The influence of substrate chemistry on the adhesion of electrolessly deposited Ni(P) on metal oxide coated ceramics

Citation for published version (APA):

Severin, J. W., Weert, van, A. A. M., & With, de, G. (1994). The influence of substrate chemistry on the adhesion of electrolessly deposited Ni(P) on metal oxide coated ceramics. *Thin Solid Films*, 250(1-2), 115-125.
[https://doi.org/10.1016/0040-6090\(94\)90174-0](https://doi.org/10.1016/0040-6090(94)90174-0)

DOI:

[10.1016/0040-6090\(94\)90174-0](https://doi.org/10.1016/0040-6090(94)90174-0)

Document status and date:

Published: 01/01/1994

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

The influence of substrate chemistry on the adhesion of electrolessly deposited Ni(P) on metal oxide coated ceramics

J. W. Severin, A. A. M. van Weert and G. de With*

Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, Netherlands

(Received December 7, 1993; accepted April 19, 1994)

Abstract

The adhesion of electrolessly deposited Ni(P) on alumina ceramic substrates which were coated with thin SiO₂, SnO₂, TiO₂, Al₂O₃, Y₂O₃, ZrO₂ and (In,Sn)O_x (ITO) films was studied. The adhesion was measured with the aid of the 90° peel test. Strong adhesion of Ni(P) was found for the substrates with ZrO₂ and Al₂O₃ coatings and weak adhesion for the substrates with SiO₂, TiO₂, SnO₂, Y₂O₃ and ITO coatings. The fracture path and the type of interfacial bonding were analysed using scanning electron microscopy, energy-dispersive analysis of X-rays and X-ray photoelectron spectroscopy. In the case of the strongly adhering samples, fracture took place through the metal layer and along the interface. In the case of the weakly adhering samples only interfacial failure was observed between the Ni(P) layer and the metal oxide coating. Cross-section transmission electron microscopy studies of the interfaces suggested that the differences in peel energy values are caused by differences in micromechanical interlocking at the metal oxide–Ni(P) interface. In addition, a weak boundary layer which was found to be present at the Ni(P)–alumina interface was absent in the case of the strongly adhering samples with the ZrO₂ substrate coating.

1. Introduction

Up to now, we have investigated the adhesion of electrolessly deposited Ni(P) on polycrystalline alumina substrates [1–5]. From these studies evidence has been obtained that, in contrast to what is commonly believed [2], the adhesion is influenced not only by mechanical interactions but also by interface chemical interactions [4, 5]. Osaka *et al.* [6] reported similar evidence. This implies that it should be possible to influence the adhesion not only by changing the surface roughness, but also by changing the chemical composition of the substrate surface. This paper describes the results of an investigation into the dependence of the adhesion of electrolessly deposited Ni(P) on the composition of the substrate surface.

This investigation was carried out using a number of metal oxide coatings on polycrystalline alumina ceramic substrates. In order to keep the roughness constant, the same polycrystalline alumina ceramic substrates were used in this study as in the previous studies. Two substrate types, with different roughnesses, were used. On these alumina substrates various metal oxide films were vapour-deposited. The thickness of these films ($\approx 0.1 \mu\text{m}$) was small compared with the roughness of

Electrodeposited Ni	(Approx. 7 μm)
Electroless Ni(P)	(Approx. 0.3 μm)
Metal-oxide substrate coating	(Approx. 100 nm)
Alumina ceramic substrate	

Fig. 1. Schematic presentation of stack of layers used for samples in this study. A metal oxide substrate coating was applied to the alumina substrates followed by electroless deposition of Ni(P). Electrodeposited Ni was finally applied in order to obtain a metal layer with sufficient strength and stiffness for the peel test.

the ceramic substrates. This ensured a constant mechanical contribution to the adhesion, which allows conclusions to be drawn on interfacial chemical effects. For reference, uncoated alumina substrates were also metallized and analysed. A schematic representation of the stack of layers used for samples in this study is shown in Fig. 1.

For the adhesion measurements use was made of the 90° peel test. This test provides information on the intrinsic interfacial interactions [4]. Before and after the required nucleation treatment [1], the surface composi-

*Also affiliated with the Eindhoven University of Technology.

tion was quantitatively analysed with the aid of X-ray fluorescence (XRF) in order to obtain information on the interface formation. The fracture surfaces were analysed with the aid of scanning electron microscopy (SEM), energy-dispersive analysis of X-rays (EDX) and X-ray photoelectron spectroscopy (XPS) in order to obtain information on the fracture path and the type of interfacial bonding. The interfaces of the samples without substrate coating and those of the samples with ZrO_2 and SiO_2 coatings were studied using cross-section transmission electron microscopy (TEM).

2. Experimental procedures

An overview of the approach followed in this study is presented in Table 1. Details of the various steps in Table 1 are described in subsequent sections.

2.1. Sample preparation

2.1.1. Substrates and metal oxide coatings

For the sample preparation a rough-type 96% purity alumina from Maruwa (Seto, Japan) and a smooth-type 99.5% purity alumina from MRC/Coors (USA) were used as the substrates. An impression of the surface roughnesses can be obtained from the SEM micrographs in Figs. 2–6. All metal oxide substrate coatings were deposited by means of e-beam evaporation, except for the $(\text{In},\text{Sn})\text{O}_x$ (ITO) coating, which was deposited by sputtering. The coating thickness was always about $0.1\ \mu\text{m}$ (see Section 3.2). Prior to the deposition of these coatings, the substrates were cleaned by rinsing with ethanol and hexane.

