4 nm/s for 50 s. The substrates were not heated during deposition. A background pressure of 10^{-5} mbar was maintained, the process pressure being $2.5 \cdot 10^{-2}$ mbar. Ar, Ti and Pd films 20 nm thick were also deposited by evaporation using a similar procedure, both at a rate of 0.5 nm/s and at room temperature. The background pressure was $2.5 \cdot 10^{-6}$ mbar.

Electroless Ni(P) was deposited using a commercial Enlyte 512 bath (OMI) at a temperature of 60 to 65°C. For the electrodeposition of a low stress Ni layer a sulfamate bath was used.^{8,12} For the adhesion strength measurements Ni layers of 2 to 4 μm thickness were used, except for the evaporated Ti-Pd samples (14–30 μm). For the fracture energy measurements a Ni layer of 40 μm thickness was used in order to avoid rupture of the layer during peeling.

The adhesion was measured by a direct pull-off (DPO) adhesion strength measurement¹⁴ and by a 90° peel test which provides information concerning the fracture energy.^{15,16} For the DPO test, aluminum pull studs with an epoxy adhesive were bonded to the Ni layer at 150°C for 1 h in air. This heat-treatment may affect adhesion but is difficult to avoid. The samples for the peel test received the same heat-treatment before attaching the peel strip to the load cell. The fracture surfaces of the peeled sample were analyzed with scanning electron microscopy (SEM) and energy dispersive analysis of x-rays (EDX).

Cross-sectional transmission electron microscopy (TEM) micrographs were made using a Philips EM 400 transmission electron microscope at an electron energy of 120 keV. For the high-resolution cross-sectional TEM micrographs a Philips CM 30 microscope was used at an electron energy of

4	Galvanic Ni	(several μm)
3	Electroless Ni(P)	(0.3 μm)
2	Pd	(20 nm)
1	Ti	(20 nm)
Al ₂ O ₃ ceramic		

Fig. 1. Stack of metal layers used in this investigation.

300 keV. Samples were prepared by grinding, polishing, and ion milling as described in Ref. 17. The equipment and measuring conditions for the static secondary ion mass spectrometry (static-SIMS) surface analyses are described in Ref. 18. A reflectron-type time-of-flight static-SIMS apparatus from IonTOF GmbH was used for the surface analysis of the first monomolecular layers of the fracture surfaces. The mass resolution of the spectra was such (3000–5000 in the mass range from 20 to 150 amu) that peaks from the metal ions could be separated from those of hydrocarbon ions of the same nominal mass.

For the XPS analyses of the Ti layer at the initial stages of deposition, MRC substrates were used which were cleaned by sputtering at elevated temperature. Then Ti was evaporated in a VG Semicon V80M MBE chamber and the XPS analysis was carried out in a VG Scientific ESCALab using Mg K α radiation. A Ti wedge of about 40 mm length and a maximum average thickness of 0.32 nm was deposited by evaporation from a resistively heated Ti filament (>99.9% pure) at a rate of the order of 0.1 monolayer/min. This wedge was prepared and analyzed in a similar manner to the Fe/Cr wedge/Fe (100) sample in Ref. 19. A moving shutter was used for the wedge preparation. The background pressure was equal to the process pressure, being 10^{-10} mbar. The Ti layer thickness was determined by analysis of the integrated Al 2s and Ti 2p_{3/2} XPS peak intensities. A linear increase of the Ti thickness along the wedge was confirmed, suggesting that Ti initially grows as relatively flat patches. The absolute accuracy in determining the layer thickness is about 10%, however, by using the wedge geometry, the relative thicknesses are extremely well defined.

Results

Adhesion measurements.—Direct pull-off tests.—In Table I the results of the DPO adhesion strength measurements are listed for the samples with sputtered and evaporated interlayers, prepared as shown in Fig. 1 and as described in the Experimental Procedures section.

Table I. Mean fracture strength $\bar{\sigma}_f$ (MPa), sample standard deviation s_{n-1} (MPa) and number of samples N for samples with sputtered and evaporated Ti-Pd layers. MRC and HCT refer to the smooth and rough types of alumina, respectively.

Sample type	Substrate no.	$\bar{\sigma}_f$	s_{n-1}	N	Failure ^a
Sputtered MRC	1A	55	8.5	33	Substrate
	1B	55	6.0	32	Substrate
Evaporated HCT	2	76	4.1	6	Stud

^a See text for explanation.

Fig. 2. Peel profile of Ni/Ni(P) layer with evaporated Ti-Pd activator layer.

