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The Influence of Thermal Treatments on the Adhesion of Electrolessly Deposited Ni(P) Layers on Alumina Ceramic

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ABSTRACT

The adhesion of electrolessly deposited Ni(P) on 96 and 99.5% pure alumina was studied as a function of annealing temperature, up to 580°C. The adhesion was measured with the direct pull-off test and the peel test. The interface structure was analyzed with cross-section transmission electron micrographs. Fracture surfaces were analyzed with scanning electron microscopy/energy dispersive x-ray analysis, static-secondary ion mass spectroscopy, and x-ray photoelectron spectroscopy. The optimum annealing temperature was found to be 400°C, at which an increase in peel energy and adhesion strength by a factor of two to three was measured, with respect to the as-deposited value. The weak boundary layer, which was previously reported to be present in this system, is still present after annealing and the fracture path remains through this interfacial layer of a few nanometers in thickness. Therefore, the adhesion improvement is ascribed to stronger cohesion of the material in the weak boundary layer.

Electroless metallization of oxidic surfaces is frequently used for electronic applications. The thermal behavior of the metal-ceramic interface is of great importance for these applications. Thermal shocks occur with soldering and thermal cycling is a standard test procedure for most electronic parts. Retention of strong adhesion is required since differences in thermal expansion, for example between electronic components and the printed-circuit board or between metal layers and substrates cause mechanical stresses. Interfacial fracture may rapidly lead to electronic failure.

Ni(P) denotes the amorphous, nonstoichiometric Ni and P containing alloy which is formed by electroless deposition from an Ni bath containing a hypophosphite reducing agent. Depending on the pH value of the bath, the P content may vary between 3 and 13 weight percent (w/o). In our case the P content is 10 w/o. In Ref. 1 and 2 backgrounds of the electroless metallization process and properties of the deposits are described. Literature data of the adhesion of electrolessly deposited Ni(P) layers on alumina ceramic have been reviewed elsewhere.³

Generally, the adhesion strength of metal layers on oxidic substrates increases with annealing temperature.^{4,5} An annealing treatment after deposition might therefore be a simple method for improving the adhesion of electrolessly deposited Ni(P) layers. However, for Ni(P) on 96% pure alumina diverging results on the effect of temperature upon adhesion have been reported, as measured with the direct pull-off (DPO) test. Honma and Mizushima⁶ found an increase in adhesion strength with annealing time and annealing temperature. The greatest effect, an increase of a factor of three to four, was found after annealing for 1 h at 250°C in air. In contrast, in a later publication than Ref. 6 Honma and Kanemitsu⁷ did not measure significant changes in the adhesion strength after annealing at 250°C in air for between 0.5 and 24 h, with respect to the as-deposited value. In addition, Osaka *et al.*⁸ did not find significant differences between the adhesion strengths before and after annealing for 1 h in vacuum at temperatures of 300 and 500°C. Since these literature data do not allow a definitive conclusion to be drawn on the influence of thermal treatments upon the adhesion, more insight into this matter is required.

On the basis of adhesion strength data only, as measured by the direct pull-off (DPO) test in the references cited above, it is very difficult to explain changes in the adhesion. According to the Griffith-Irwin theory, the adhesion strength is determined on the one hand by interfacial interactions on a molecular scale (intrinsic adhesion) and on the other hand by the size of interfacial flaws due to, for example, pores or foreign particles. Strength is thus a hybrid

quantity. See Ref. 9 and 10 for a general discussion on this matter. For that reason not only adhesion strength measurements but also fracture energy measurements were performed in this study, which provide information on the intrinsic adhesion. Moreover, various interfacial analyses were carried out in order to obtain more information on changes of the intrinsic adhesion with annealing temperature. The approach for both the mechanical and the interfacial analyses was similar as described in Ref. 11.