Fig. 2. SEM micrograph of a smooth-type substrate fracture surface of the sample with a ZrO_2 substrate coating after peeling off of the metal film. The white spots are the remaining metal particles.

Fig. 3. SEM micrograph of a smooth-type substrate fracture surface of a sample with an ITO substrate coating after peeling off of the metal film.

TABLE 1. Overview of successive procedures and analyses

Step	Procedure/analysis	Remark
1	Substrate cleaning	Ethanol and hexane rinsing
2	Metal oxide coating	Evaporation: SiO_2 , ZrO_2 , Al_2O_3 , SnO_2 , Y_2O_3 , TiO_2 Sputtering: $(\text{In},\text{Sn})\text{O}_x$ (ITO)
3 ^a	Annealing (A)	1 h, 300 °C, air
4	Surface analysis	XRF
5	Cleaning	Detergent solution
6	Nucleation ^b	Sn, Ag and Pd solutions
7	Surface analysis	XRF
8	Ni(P) electroless deposition	pH = 4.7, 65 °C
9	Ni electrodeposition	Sulphamate bath, 50 °C
10	Peel test	90°, rate 1 mm min ⁻¹ , in air
11	Annealing (B)	1 h, 150 °C, air
12	Peel test	90°, rate 1 mm min ⁻¹ , in air
13	Fracture surface analyses	SEM/EDX and XPS

^aFrom Step 3 onwards uncoated rough-type and smooth-type substrates were also metallized and analysed as reference samples

^bIn the case of the sample with the ITO coating Step 6 was carried out twice due to slow and inhomogeneous initiation after the standard single nucleation procedure

Fig. 4. SEM micrograph of a smooth-type substrate fracture surface of a sample without substrate coating after peeling off of the metal film.

Fig. 5. SEM micrograph of a rough-type substrate fracture surface of a sample without substrate coating after peeling off of the metal film.

Fig. 6. SEM micrograph of a rough-type substrate fracture surface of a sample with a ZrO_2 substrate coating after peeling off of the metal film. The white spots are the remaining metal particles.

The evaporation process was carried out with a Balzers BA510 apparatus, equipped with an e-gun. Oxidic starting materials were used. The process pressure varied from 10^{-6} mbar, which is the background pressure, to 10^{-4} mbar. The deposition rate was 30 nm min^{-1} and the substrate temperature was about 300°C .

ITO was microwave-sputtered using a Perkin-Elmer 2400 system starting from an In/Sn alloy (85/15 at.%). During sputtering, Ar and O_2 , the reactive gas, were introduced at flow rates of 120 and 30 sccm, respectively. The background pressure and the process pressure were 10^{-6} and 7×10^{-3} mbar, respectively. The deposition rate was 10 nm min^{-1} and the substrate temperature was 300°C . Before further processing, all coated substrates were annealed for 1 h at 300°C in air in order to obtain stable, completely oxidized coatings. This step is denoted by “Annealing (A)”.

2.1.2. Metallization

The two substrate types, provided with the various metal oxide coatings, were metallized using the following procedure. The samples were cleaned with a detergent solution and nucleated through successive immersion in solutions containing Sn, Ag and Pd ions [1]. By means of electroless metallization, Ni(P) layers with thicknesses of about $0.3 \mu\text{m}$ were deposited. On top of the electrolessly deposited Ni(P) layers, Ni layers were electrodeposited from a low-stress sulphamate bath. The metal layer thickness was about $7 \mu\text{m}$. The electrodeposited Ni layer was only applied in order to facilitate adhesion measurements, because for the peel test a metal layer with sufficient strength and stiffness is required. Details and backgrounds of the conditions of these wet chemical processes are given in refs. 1 and 4.

2.2. Analyses

The adhesion measurements were carried out with the aid of 90° peel tests as described in ref. 4. The measuring accuracy of this test is within 1% and the reproducibility within 10% [4]. These tests were carried out before and after treating the metallized samples for 1 h at 150°C in air. This annealing treatment is denoted by “Annealing (B)”. SEM/EDX were carried out as described in the same paper [4]. The XPS measurements were done on a PHI 5400 apparatus equipped with a hemispherical analyser, using MgK_α radiation (1253.6 eV) and an emission voltage of 13.5 keV. Calibration was done using the carbon peak. The background pressure was lower than 10^{-9} Pa. The analyser was positioned at an angle of 45° relative to the substrate surface. A depth profile was made by alternately measuring and sputtering with 3 kV Ar^+ ions at a rate of 0.7 nm min^{-1} . By rastering the sputter beam, a crater of $7 \times 7 \text{ mm}^2$ diameter was formed. The information depth was 0.5 to 2 nm, which corresponds to 2 to 10 atomic layers. The spot size was $\approx 2 \text{ mm}^2$. Survey spectra, multiscan detail measurements and depth profiles were made. The exact peak positions were measured using curve fitting. The relative concentrations were calculated from the measured peak areas, assuming a homogeneous surface composition, both

laterally and in depth. For this calculation Perkin-Elmer software was used (ESCA series model 8503A version V4.0 Rev. B 19-02-'91). The dependence of the information depth upon kinetic energy is taken into account in the sensitivity factors in this software. The equipment and measuring conditions for the XRF analyses are described in ref. 7. The sample preparation, the analytical method and the equipment used for the cross-section TEM studies are described in ref. 1.