The strength values listed for the samples with sputtered Ti-Pd (No. 1A and B) are lower than those with the evaporated Ti-Pd layers (No. 2). However, this does not mean that the adhesion strength is lower. In the case of the sputtered interlayers (No. 1A and B) failure took place by fracture of the substrate. Therefore it is only possible to conclude that apparently the adhesion strength is higher than the values measured in these tests. In order to overcome this problem, the substrates were strengthened by bonding a thick rigid body on the back of the substrate for the subsequent adhesion strength measurements of the samples with evaporated Ti-Pd interlayers (No. 2). In this case the substrate did not break, but failure always took place in the adhesive with which the studs are bonded on the samples. Again, the adhesion is apparently stronger than the values measured in these tests. Since this did not provide extra information on the metal-ceramic interfacial strength, only a few samples of this type have been measured.

Peel tests.—Three peel measurements were carried out. For practical reasons (sample size) this test was only done with the evaporated Ti-Pd activator layer. From two measurements on one part of the sample a reproducible peel energy of 226 J/m² was measured. From a third measurement on another part of the sample a value of 306 J/m² is obtained. This last measurement was done near to the edge of the substrate where the layer thickness was 30 μm instead of the average value of 40 μm . In Fig. 2 the peel profile is depicted with a corresponding peel energy of 306 J/m².

For reasons described above, only from the peeled samples (with evaporated Ti-Pd) could the fracture surfaces be analyzed. A variety of structures is visible on these surfaces as shown in the SEM micrographs in Fig. 3A to D. On the metal side a large fraction of the surface is covered by individual alumina grains or by larger ceramic pieces (Fig. 3A). On the alumina side, ceramic-ceramic fracture surfaces are seen (Fig. 3B). This means that fracture took place mainly throughout the ceramic. On the relatively smooth surfaces of grains which remained on the substrate, a microroughness becomes apparent (Fig. 3C). This is, however, a relatively small fraction of the whole fractured area. EDX analysis shows the presence of Ni on these alumina grain surfaces. Ni is also detected with a stronger EDX signal at the grain boundaries than on the grain surfaces. On the metal side (Fig. 3D), metal-metal fracture is observed on sites corresponding to substrate grain boundaries. Apparently, the amounts of Ti and Pd on these fracture surfaces are below the EDX detection limit. In order to obtain more detailed information, additional analyses were carried out with static-SIMS.

Interface chemistry analysis by static-SIMS measurements.—In Fig. 4A the positive-ion static-SIMS spectrum of the Al₂O₃ side of the peeled interface (with evaporated Ti-Pd activator layer) is shown. The spectrum is dominated by the Al signal at mass/charge ratio (m/z) 27. Smaller peaks from Ni, Ti, and Pd are also observed. The relatively high intensity of the peaks from alkaline and alkaline earth

metal ions is caused by their high ionization probability. The corresponding spectrum recorded from the metal side of the interface (Fig. 4B) is very similar to the former one, also with a dominating Al signal. This is in agreement with the observation with SEM/EDX that fracture took place mainly through the ceramic. The peaks that are not assigned are mostly due to alkyl fragments, generally observed in such measurements and probably mainly originating from the laboratory atmosphere. These fragments are present in the spectra at m/z 15, 29, 39, 41, 55 and 57. The signal at m/z 39 is due to the hydrocarbon ions $C_3H_3^+$ and to K^+ in a 1:1 ratio. The signal at m/z 27 is mainly due to Al^+ . The peak of $C_2H_3^+$ at m/z 27 has an intensity which is about 10 lower than the intensity of Al^+ .

Once it had become apparent from the SEM/EDX and static-SIMS measurements that fracture took place cohesively, it was also clear that further mechanical characterization could not give any additional information on the interface. Therefore, it was decided that TEM and XPS measurements were more appropriate to investigate the nature of the metal-ceramic interface itself.

Interface structure from cross-sectional TEM.—Cross-sectional TEM micrographs of the samples with sputtered and with evaporated activator films on both types of substrates have been made. In Fig. 5A the micrograph of the sample with the rough-type alumina is shown. The images obtained from samples with sputtered and evaporated layers are similar. In both cases a stack of layers is seen as schematically given in Fig. 1. The ceramic substrates are well covered, and no interface voids are observed. Intimate contact is also observed for the other metal-metal interfaces. At the interface between Ti and alumina (Fig. 5A) a contrast is observed which could be assigned to an interfa-

cial layer of less than 1 nm thickness. However, a clear interfacial layer could not be distinguished in the lattice image observed with high resolution TEM (HRTEM) (Fig. 5B) on the same sample.

Interface formation studied with XPS analyses.—Figure 6 shows the XPS overview spectra, recorded before (Fig. 6a) and after (Fig. 6b) deposition of the Ti wedge. Subsequently, detail spectra of the main Ti peaks from the layer and the main Al and O peaks from the substrate were recorded at five positions on the wedge, each at a different layer thickness. In Table II the peak positions (± 0.3 eV) are listed for the five thicknesses. A rigid shift in the position of the Al and O peaks is observed along the wedge. The mean shift values of the Al and O peaks relative to the reference values,²⁰ were used to correct the position of the Ti peaks for the minor electric charging of the insulating sample. The electric charging decreased with increasing layer thickness, probably due to improved conduction of the thicker Ti layer.