In previous investigations,^{11,12} cross-sectional transmission electron microscopy (TEM) micrographs revealed the presence of an interfacial layer between the alumina substrate and the Ni(P) layer for as-deposited samples. The thickness of this interfacial layer was a few nanometers. Static secondary ion mass spectroscopy (static-SIMS) and x-ray photoelectron spectroscopy (XPS) analyses of the fracture surfaces showed that this interfacial layer mainly consisted of remaining components of the metallization solution (Ni^{+2} , PO_4^{3-} , Na^+ , Cl^- , and organic complexing agents

Fig. 1. Peel energy G_p vs. annealing temperature T of samples with smooth-type (circle symbols) and rough-type (solid dot and square symbols) alumina substrates for samples annealed for 1 h in vacuum. The numbers along the line with solid dot symbols represent the cumulative annealing time (min) in air.

Fig. 2. Relative decrease in peel energies by placing a water drop at the peel front for samples with rough-type substrates, heat-treated at various temperatures T . G_p denotes the peel energy measured in laboratory air (circles) and ΔG_p the relative decrease in peel energy due to water (solid dots).

acetate, lactate, or glycine, depending on bath composition) and of nucleation material (Sn, Ag, Pd, and Cl ions). Moreover, these analyses showed that fracture took place through this layer. The cohesive interactions within this layer are therefore considered to be of decisive influence for the fracture energy. In this paper an analysis will be made of how the interfacial interactions and the fracture path change for samples that have received a heat-treatment.

Experimental Procedures

Sample preparation.—For the sample preparation a rough-type 96% pure alumina and a smooth-type 99.5% pure alumina were used as the substrates, both from Maruwa. These ceramic substrates were cleaned with a detergent, etched with an HF solution and nucleated with solutions containing Sn, Ag, and Pd salts. The resulting coverage by nucleation material amounts to ca. $3 \cdot 10^{15}$ atom/cm².¹² By electroless metallization using an OMI Enlyte 512 bath, Ni(P) layers of about 0.3 μm thickness were deposited. On top of these layers, Ni layers were electrodeposited from a low-stress sulfamate bath. The total metal layer thickness was about 2 μm for the DPO test samples and about 7 μm for the peel test samples. Details of materials, solutions, and deposition conditions are given in Ref. 11 and 12.

The electrodeposited Ni layer was only applied in order to facilitate adhesion measurements. For the peel test a metal layer with sufficient strength and stiffness is required. For the DPO test the electrodeposited Ni layer prevents the penetration of the epoxy adhesive of the pull studs into cavities of the rough substrate surface during bonding. However, as described in subsequent sections, in certain cases the electrodeposited Ni layer may influence the results of adhesion measurements after thermal treatments. Therefore, in order to eliminate this possible influence, a number of measurements also were performed on samples without electrodeposited nickel. For these samples Ni(P) layers were electrolessly deposited with a thickness of 2 to 4 μm . After metal deposition, the samples were annealed at temperatures between 100 and 600°C. Details of the annealing conditions are given in the adhesion measurement section.

Analyses.—The adhesion strengths were measured by the DPO test. An aluminum pull-stud (QUAD Sebastian) was bonded with an epoxy adhesive to the metallized ceramic surface by heating for 1 h at 160°C and the force at which fracture occurs at the metal-ceramic interface was measured using a testing machine (ELE 205) at a cross-head speed of 0.5 mm/min in air atmosphere. All adhesion measurements were performed at room temperature ($21 \pm 2^\circ\text{C}$). The diameter of the bonded area was 2.5 mm, the height of the studs was 12.5 mm, and the angle between nail head and shank of the stud was 140° . The thickness of the adhesive layer varied between 2 and 10 μm and no interfacial voids were observed in cross sections. At the edge of the stud an adhesive spew fillet of about 0.1 mm was formed. For the strength the nominal value given by the pull-off force divided by the bonded area under the stud was used.