3. Results

3.1. Adhesion measurements

Table 2 shows the results of the peel measurements. The peel energy measurements show that:

- The peel energy values obtained for the rough-type ceramic are considerably higher than those for the smooth-type ceramic.

- For both the rough- and the smooth-type surfaces and both before and after annealing the highest peel energy values were measured for the ZrO₂ substrate coating.

- The peel energy of the Ni(P)–Ni layers on samples with ITO substrate coatings was below our detection limit of $\approx 0.5 \text{ J m}^{-2}$ for both substrate types. There was virtually no adhesion.

- The peel energy of as-deposited Ni(P)–Ni on the SnO₂ surface was higher than on the uncoated alumina for both substrate types. After annealing the peel value strongly decreased and visual inspection showed that the (yellow) SnO₂ layer had peeled off the alumina ceramic surface.

- The peel energy values of the Ni(P)–Ni layers on the other metal oxide surfaces are higher than those of the uncoated alumina ceramic, both before and after annealing for 1 h at 150 °C, with the exception of the values obtained for the samples with the ITO coating and the Y₂O₃ coating on smooth type substrates.

- In most cases the peel energy after annealing for 1 h at 150 °C was lower than before the annealing.

3.2. Analyses of surface composition

The chemical composition of the substrate surfaces was determined with the aid of XRF before and after the wet chemical cleaning and nucleation treatments. The average thickness of the substrate coating and the coverage by nucleation material were measured. The analysed area was about 20 mm². The relative accuracy of these measurements is estimated to be within 10% in the case of the lower coverages (nucleation material) and within a few per cent for the higher coverages (oxidic layers). The results are presented in Table 3.

The XRF results show that:

- The oxide layer was affected by the nucleation treatment only in the case of samples with the Y₂O₃ substrate coating.

- In the case of samples with the TiO₂- and ZrO₂-coated substrates high coverages of Sn, Ag, Pd and Cl from the nucleation treatment were found compared with the coverage of the uncoated substrate after nucleation. In particular, the coverages of Ag and Cl were very high.

- In the case of the sample with the SiO₂-coated substrate very high Ag and Cl coverages are found. For the other elements from the nucleation treatment the coverages were comparable with those of the uncoated alumina substrate after nucleation.

- The Ag and Pd coverages of the sample with the SnO₂-coated substrate were in the same range as those of the reference sample. This is an indication that Sn from the oxide layer does not play an important role in the nucleation. The same holds for the sample with the ITO substrate coating, which had to be submitted to the nucleation treatment twice in order to achieve quick and homogeneous initiation of Ni(P) deposition. The difference in the thicknesses of the SnO₂ coatings before and after nucleation is too large to be ascribed to

TABLE 2. Peel energy (G_p) values of Ni(P)–Ni bilayers on rough- and smooth-type alumina substrates provided with various thin metal oxide coatings. Peel tests were performed before and after the metallized samples had been annealed for 1 h at 150 °C

Metal oxide substrate coating	Rough-type substrate		Smooth-type substrate	
	As-deposited G_p (J m ⁻²)	Annealed G_p (J m ⁻²)	As-deposited G_p (J m ⁻²)	Annealed G_p (J m ⁻²)
Uncoated	22.7	15.7	3.7	2.3
ZrO ₂	55.9	> 97.3	17.9	15.7
Al ₂ O ₃	39.5	39.0	8.3	13.9
TiO ₂	24.1	26.3	7.9	3.1
SiO ₂	24.1	17.2	4.8	3.1
SnO ₂	30.8	15.5	5.7	1.2
Y ₂ O ₃	25.4	19.1	3.3	2.2
ITO	— ^a	— ^a	— ^a	— ^a

^aBelow detection limit of 0.5 J m^{-2} .

TABLE 3. XRF analyses of the chemical composition of the coated and uncoated substrate surfaces before and after the wet chemical cleaning and nucleation procedures

Substrate coating	Substrate type ^a	Nucleation ^b	Thickness (nm)	Coverage (10^{15} atoms cm^{-2})			
				Sn	Ag	Pd	Cl
SiO ₂	R	B	73	—	—	—	—
SiO ₂	R	A	75	0.74	14.7	0.55	12.4
SiO ₂	S	B	99	—	—	—	—
SiO ₂	S	A	100	0.90	10.1	0.73	8.0
TiO ₂	R	B	100	—	—	—	—
TiO ₂	R	A	98	2.6	15.6	1.9	11.0
TiO ₂	S	B	96	—	—	—	—
TiO ₂	S	A	96	4.1	19.5	2.6	14.9
SnO ₂	R	B	100	—	—	—	—
SnO ₂	R	A	109	— ^c	1.6	0.78	2.2
SnO ₂	S	B	96	—	—	—	—
SnO ₂	S	A	95	— ^c	4.5	0.85	4.2
Al ₂ O ₃	R	A	— ^d	0.23	0.43	0.52	1.3
Al ₂ O ₃	S	A	— ^d	0.19	0.47	0.33	1.5
ZrO ₂	R	B	74	—	—	—	—
ZrO ₂	R	A	74	2.4	12.4	3.2	14.1
ZrO ₂	S	B	65	—	—	—	—
ZrO ₂	S	A	66	1.9	8.2	2.5	9.9
Y ₂ O ₃	R	B	68	—	—	—	—
Y ₂ O ₃	R	A	<1	2.0	2.7	0.93	3.0
Y ₂ O ₃	S	B	67	—	—	—	—
Y ₂ O ₃	S	A	<1	1.2	1.4	0.49	1.1
Uncoated	R	A	—	1.0	2.2	0.61	2.0
ITO	S	A	—	1.8	2.2	0.55	1.9

^aR and S denote rough and smooth types of substrates, respectively.