The gradual change in the spectra of the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks as a function of Ti layer thickness can be seen in Fig. 7. The binding energy scale of each curve has been corrected for electric charging as shown in Table II. At the lowest coverage the spectrum is characteristic of TiO_2 , while the spectrum of Ti at the highest coverage is characteristic of metallic Ti (see the reference binding energies in Table II). At intermediate coverages the transition can be followed as a change in relative contribution of both these spectra. For reasons of clarity of presentation the intensity of the spectra has been normalized to the most intense peak of Ti at all coverages. This explains the relatively large amount of noise in the spectra for the lower coverages. Since the increase of the Ti $2p_{3/2}$ peak intensity in the sub-monolayer regime (as determined with the Al 2s intensities)

Fig. 3. (a, top left) SEM fractograph of the metal side: most of the metal fracture surface is covered by alumina grains (right side). On the left side fracture occurred close to the metal-ceramic interface. (b, top right) SEM fractograph of the alumina side: ceramic-ceramic fracture surface at the upper part of the figure. At the lower part the top grains remained on the ceramic. (c, bottom left) SEM fractograph of the alumina side: by EDX it is shown that the roughness on the alumina grains at least partly consists of Ni. More Ni is present at grain boundaries. (d, bottom right) SEM fractograph of the metal side. Metal fracture at positions corresponding with substrate grain boundaries.

Fig. 4. Static SIMS positive-ion spectra of alumina (A) and nickel (B) fracture surfaces. A linear intensity scale is used.

was exactly linear with the position along the wedge as measured in the first 4 spectra (Fig. 7, spectra 1, 2, 3, and 4), it is concluded that the Ti grows in a close to "layer by layer" mode.

It has been established that oxidation of the Ti layer in the vacuum did not influence the measurements. Even after 20 h storage in this environment, only a small change in the shape of the Ti XPS peaks is observed, see curve 5 and 5' in Fig. 7. The peak position did not significantly shift. The other spectra shown in Fig. 6 and 7 were recorded within 1 h after deposition of the metal. From this observation it can also be concluded that other reactions, *e.g.*, with the substrate, do not play a role on this time scale.

Discussion

Adhesion.—In Table III a comparison is made for the adhesion obtained with a wet-chemical activator²¹ and with the Ti-Pd activator. In this table it is shown that with the Ti-Pd activator fracture takes place cohesively and at higher strengths and at higher peel energies than in the case of the wet-chemical activator, where adhesive fracture occurred.

In Fig. 8 the fracture path through the stack of Fig. 1 is schematically shown as observed after the peel test. The dips in the ceramic represent grain boundaries. Fracture takes place mainly through the ceramic substrate but also on some places through the Ni(P) layer. The fracture through the ceramic takes place at a more or less constant depth, relative to the interface. At the places where fracture takes place near to the interface, small particles are observed on the grain surfaces. These particles not only consist of Ti or Ti plus Pd, but also Ni and P are detected at these places with EDX. On the grain surfaces, which are relatively smooth, the possibility of mechanical adhesion is excluded. Therefore, these areas show that the strong adhesion must be due to chemical bonding at the interface.

For the samples prepared with wet-chemical deposition of the Pd nuclei, it has been found that the peel energy is equal to the fracture energy.²¹ For those samples, the peel energy did not depend on the layer thickness. However, for the samples with the vacuum-deposited activator layer, the

situation is somewhat more complicated. Since the adhesion is stronger, peeling only starts at higher loads. In order to avoid plastic deformation of the Ni film, a layer thickness of about 40 μm is chosen, instead of about 10 μm . Still, from the difference in shape of the onset and the end part of the peel curve it is concluded that at least some bulk plastic deformation of the metal film has occurred. This may also explain the dependence of peel energy on location, probably due to variation in layer thickness. An additional phenomenon which may have contributed to the large peel energy, is the formation of many small cracks (pulverization) in the brittle alumina layer which is peeled from the substrate.

Chemical bonding.—The results from the XPS analyses on the Ti layer on the MRC ceramic at the initial stages of deposition show a similar trend to that reported by Chaug *et al.*⁹ who used a polished single-crystal sapphire as the substrate. However, a notable difference seems to be present in the binding energies. Chaug *et al.* found a shift in

Fig. 5. (a, top) Cross-sectional TEM micrograph of sample with evaporated Ti-Pd activator on rough type ceramic. (b, bottom) Cross-sectional HRTEM micrograph of sample with evaporated Ti-Pd activator on rough type ceramic.