The fracture energy was measured using the 90° peel test at a cross-head speed of 1 mm/min. A 1N load cell was used and the overall measuring accuracy was $<1\%$. The metal strips were cut with a razor blade to a length of about 50 mm and a width W of 15 mm. More details on the adhesion measurements are given in Ref. 11. The influence of humidity upon the fracture energy was measured by peeling after applying a drop of water at the peel front.

Scanning electron microscopy and energy dispersive x-ray analysis (SEM/EDX), cross-sectional transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS) and static-SIMS analyses were carried out as described in the same paper.¹¹ For the static-SIMS analyses, the metal layers were peeled in the vacuum chamber of the apparatus in order to avoid contamination of the fresh fracture surfaces in the air. The crystallization of the samples with an electrolessly deposited Ni(P) layer only, was followed by x-ray diffraction (XRD).

Results

Adhesion measurements.—Peel tests.—The peel test results are shown in Fig. 1. The relative accuracy of the peel test results is within 10%.¹¹ This accuracy is mainly determined by the reproducibility of the sample preparation. The lower line with open circle symbols represents the peel energy *vs.* annealing temperature for samples with smooth-type substrates. These samples were annealed for 1 h in vacuum. From 150 to 580°C an increase in peel energy is observed of a factor of two to three. Samples without electrodeposited Ni, onto which electroless Ni(P) layers with a thickness of ca. 3.5 μm was applied, could only be peeled after annealing at temperatures of 200°C or lower. For as-deposited samples and samples annealed for 1 h at 150 and 200°C in air, peel values of 2.8, 4.3, and 5.1 J/m², respectively, were recorded. Samples annealed at higher temperatures could not be peeled because the peel strip broke before peeling started, owing to increased brittleness of the Ni(P) material caused by annealing.

The peel energy *vs.* annealing temperature for samples with rough-type substrates is represented by the line with the square symbols in Fig. 1. These samples were provided with an electrodeposited Ni layer as described before. They were heat-treated for 1 h each at a different temperature in vacuum. After an initial decrease in peel energy by about 30% after annealing at 150°C, a gradual increase of up to a factor of three is observed after annealing at 450°C.

The line with solid dot symbols in Fig. 1 represents the peel energy *vs.* annealing temperature in the range between room temperature and 300°C for a sample with the rough-type alumina substrate. In this experiment the coating was first partially peeled and then alternately annealed in air and partially peeled further. Annealing was done by placing the sample in a preheated furnace and taking it out after the annealing time. Every time annealing was done for a longer time or at a higher temperature, resulting in a cumulative thermal load of the sample. The numbers along this line in Fig. 1 denote the cumulative annealing time for each temperature. Due to oxidation of the nickel layer in air, no annealing temperature higher than 300°C could be applied in this experiment. Similarly as for the other mea-

Fig. 3. Direct pull-off adhesion strengths (σ_f) vs. annealing temperature for samples with 2 μm electroless Ni(P) only. The symbols $\circ$ and $\times$ represent samples with smooth-type and rough-type substrates, respectively.

measurements with samples with smooth-type and rough-type substrates, adhesion improvement with temperature was found for this sample with the rough-type substrate. The initial decrease in peel energy was not observed for this sample with this annealing procedure. For Fig. 2 the measurement of peel energy vs. annealing temperature for samples with rough-type substrates, with square symbols in Fig. 1, was repeated. Furthermore, the relative decrease ΔG_p is shown which was found after a drop of water had been placed at the peel front. This relative decrease is significantly higher for samples annealed at temperatures above 250°C than for samples annealed at lower temperatures. These results will be discussed in the subsection on mechanical behavior in the Discussion.

Since plastic deformation may contribute to peel energy values, it was necessary to estimate relative changes in the yield strength of the metal layer due to the thermal treatments. This was done by hardness measurements using the Vickers test. With an indentation load of 0.01N, Vickers hardness values of 400, 130, and 100 MPa were measured for samples annealed at 150, 250, and 450°C, respectively. This means that a decreasing trend in the hardness of the metal layer was observed with increasing temperature. To eliminate the influence of changing mechanical properties of the electrodeposited nickel layer, the DPO tests were performed with samples with only electrolessly deposited nickel.