^bA and B denote after and before wet chemical cleaning and nucleation treatments, respectively.

^cSn from nucleation could not be distinguished from coating material.

^dCoating material could not be distinguished from substrate material.

deposition of Sn as a result of the nucleation treatment. It is therefore probably due to non-uniformity in the as-deposited SnO₂ thickness.

- The Sn and Ag coverages of the sample with the Al₂O₃ coating were a factor of 2 or more lower than measured for all the other samples. The Pd and Cl coverages of these samples were also relatively low.

- The coverage of the nucleation material on the uncoated alumina substrate differs by less than 30% from the values reported earlier on the same type of ceramic [1].

3.3. Fracture surface analyses

3.3.1. SEM/EDX

SEM and EDX analyses led to the following observations on the structure and the chemical composition of the fracture surfaces.

- ZrO₂, Al₂O₃ and TiO₂: EDX measurements showed that the white spots observed on the substrate surfaces for the samples with the ZrO₂ coatings in Figs. 2 and 6 are Ni(P)–Ni particles. Apparently, a high coverage of these particles is present, both at grain boundaries and on grain surfaces. The metal fracture

surfaces showed corresponding images. Zr was not detected on the metal fracture surface. The surface structure of the ZrO₂ film was visible. It was copied in the metal fracture surface. The fracture path was along the interface and through the metal layer. Similar observations were made for the samples with the Al₂O₃ and TiO₂ coatings, but for the latter sample type fewer metal particles remained on the coated substrate surface than for the first two sample types, and hence the failure type was more interfacial.

- SnO₂: an irregular type of surface roughness was observed. The metal and substrate fracture surfaces were covered with particles. With EDX Sn was detected on both the metal and the ceramic side. Apparently, fracture took place through the SnO₂ layer.

- ITO and SiO₂: for samples with the ITO and SiO₂ substrate coatings, complete interfacial failure was revealed by both SEM and EDX. Fracture took place along the interface only (Fig. 3).

- Uncoated and Y₂O₃: interfacial failure was observed. In gaps between surface grains small amounts of remaining metal were observed in the case of the samples with rough-type substrates (Fig. 5) but not in the

case of the samples with smooth-type substrates (Fig. 4). For the samples with Y_2O_3 substrate coatings, Y was not detected with EDX on either side. The structures of the fracture surfaces are very similar to those of the samples without substrate coatings. Apparently, the Y_2O_3 coating has disappeared.

For each substrate coating similar fracture behaviour was observed in the case of the two substrate types, except for a difference in mechanical interlocking which was not observed in the case of the smooth-type substrates. The substrate surface morphology of the coated and the uncoated substrates is very similar. Only a microroughness was observed in the case of some of the substrate coatings, while the uncoated alumina grains generally show smooth crystal faces.

3.3.2. XPS fracture surface analysis

With the aid of XPS the composition and the chemical state of the Ni(P) and metal oxide fracture surfaces of a few samples with strong and weak adhesion were analysed. The samples investigated were those with ZrO_2 , SiO_2 and Al_2O_3 coatings and the one without metal oxide coating, all with smooth-type substrates. The fracture surfaces were analysed after peeling off in a dry nitrogen atmosphere at various depths by sputtering several nanometres deep; see Table 4. The sputter rate was to 0.6 nm min^{-1} .

The following remarks can be made on the XPS results.

- On the metal fracture surfaces the Ni was always in the metallic state. This means that no significant oxidation took place during handling after peeling in the glove box filled with nitrogen. Therefore the oxidation states measured for the other fracture surfaces represent the situation at the interface (Tables 5–8).

- On all substrate fracture surfaces oxidized Ni and P were detected, which indicated that metallization bath compounds were still present in the case of all sample types. Another indication of the presence of remaining bath components is the XPS signal ascribed to an organic sulphur-containing compound, which can only have come from the electroless deposition bath (Tables 5–8).

- On the samples with high peel energy values metallic Ni and P were also detected on the substrate side; in the case of the ZrO_2 substrate coating this was even 50% of the total Ni coverage (Table 5).

- In the case of all samples, Sn, Ag, Pd and Cl, deriving from the nucleation treatment, were detected. The highest coverages of these elements were found on the metal fracture surfaces for all of the samples analysed (Table 4). Generally, Sn and Ag were found in the oxidized state and Pd in the metallic state (not indicated in the tables).

TABLE 4. Chemical composition in at.% of peeled metal oxide and Ni(P) fracture surfaces measured with the aid of XPS before and after sputtering for time t at a rate of 0.6 nm min^{-1}