Fig. 6. XPS survey spectra recorded from the alumina substrate (A) before and (B) after Ti deposition.

Ti binding energy relative to metallic Ti of 2.6 eV, in between the values reported for TiO (2.1 eV) and Ti_2O_3 (3.7 eV). Therefore, they concluded that the oxidation state of Ti at the interface is between 2+ and 3+. In this work a shift of 4.7 eV is found, corresponding with a 4+ oxidation state. A possible explanation can be found in the layer thicknesses. Chaug *et al.* used layer thicknesses from 0.1 to 0.7 nm Ti on sapphire, whereas in the present case this was 0.02 to 0.35 nm, which is about five times less on the thinnest place. At 0.095 nm the shift (Fig. 6, spectrum 2) has already decreased to 3.9 eV, relative to metallic Ti, close to the value corresponding with Ti^{3+} and approaching the value reported in Ref. 9, obtained at a similar layer thickness. A further reduction in Ti thickness to the extreme submonolayer regime, as reported here, is required to encounter the 4+ oxidation state.

On increasing the Ti layer thickness above about 0.02 nm, the absence of sufficient surface O makes it increasingly difficult for the additional Ti atoms to achieve the 4+ oxidation state. Consequently, lower oxidation states are encountered at lower binding energies. For the thickest layers, metallic Ti is encountered (Fig. 7, spectrum 4, 5). At the higher binding energy side of both these Ti 2p peaks, satellite peaks are observed the absolute intensity of which remains fairly constant with increasing Ti layer thickness. This suggests that at all Ti thicknesses considered, a strongly chemically bonded interface with the Al_2O_3 is formed in the first Ti monolayer.

The results of the XPS measurements also agree with the observation with HRTEM, that no separate, structurally different interfacial reaction layer is formed. An atomically sharp interface is present, although small lattice deformations may be present within 0.5 nm from the interface. It is worth noting in addition that these TEM images were made

Fig. 7. XPS detail spectra of the Ti $2p_{3/2}$ and $2p_{1/2}$ peaks recorded from five places on the Ti wedge: 0.02 nm (1), 0.055 nm (2), 0.095 nm (3), 0.165 nm (4), and 0.32 nm (5). Spectrum 5' was recorded from place 5 after 20 h exposure to the vacuum environment.

Fig. 8. Schematic representation of fracture path through stack. The dips in the ceramic surface represent grain boundaries.

of samples which were several months old and which had been heated for 1 h at 150°C before the DPO test. This means that the sharp interface is very stable under these conditions.

Conclusion

Strong adhesion is obtained between electroless nickel layers and alumina substrates by using vacuum-deposited Ti-Pd activator layers. In the peel tests, cohesive failure takes place mainly in the alumina ceramic. Due to the high interfacial strengths, cohesive failure occurred and with the DPO test only lower limits of the adhesion strength could be obtained. No differences are observed then in the adhesion with sputtered and evaporated Ti-Pd activator films. From the fracture surface analyses it is concluded that the strong adhesion is brought about by interface chemical interactions.

At small coverages, XPS indicates that Ti exists in an oxidized state on the alumina surface, most probably in the 4+ state. With increasing coverage a decrease in the relative amount of oxidized Ti is found. At a few monolayers thick-

Table II. XPS binding energy peak positions (eV) of Al, O and Ti peaks at various Ti layer thicknesses T (nm).

No.	1	2	3	4	5	Ref. 20
T (nm)	0.02	0.055	0.095	0.165	0.32	—
Al	76.1	76.1	75.7	75.1	74.6	74.7 (Al_2O_3)
O	532.6	532.6	532.3	532.0	531.6	531.6 (Al_2O_3)
Ti	459.9	459.2	458.5	455.7	453.8	458.5 (TiO_2), 453.8 (Ti)
Ti^a	458.8	458	457.7	455.3	453.8	

^a After correction for the shift in substrate signals due to electric charging

Table III. Comparison of mechanical data on adhesion with Ti-Pd activator layer and with wet-chemical activator layer.

Substrate	Activator	Strength (MPa)	Peel energy (J/m ²)	Fracture path
HCT	Wet-chemical (21)	12	41	Interfacial
MRC	Wet-chemical (21)	5	8.5	Interfacial
HCT	Ti-Pd	>76	226	Cohesive
MRC	Ti-Pd	>55	—	Cohesive

ness mainly metallic Ti is measured, but most probably, the original oxidized Ti layer is still present. The Ti layer is bonded to the alumina substrate by an interaction of the first monolayer of Ti atoms with oxygen in the top layer of the alumina substrate. It is concluded that this interaction is responsible for the strong adhesion at the metal-ceramic interface. The other interfaces are strong metal-metal interfaces.

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