DPO tests.—Since electrodeposited Ni had not been applied for the DPO test samples, a much thicker electrolessly deposited Ni(P) layer was applied with a layer thickness of $2 \pm 0.4 \mu\text{m}$. The DPO strength vs. annealing temperature is plotted in Fig. 3 for samples with the rough-type and the smooth-type substrates. The numbers of test samples and the standard deviations are given in Table I. The samples were annealed for 1 h in an argon atmosphere at the top temperature indicated in the figure. Since pull-studs were bonded with an epoxy adhesive at 150°C for the DPO test, DPO strength values of the as-deposited sample could not

be obtained. At temperatures of 250°C or lower no systematic trend was observed in the adhesion strength, but at 300 and 400°C a two- to three-fold increase in the adhesion strength was clearly seen. For both substrate types a remarkable decrease in the DPO strength was measured after annealing at 500°C.

The XRD pattern of the DPO samples with rough-type and smooth-type substrates annealed at temperatures lower than 400°C only showed a broad band due to an amorphous Ni(P) phase, apart from peaks originating from the alumina substrates. The samples annealed at 400°C gave rise to an Ni_3P diffraction pattern. In addition, a small contribution from amorphous material was still observed. The XRD patterns of samples annealed at 500°C showed peaks characteristic of Ni_3P and Ni phases. With these samples an indication of the presence of an amorphous phase was not visible in the XRD patterns anymore.

Interface and fracture surface structure.—**SEM/EDX.**—In order to explain the large differences in peel energies between the two substrate types, cross sections were made of the metal-ceramic interfaces. Optical micrographs of these cross sections, shown in Fig. 4, show the penetration of the metal layer into the surface pores of the rough-type substrates. This type of roughness with narrow structures and cavities is difficult to measure with, for example, a step-profiler. It is obvious that this roughness gives rise to a much stronger adhesion due to mechanical interlocking than on the smooth-type substrate surface shown in Fig. 4B, where such interlocking structures are not present. The SEM micrographs of rough-type alumina fracture surfaces of samples annealed at 150 and 450°C, shown in Fig. 5, reveal a larger density of remaining metal particles on the sample annealed at the higher temperature. On the smooth-type alumina fracture surfaces (not shown), such remaining metal particles were not found for samples annealed at 150, 320, and 450°C. With EDX, nevertheless, a very small Ni signal was observed for the sample annealed at 320°C and a stronger Ni signal for that annealed at 450°C. When a relatively large area of about 50 μm diam was scanned with the electron beam, the same intensities were found as when a small area of about 1 μm on a smooth alumina grain surface was irradiated. This means that a very thin, Ni containing layer is present all over the alumina fracture surfaces of smooth-type samples annealed at 320 and 450°C. Ni was not detected with EDX on the surface of the sample annealed at 150°C.

Cross-sectional TEM.—The TEM images shown in Fig. 6 provide information on the material structure both at the interface and in the bulk of the metal layers after annealing at 150 and 580°C in vacuum. The columnar structure of the as-deposited Ni(P) material (Fig. 6A) has completely disappeared after annealing at 150°C (Fig. 6B) and 580°C (Fig. 6C). Instead, microcrystalline particles are observed, and extensive microcracking has taken place all over the Ni(P) layer and in all directions (Fig. 6C). The size of these microcrystals is too small to give rise to a crystalline-type XRD pattern. On top of the microcrystalline Ni(P) layer, Ni crystals are visible from the electrodeposited Ni layer. No cracks along the metal-ceramic interface are observed. The interfacial layer which is observed for the low-temperature sample remains present after annealing (Fig. 6D). The con-

Table I. Mean adhesion strength σ_f of electroless Ni(P) on rough- and smooth-type alumina ceramic as a function of annealing temperature T as measured by the DPO test. N is the number of test samples and s_x is the standard deviation in the mean.