Surface	<i>t</i> (min)	Surface composition (at.%)											
		C1s	O1s	Ni2p _{3/2}	P2p	S2p	Zr3d _{5/2}	Al2p	Si2p	Sn3d _{5/2}	Ag3d _{5/2}	Pd3d _{5/2}	Cl2p
<i>Sample with ZrO₂ coating</i>													
ZrO ₂	0	29	46	9.5	4.8	—	10.5	—	—	0.3	0.1	—	—
	170	—	63	2.8	0.4	—	23	11	—	—	—	—	—
Ni(P)	0	33	23	30	10.5	—	—	—	—	0.3	2.4	0.5	0.3
	30	—	0.7	90.2	8.3	—	—	—	—	—	0.4	—	—
<i>Sample with Al₂O₃ coating</i>													
Al ₂ O ₃	0	22	47	8.2	3.8	—	—	18	—	0.1	—	—	—
	190	—	59	11	0.8	—	—	29	—	—	—	—	—
Ni(P)	0	39	28	29	1.3	0.3	—	—	—	0.2	0.4	0.1	—
	30	—	—	92.6	7.4	—	—	—	—	—	—	—	—
<i>Sample with SiO₂ coating</i>													
SiO ₂	0	23	51	10.9	1.6	—	—	0.9	13	0.07	0.03	—	—
	190	—	67	1.8	—	—	—	13	18	—	0.1	—	—
Ni(P)	0	38	23	24	11	1.0	—	—	1.3	0.2	0.7	—	—
	30	—	—	93	7.4	—	—	—	—	—	0.6	—	—
<i>Sample without coating</i>													
Al ₂ O ₃	0	19	52	6	1.6	—	—	21	—	0.05	—	—	—
	190	—	64	0.6	—	—	—	35	—	—	—	—	—
Ni(P)	0	38	39	16	6.3	0.4	—	—	—	0.6	0.3	—	—
	30	—	0.7	91	8.0	—	—	—	—	0.2	—	—	—

TABLE 5. Assignment of exact XPS peak positions to chemical compounds on both fracture surfaces of the sample with the ZrO₂ substrate coating

Element	Binding energy (eV)	Relative amount (%)		Environment
		Ni(P)	Substrate	
C1s	284.8	82	94	-C-H
	286.2	8	6	-C-O
	288.4	10	—	-O-C=O
O1s	530.1	—	35	NiO/ZrO ₂
	531.2	78	—	NiO _x
	531.5	—	61	org. -C-H-O
	532.4	22	—	org. -C-H-O
	533.6	—	4	org. -C-H-O
Ni2p _{3/2}	852.7	100	48	Ni, NiP _x
	856.5	—	52	NiO _x
P2p	129.4	29	23	Ni(P)
	130.2	41	—	Ni(P)
	132.9	30	—	PO ₃ , PO ₄
	133.4	—	77	PO ₃ , PO ₄
S2p	161.8	68	—	NiS
	163.1	32	—	org. S
Zr3d _{5/2}	182.1	—	100	ZrO ₂
Cl2p	198.3	100	—	

TABLE 6. Assignment of exact XPS peak positions to chemical compounds on both fracture surfaces of the sample with the Al₂O₃ substrate coating

Element	Binding energy (eV)	Relative amount (%)		Environment
		Ni(P)	Substrate	
C1s	284.8	86	100	-C-H
	286.4	7	—	-C-H
	288.7	7	—	-O-C=O
O1s	531.0	61	56	Ni oxide, Al ₂ O ₃
	532.0	39	44	-C-O
Ni2p _{3/2}	852.7	100	8	Ni, Ni(P)
	854.1	—	92	Ni oxide
P2p	129.0	—	20	Ni(P)
	129.3	31	—	Ni(P)
	129.9	—	7	Ni(P)
	130.2	38	—	Ni(P)
	130.5	—	6	Ni(P)
	133.2	31	6	PO ₃ , PO ₄
	133.8	—	61	PO ₃ , PO ₄
	161.9	63	—	NiS
S2p	163.3	37	—	SO ₃ , SO ₄
	165.8	—	100	C-S org.
Al2p	74.5	—	100	Al ₂ O ₃

● The ratio of the Ni coverage and the coverage of Zr, Si or Al substrate material varied between 1/1 and 1/3 (Table 4). It did not show a correlation with the peel energy.

● The SiO₂ substrate coating was not completely oxidized by the annealing treatment at 300 °C in air (Table 7).

TABLE 7. Assignment of exact XPS peak positions to chemical compounds on both fracture surfaces of the sample with the SiO₂ substrate coating

Element	Binding energy (eV)	Relative amount (%)		Environment
		Ni(P)	Substrate	
C1s	284.8	86	95	-C-H
	286.2	8	5	-C-O
	288.1	6	—	-O-C=O
	288.4	—	—	-O-C=O
O1s	531.2	77	44	Ni oxide, -C-O
	532.8	23	56	SiO ₂
Ni2p _{3/2}	852.7	100	—	Ni, Ni(P)
	856.7	—	100	Ni oxide
P2p	129.3	31	—	Ni(P)
	130.1	36	—	Ni(P)
	132.9	33	—	PO ₃ , PO ₄
	133.2	—	100	PO ₃ , PO ₄
S2p	162.2	69	—	NiS
	163.9	31	—	-S-C
Si2p	102.0	—	9	Si ³⁺ a
	103.2	—	91	≡ Si-OH ^b

^aSubstoichiometric silicon dioxide.

^bSiOH, due to either evaporation or exposure to H₂O in various solutions and in atmosphere [21].