T (°C)	Rough-type substrates			Smooth-type substrates		
	N	σ_f (MPa)	s_x (MPa)	N	σ_f (MPa)	s_x (MPa)
150	21	16.4	0.9	20	28.2	3.3
200	21	25.0	1.8	21	19.1	1.4
250	19	20.2	1.6	19	19.2	2.2
300	19	44.8	2.3	19	39.9	5.0
400	21	51.6	2.3	21	53.1	2.9
500	21	27.4	1.8	20	17.9	3.4

Fig. 4. Optical micrographs of cross sections of samples with rough-type substrate (A, left) and smooth-type substrate (B, right).

Fig. 5. SEM micrographs of rough-type alumina fracture surfaces from samples annealed at 150°C (A, left) and 450°C (B, right). The sample annealed at the higher temperature shows more remaining metal particles on the substrate surface. Some of the metal particles are indicated with arrows.

trast between the interfacial layer and the neighboring phases is much weaker for the annealed sample than for the as-deposited sample. This may be an indication that the density of the interfacial layer increases upon annealing.

XPS fracture surface analyses.—With XPS the fracture surfaces were analyzed of samples with rough-type substrates, annealed at 150 and 450°C in vacuum. The peel energy values of these samples are given in Fig. 1 (square symbols). The SEM micrographs of the alumina fracture surfaces of these samples are depicted in Fig. 5A and B. For the XPS analyses fresh fracture surfaces were prepared by peeling a small part of the film in a glove box filled with N_2 , with less than 0.2 ppm O_2 and H_2O . After peeling, the Ni(P) and alumina fracture surfaces were transferred in a vacuum-tight vessel into the XPS apparatus. The surface compositions of the Ni(P) and alumina fracture surfaces of both samples are listed in Table II. The relative accuracy of the XPS relative coverages is within 10%. The spot area during the XPS measurement was *ca.* 2 mm², which means that the results are not influenced by inhomogeneities with the size of a few micrometers.

All surfaces show a similar coverage with C, which is probably at least partly due to organic contaminations in the XPS apparatus or during handling. For that reason, the coverage with this element will not be discussed further. More remarkable is the relatively high coverage of the alumina fracture surfaces with Ni. For both annealing temperatures the intensity of the Ni signal is in the same range as that from Al from the substrate. After annealing at 150°C the Ni/Al ratio is 1.05 and this changes slightly to 1.25 upon annealing at 450°C. The P coverage on alumina is considerably higher after annealing at the higher temperature. This

is also the case for the P coverage on the Ni(P) fracture surface after annealing at the higher temperature. This points to enrichment of the interface with P, originating from the Ni(P) bulk. The oxygen content on the alumina surface does not differ for the two temperatures and is probably determined by the oxidic bulk. The nucleation material remains almost entirely on the Ni(P) fracture surface and the coverage is lower after annealing at the higher temperature. Apart from P, S also tends to segregate to the interface at higher temperatures as observed on the Ni(P) fracture surface. This element probably originates from the SO_4^{2-} ions in the electroless metallization solution. Another interesting observation is the significantly lower amount of O after annealing at 450°C. Al was not detected on the Ni(P) side, which means that few or no alumina grains are detached from the substrate surface during peeling.

An assignment of the peaks of the elements listed in Table II to compounds, ions, or molecules with relative amounts, obtained by multiscan measurements, is listed in Table III. The relative coverages are given in atom percent (a/o). Reference data are used from Ref. 13.

Ni and P which are present on the alumina fracture surface after peeling are entirely (Ni) or for the greater part (P) in the oxidized state, for both annealing temperatures. On the Ni(P) fracture surface Ni and P are for a greater part in the metallic state after annealing at 450°C than after annealing at 150°C. At the lower temperature the ratios Ni^{n+}/Ni^0 and P^{n+}/P^0 are 3.8 and 2.3 while at the higher temperature these ratios are 1.4 and 1.5, respectively. Nickel-carbon compounds were not formed at either temperature.

Static-SIMS measurements.—The alumina and nickel fracture surfaces of the annealed and as-prepared samples

Fig. 6. TEM cross section images of samples with smooth-type substrates. (A, top left) as-deposited; (B, top right) after annealing at 150°C; (C, bottom left) after annealing at 580°C; and (D, bottom right) as C.

were analyzed with static-SIMS. Since peeling was done inside the static-SIMS apparatus, only samples with low peel energy and therefore only samples with smooth-type substrates could be analyzed in this experiment. The change in relative intensities of various inorganic fragments in the static-SIMS spectra contained interesting information on the change in the composition of the fracture surfaces. An overview of the most important results for the alumina fracture surfaces is given in Table IV. The intensities are normalized to the most intense peak from the substrate, which is Al^+ for the positive ion spectra and O^- for the negative ion spectra. The intensity ratios listed in Table IV are obtained from two different positions on the fracture surfaces. For each measurement the analyzed area is about $2000 \mu\text{m}^2$. The spread in results represents the spread in surface composition. The accuracy of the relative static-SIMS intensities is on the order of 10%.

The positive and negative ion spectra of the alumina fracture surfaces of an as-prepared sample and a sample annealed at 450°C are shown in Fig. 7. The $^{58}\text{Ni}^+/\text{Al}^+$, PO_2^-/O^- , and PO_3^-/O^- intensity ratios in Table IV show a strongly increasing coverage of Ni and P containing compounds with increasing annealing temperature. The nucleation elements Sn, Ag, and Pd were also detected on the nickel fracture surface but the signal intensity of these elements was too weak for significant changes in relative coverages to be observed. The relative coverage of F decreases with increasing temperature while increasing relative intensities are observed for Cl and Na. This may be associated either with diffusion and segregation or with a different fracture path, a point which will be discussed in greater detail in the following section.

Discussion

Mechanical behavior.—Energy balance.—During peeling, energy is consumed by fracture (G_c) and possibly by

bulk plastic deformation of the film (G_{def}), while energy is supplied externally by peeling (G_p) and internally by relaxation of residual stresses present in the film (G_{el}). Therefore, the following energy balance is valid for the peel test¹¹

$$G_c = G_p + G_{\text{def}} - G_{\text{el}} \quad [1]$$

All energy terms are per unit area. The fracture energy term G_c is made up of an intrinsic contribution, which represents the energy required for breaking interfacial bonds, and a dissipation contribution which is due to crack-tip plasticity.¹⁴ The influence of each of these terms upon the peel energy G_p will be considered in the discussion which follows.

Residual strain energy.—In a previous investigation¹¹ it has been shown that built-in elastic strain energy due to the deposition process itself does not play a significant role in the energy balance. As shown in the discussion below, the internal strain energy due to thermal effects are more important. The amount of energy per unit area G_{el} , stored in the metal layer at elevated temperatures owing to the difference in thermal expansion coefficients $\Delta\alpha$ between the layer and the substrate, can be estimated with Eq. 2¹¹

$$G_{\text{el}} = \frac{DE(\Delta\alpha\Delta T)^2}{2} \quad [2]$$

where D is the metal layer thickness, E is the Young's modulus of the layer and ΔT is the temperature difference with the deposition temperature. G_{el} is about 11 J/m^2 for the current layer thickness of $7 \mu\text{m}$ in the peel test with ΔT is 550°C, E is 200 GPa,¹ and $\Delta\alpha$ is $6 \cdot 10^{-6} \text{ K}^{-1}$.^{1,15} This means

Table II. Relative atom concentrations (%) on the Ni(P) and the Al₂O₃ fracture surface of samples with rough-type substrates after annealing at 150 and at 450°C.