TABLE 8. Assignment of exact XPS peak positions to chemical compounds on both fracture surfaces of the sample with the uncoated alumina substrate

Element	Binding energy (eV)	Relative amount (%)		Environment
		Ni(P)	Substrate	
C1s	284.8	78	97	-C-H
	286.2	14	1	-C-O
	288.4	8	2	-O-C=O
	288.7	—	—	-O-C=O
O1s	531.4	70	80	Ni oxide, Al ₂ O ₃
	532.8	30	20	O-C-
Ni2p _{3/2}	852.4	100	—	Ni, Ni(P)
	856.2	—	100	Ni, oxide
P2p	129.1	21	—	Ni(P)
	130.0	31	—	Ni(P)nnn
	133.4	48	100	PO ₃ , PO ₄
	161.5	25	—	NiS
S2p	162.5	75	—	S-C-, SO ₃ , SO ₄
	165.8	—	100	Al ₂ O ₃

● In the case of the sample with the SiO₂ substrate coating a small Si coverage was found on the Ni(P) fracture surface (Table 4).

3.4. Cross-section TEM interface structure analysis

The cross-section TEM micrograph of a sample with a smooth-type alumina substrate, without metal oxide substrate coating (Fig. 7), shows the presence of a thin interfacial layer between the Ni(P) layer and the substrate. Previous analyses have shown that this layer

Fig. 7. Cross-section TEM micrograph of a sample with a smooth-type alumina substrate and without metal oxide substrate coating.

Fig. 8. Cross-section TEM micrograph of a sample with a smooth-type alumina substrate and with a ZrO_2 substrate coating.

consists of nucleation material and compounds remaining from the electroless metallization solution [4]. Apart from this, a good interfacial contact between the layer and the substrate is observable, at nanometre level. The alumina grain surfaces show relatively large almost atomically smooth areas.

Figure 8 shows a cross-section TEM micrograph of a sample with the same substrate type, but with a ZrO_2 substrate coating. A number of differences with respect to the previous case are evident. The ZrO_2 substrate coating shows a microcrystalline structure, which causes a rough surface, on a nanometre scale. Here again, excellent contact is observed between the Ni(P) layer and the metal oxide material. However, the previously observed interfacial layer is not observed in the case of this sample. The implications of these observations for adhesion will be discussed in Section 4. Because the tilt angle of this sample in the TEM was optimized in order to

obtain a sharp image of the Ni(P)– ZrO_2 interface, the interface between ZrO_2 and the alumina substrate seems diffuse. With a different tilt angle, however, a sharp image of the latter interface was obtained, within the resolution of the TEM of approximately 0.3 nm.

The metal layer of the sample with the SiO_2 substrate coating was detached from the substrate surface during the TEM sample preparation due to its weak adhesion. Therefore information on the interface structure could not be obtained. However, unlike the ZrO_2 coating, the structure of the SiO_2 substrate coating was too amorphous and had a very smooth surface. The smoothness was similar to that of the uncoated alumina grain surfaces.

4. Discussion

The influence of various processing parameters upon the adhesion of electrolessly deposited Ni(P) to alumina ceramics is reviewed in ref. 2. The conditions of the etching treatment were found to be of much greater influence on the adhesion strength than the nucleation and metallization conditions. Therefore it is the general opinion of most researchers in the field that the adhesion is controlled by mechanical interactions between the Ni(P) layer and the rough ceramic surface due to mechanical interlocking. Etching causes the removal of the glass phase from between surface alumina grains, which results in a surface roughness with a characteristic dimension of several micrometres. Only Osaka *et al.* [6] found evidence that other, non-mechanical, interfacial interactions contribute to the adhesion.

In a previous study using cross-section TEM [4] we discovered that an amorphous layer 1–2 nm thick was present at the interface between the electroless Ni(P) layer and the alumina ceramic substrate. Fracture surface analyses with the aid of XPS, static SIMS and SEM/EDX showed that fracture always took place through this layer, except in interlocking places. The interfacial layer consisted of all compounds present in the metallization solution and of nucleation material. The cohesion of the material within this layer was therefore of decisive influence on the adhesion of Ni(P) to smooth-type substrates, where evidence for the occurrence of mechanical interactions was not obtained. A peel energy of 8.5 J m^{-2} was measured for these smooth-type substrates. A much higher peel energy of 44 J m^{-2} was measured for the rough-type substrates, which is largely explained by mechanical interactions. After annealing of these samples at temperatures above 250°C , a two- to threefold higher peel energy was measured [5]. Since the fracture path remained through the interfacial layer, the improved adhesion was ascribed to stronger cohesion within the layer after annealing.

With a vacuum-deposited Pd nucleation layer, with an underlying Ti adhesion promoter layer, excellent adhesion was found of Ni(P) to alumina ceramics. Fracture took place cohesively in these systems [3]. The strong adhesion was explained by the absence of the amorphous interfacial layer as demonstrated by cross-section TEM. This allowed strong interfacial metal-metal bonds to be formed.

The results of these previous investigations demonstrate the importance of the interfacial layer for the adhesion. We assume that this layer is formed as a result of incomplete removal of the metallization solution from the hydrophilic substrate surface by the newly formed Ni(P) metal phase at the initial stages of the metallization process. After the evaporation of water, the dissolved bath components remain at the interface and prevent intimate contact on an atomic scale and thus direct chemical interactions between the metal layer and the substrate. This explains why the adhesion of Ni(P) directly to the alumina ceramic depends so much on the nature of mechanical interactions. In the present discussion the question is whether the improvement of the adhesion of Ni(P), observed for some of the metal oxide substrate coatings, is caused by interfacial chemical interactions or mechanical interactions.