Surface	T (°C)	C 1s	O 1s	Ni 2p	Al 2p	P 2p	Sn 3d	Ag 3d	Pd 3d	S 2p
Al ₂ O ₃	150	14.6	53.1	15.6	14.9	1.9	—	—	—	—
Al ₂ O ₃	450	14.6	52.6	14.5	11.5	6.8	—	—	—	—
Ni(P)	150	14.0	41.5	40.7	—	2.6	0.2	0.2	<0.1	0.8
Ni(P)	450	15.2	31.7	43.2	—	6.6	—	<0.1	0	3.4

“—”: Below detection limit.

that the layer on the smooth-type sample can spontaneously debond at 580°C because the thermal elastic strain energy exceeds the initial fracture energy of 8.5 J/m² (Fig. 1). The fact that this spontaneous debonding was not observed can be explained by increased intrinsic interfacial bonding, exceeding the buildup of thermal elastic strain energy. From Eq. 2 it also follows that no residual strain energy is present in the Ni(P)/Ni layers after annealing, owing to differences in thermal expansion between the metal layer and the substrate, since the temperature at which the peel measurements are carried out (room temperature) is only slightly lower than the deposition temperature of the electrodeposited Ni layer (50°C). Only irreversible changes in the metal layers such as plastic deformation due to thermal stresses during annealing, or crystallization shrinkage of Ni(P), can cause residual stresses. The elastic strain energy G_{el} , associated with such stresses is released upon debonding and lowers the peel energy G_p , measured; see Eq. 1. Accordingly, these processes cannot cause an increase in peel energy with annealing temperature. If such irreversible processes, such as the crystallization of Ni(P), have introduced additional residual strain energy G_{el} , then the actual fracture energy G_c has increased more than the measured increase in peel energy G_p .

Changes in plasticity.—As we see in Eq. 1, various other phenomena may contribute to the increase in peel energy with increasing annealing temperature. First, the intrinsic adhesion due to interfacial interactions may have become greater, thereby increasing G_c . Second, more energy may be dissipated by plastic deformation at the crack tip. This also increases G_c . Third, more energy dissipation may take place in the bulk of the film during peeling (G_{def}). The hardness measurements showed a decreased hardness of the electrodeposited Ni film with increasing annealing temperature so that more plastic deformation can be expected to take place during peeling in the bulk of the film, G_{def} . On the other hand, the hardness of the underlying electrolessly deposited Ni(P) layer, relative to the as-deposited value¹ increases by a factor of two upon annealing at 450°C. Therefore, near the crack tip, a decreasing amount of energy can probably be dissipated with increasing temperature (G_c). Since two counteracting effects may play a role in the contribution of plastic deformation to the peel energy, it is difficult to estimate the overall change in plasticity during peeling as a consequence of thermal treatments.

Because of changes in plasticity described above, it is difficult to draw definite conclusions as to changes in interfacial bonding on the basis of these peel tests only. However, the samples without electrodeposited Ni, on which a relatively thick electroless Ni(P) layer was deposited, provided additional evidence for enhanced interfacial interactions. As described in the subsection on Adhesion Measurements, an increase in peel energy with annealing temperature was measured for these samples in the limited temperature range of 20 to 200°C. In addition, the results of the DPO tests, for which similar samples were used, showed the same trend as the peel test results. Consequently, the increased DPO strength cannot be ascribed to increased plasticity of the metal layer, because the Ni(P) metal layer becomes more brittle during annealing below 500°C. Hence, it must be concluded from the whole set of adhesion measurements that the improved adhesion is brought about by stronger interfacial interactions.