4.1. Adhesion mechanism

The oxidized Ni and P species, the nucleation material and the sulphur compounds, detected with the aid of XPS on fracture surfaces of all of the sample types, indicate the presence of similar compounds as found in the previous studies [4, 5]. On the other hand, the TEM cross-section micrograph of the sample with the ZrO₂ substrate coating does not show a discrete interfacial layer. Therefore it can be concluded that the material detected with the aid of XPS as described above did not form a continuous layer. It was probably present in the pores of the ZrO₂ layer surface. The absence of the interfacial layer allows direct contact between the Ni(P) layer and the substrate. The first possibility, therefore, is that interfacial chemical interactions, due, for example, to differences in acid-base properties of the metal oxide surfaces [8–10], have a much greater effect on the adhesion of this type of system than on that of the system without substrate coating.

The second possibility is the occurrence of more efficient mechanical interactions. Whereas the substrate roughness on a micrometre scale was not influenced by the thin substrate coatings, a strong increase in roughness was observed on a nanometre scale. It is well known [11–15] that e-beam evaporated metal oxide films have porosities of 10–30%, in spite of a deposition temperature of about 300 °C. The material may grow in columns and open gaps may remain between these columns [16]. In addition, films with other microstructures,

such as fine-grained or amorphous films, can also contain various types of pores. If these gaps or pores are wider than a few nanometres, Ni(P) is likely to penetrate and form microscopic anchoring sites. The Ni(P) films generally follow the surface topography of the substrate on this scale [1, 4, 5]. This type of roughness was termed microroughness by Venables [17], who observed an improvement of adhesion of polymer layers to phosphoric acid anodized aluminium due to roughness structures of 5–10 nm.

For the high coverages with nucleation material, indicated in Table 3, the porosity of the metal oxide substrate coatings may play an important role. The higher coverages correspond to up to 25 monolayers of solid material, and are much higher than observed for nucleation of alumina ceramic surfaces, both in ref. 1 and in this work; see also Table 3. Vapour-deposited metal oxide coatings can absorb water [18] and therefore nucleation material can penetrate into the coating. The analysis depth of the XRF measurement is such that all nucleation material present in the substrate coating is detected, whereas in XPS measurements only the outermost 3 nm are analysed. This can explain the fact that the amount of nucleation material measured with the aid of XPS is of the order of 0.1 monolayer for both fracture surfaces together. The deposition of the nucleation material can be described by the same processes as reported in ref. 1 for the non-porous alumina ceramic surface. The high coverages of Ag and Cl, relative to those of the other elements used in the nucleation treatments, can possibly be explained by precipitation of AgCl. The AgCl precipitation may be enhanced by inefficient rinsing due to the porosity. The valencies of Ag and Pd, determined via the XPS multi-scan measurements of the fracture surfaces, are in agreement with the proposed processes during nucleation [1].

4.2. Remarks on Y₂O₃, SnO₂ and ITO substrate coatings

With EDX Y was not detected on the metal and substrate fracture surfaces of the samples with the Y₂O₃ substrate coatings. The XRF measurements before and after nucleation show that Y disappears already in the acidic nucleation treatment. This may explain the observation that these samples behaved very similarly to the samples with the uncovered substrates, as far as the coverage with nucleation material, the peel energy values and the structure of the fracture surfaces are concerned.

The results obtained for the ITO substrate coatings are remarkable. In the case of both substrate types the peel energy was extremely low; see Table 2. This is an indication that both mechanical interactions and chemical interfacial interactions are very weak. The initiation on the ITO-coated substrates was slow and the Ni(P)

coverage was incomplete after a standard single activation procedure. Therefore the samples used in this study were subjected to the nucleation procedure (step 6 in Table 1) twice and the coverages indicated for ITO in Table 3 refer to this repeated nucleation procedure. With this repeated procedure quick initiation was observed, but still the adhesion was very poor. More detailed investigations are required before explanations or even reasonable speculations can be formulated.

It should be noted that even in the case of the samples with high peel energy values the metal oxide substrate coatings were not removed from the alumina ceramic. This means that the adhesion of the metal oxide coatings to the alumina ceramic was generally very strong. Only in the case of the SnO_2 substrate coating was failure observed in the coating. However, this was of cohesive type in the SnO_2 layer and, for unknown reasons, it was only observed after annealing at 150 °C.

4.3. Final remarks

The reason for the variable change in peel energy after annealing of the metallized samples at 150 °C is not clear. Similar changes have been observed in a previous study into the influence of thermal treatments on the adhesion of Ni(P) to uncoated smooth-type and rough-type substrates [4]. Only at temperatures above 250 °C was a clear increase in peel energy and adhesion measured. A possible explanation for the decrease in peel energy could be the evaporation of water from the porous substrate coatings or from the interfacial layer and the build-up of pressure under the Ni(P) films. However, there are some arguments against this assumption: firstly, blisters have not been observed; secondly, different changes were sometimes observed for rough-type and smooth-type substrates; thirdly, the adhesion to the non-porous uncoated alumina substrates also decreased upon annealing and finally, debonded areas have never been observed in TEM and SEM cross-sections. Therefore, it must be concluded that this matter remains unclear.

The real widths of the interfaces between Ni(P) and metal oxide and between metal oxide and the alumina substrate are probably much smaller than those found with the XPS depth profiling measurements. This difference is due to several effects. In the first place, with an information depth of 3 nm, the underlying material is already detected whereas the actual interface lies still 3 nm deeper. Secondly, in the case of a rough surface the angle between the sputter beam and the surface varies strongly according to the position on the substrate; consequently, the sputter rate is not constant over the substrate surface [19]. Thirdly, the angle of the sputter beam relative to the surface generally differs from that of the analyser; this causes shadow effects on a

rough surface. Fourthly, redeposition of sputtered material may take place in valleys and gaps in rough surfaces. Finally, when the chemical composition of a surface is laterally inhomogeneous, local differences in sputter rate may arise as a consequence of preferential sputtering.

The peel energy values reported in this work for the samples with the uncoated rough-type and smooth-type substrates of 22 and 3.5 J m⁻², respectively, are considerably lower than the values of 44 and 8.5 J m⁻² measured using the same substrates in previous studies [4, 5]. This difference is caused by a greater internal stress in the electrodeposited Ni top layer, as confirmed by a measurement with the aid of a deposit stress analyser. This does not have consequences for the relative differences between peel energy values measured for the various sample types in this study as they were all prepared using the same Ni electrodeposition solution and had the same internal stress in the electrodeposited Ni top layer. The differences in peel energy between the various sample types are consistent for the rough-type and smooth-type samples. Moreover, the differences in the fracture paths of samples with low peel energy and samples with high peel energy strongly suggest that these differences are caused by differences in intrinsic adhesion, not by differences in bulk properties of the metal layers.

5. Conclusions

The adhesion of electrolessly deposited Ni(P) to alumina ceramics can be greatly increased by using approximately 0.1 µm thick e-beam evaporated ZrO_2 and Al_2O_3 coatings. Other oxidic substrate coatings such as e-beam evaporated SiO_2 and TiO_2 do not lead to a greatly increased adhesion. The adhesion to a sputtered ITO coating was very weak, the peel energy being below our detection limit of 0.5 J m⁻². The Y_2O_3 coating was not stable during wet chemical processing and in the case of the SnO_2 coating cohesive fracture took place in the oxidic coating at a low peel energy. A correlation between the peel energy and the coverage of nucleation material or the coverage of Pd was not found.

Cross-section TEM analyses suggest that the stronger adhesion of Ni(P) to the substrates with metal oxide coatings, relative to the adhesion to uncoated substrates, can be explained by differences in roughness on a nanometre scale. The surface structure of the adhesion-promoting metal oxide layers is assumed to cause micromechanical interlocking. In addition, stronger chemical interaction may play a role in the case of these samples because these samples, unlike those without substrate coating, did not have a weak boundary layer.

Acknowledgment

The authors would like to thank J. van Glabbeek for the deposition of the metal oxide coatings, C. Geenen for the SEM micrographs, T. Verspaget for the XRF measurements, A. de Veirman and A. Staals for the TEM cross-section micrographs, and C. van der Marel and F. van der Weegberg for the XPS measurements.

References

- 1 J. W. Severin, H. van der Wel, R. Hokke and G. de With, *J. Electrochem. Soc.*, **140** (1992) 682.
- 2 J. W. Severin and G. de With, *J. Adhesion Sci. Technol.*, **7** (1992) 115.
- 3 J. W. Severin, H. van der Wel, R. Hokke, M. T. Johnson and G. de With, *J. Electrochem. Soc.*, **140** (1993) 1611.
- 4 J. W. Severin, R. Hokke, H. van der Wel and G. de With, *J. Appl. Phys.*, **75** (1994) 3402.
- 5 J. W. Severin, R. Hokke, H. van der Wel and G. de With, *J. Electrochem. Soc.*, **141** (1994) 816.
- 6 T. Osaka, Y. Tamiya, K. Naito and K. Sakaguchi, *J. Surf. Finish. Soc. Jpn.*, **40** (1989) 835.
- 7 D. K. G. de Boer, J. J. M. Borstrok, A. J. G. Leenaers, H. A. van Sprang and P. N. Brouwers, *X-Ray Spectrometry*, in press.
- 8 G. A. Parks, *Chem. Rev.*, **52** (1965) 177.
- 9 G. A. Parks and P. L. de Bruyn, *J. Phys. Chem.*, **66** (1962) 967.
- 10 F. M. Fowkes, *J. Adhesion Sci. Technol.*, **1** (1987) 7.
- 11 G. G. Long, D. R. Black, A. Feldman, E. N. Farabaugh, R. D. Spal, D. K. Tanaka and Z. Zhang, *Thin Solid Films*, **217** (1992), 113.
- 12 A. G. Dirks and H. J. Leamy, *Thin Solid Films*, **47** (1977) 219.
- 13 M. Lottiaux, C. Boulesteix, G. Nihoul, F. Varnier, F. Flory, R. Galindo and E. Pelletier, *Thin Solid Films*, **170** (1989) 107.
- 14 A. Feldman, X. Ying and E. Farabaugh, *Appl. Opt.*, **28** (1989) 5229.
- 15 E. Farabaugh, A. Feldman, J. Sun and Y. N. Sun, *J. Vac. Sci. Technol.*, **A5** (1987) 1671.
- 16 H. A. Macleod, *Opt. Thin Films, SPIE Proc.*, **325** (1982) 21.
- 17 J. D. Venable, *J. Mater. Sci.*, **19** (1984) 2431.
- 18 H. A. Macleod and D. Richmond, *Thin Solid Films*, **37** (1976) 163.
- 19 A. Benninghoven, F. G. Rüdenauer and H. W. Werner in *Secondary Ion Mass Spectrometry*, Wiley, New York, 1987, p. 204.
- 20 J. W. Severin, *Thesis*, Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA, Eindhoven, The Netherlands, 1993.
- 21 M. L. Miller and R. W. Linton, *Anal. Chem.*, **57** (1985) 2314.