The peel energy values, shown in Fig. 1 for the smooth- and rough-type substrates differ by a factor of about three to five. On the other hand, the DPO strength values, shown in Fig. 3 for the two substrate types, do not differ largely. Assuming other influencing factors to remain constant, one should expect a similar behavior for the peel energy and the DPO test results. According to the Griffith-Irwin theory, strength is proportional to the square root of the fracture energy and inversely proportional to the square root of the size of critical flaws. These flaws are small, nonbonded areas which are virtually always present at an interface. In Ref. 6 this theory is used to interpret adhesion strength and fracture energy data for two types of Ni(P) on the same smooth and rough types of substrates. In that case also a high DPO strength was found for samples with low peel (fracture) energy. According to the Griffith-Irwin theory, this indicates the presence of very small defects of <10 µm for the high strength samples, instead of the usual 100 to 200 µm for the other samples. Presumably, similar effects concerning flaw sizes play a role here. This could be related to small gas bubbles entrapped on the roughness of the substrate. Such a bubble can easily give rise to a flaw of 100 to 200 µm, as was just mentioned.

Intrinsic adhesion.—For the intrinsic adhesion, mechanical interlocking effects should be distinguished from chemical interfacial effects. The large differences between the peel energies on smooth- and rough-type substrates are probably caused by differences in mechanical interlocking. This interlocking is likely to take place in the open pores near the surface of the rough-type substrate shown in Fig. 4, but not for the smooth-type substrate which has little porosity. However, the change in adhesion on each substrate type due to thermal treatments cannot be explained by differences in mechanical interlocking. Ni(P) does not flow into pores upon heating and increasing brittleness of Ni(P) would rather lead to a smaller mechanical interlocking contribution. It is, therefore, more likely that chemical interfacial interactions are enhanced by annealing. The effect of water upon the peel energy (Fig. 2) is consistent with this interpretation. Water has a greater effect on the peel energy of samples annealed at the higher temperatures than that of the samples annealed at the lower temperature. Water may promote the breaking of interfacial chemical bonds, including Van der Waals interactions, but it is not expected to influence mechanical adhesion.

Interface chemistry.—For the samples with the rough-type substrates, the XPS analyses did not provide evidence for a change in the fracture path. The amount of Ni detected with XPS after fracture on the substrate surface was the same for samples annealed at high and at low temperature. The amounts of aluminum on the substrate surface were also constant. The XPS measurements indicated rather a change in the chemical composition of the interface. On the metal fracture surface of the sample annealed at the higher temperature, less oxygen and oxidized Ni and P were measured, and the nucleation material had largely disappeared, probably by diffusion into the metal bulk. Nevertheless, the SEM micrographs show a significantly larger coverage of torn metal pieces on the alumina substrate surface for the sample annealed at 450°C, compared with the sample annealed at 150°C. Since the Ni(P) cannot flow into substrate surface pores, it must be assumed that

Table III. Assignment of exact peak positions to the chemical environment of the same sample as measured in Table II.

Element	Position (eV)	Relative amount (%)		Environment
		150°C	450°C	
Al ₂ O ₃ surface				
C	284.8	90	90	—C—H
	286.5	10	10	—C—O
O	531.0	100	100	Al ₂ O ₃
P	129.5	15	15	Ni(P)
	132.5	85	85	PO ₄
Ni	856.2	100	100	Ni ₂ O ₃ , Ni(OH) ₂ , NiPO ₄
Al	73.8	100	100	Al ₂ O ₃
Ni(P) surface				
C	284.8	85	85	—C—H
	288.5	15	15	—O—C=O
O	531.5	100	100	PO ₄ , Ni(OH) ₂ or Ni ₂ O ₃
S	162.1	100	100	NiS
Sn	486.0	100	—	Sn oxide
Ag	367.5	100	100	Ag oxide
Pd	335.2	100	—	Pd metallic
P	133.5	70	60	—PO ₄
	129.5	30	40	NiP
Ni	852.5	21	42	Metallic Ni, Ni(P)
	856.2	79	58	Ni(OH) ₂ , NiPO ₄ , Ni ₂ O ₃

the mechanical interlocking remained constant during annealing, and therefore that the higher coverage of nickel particles indicates a stronger intrinsic adhesion. This higher metal particle coverage does not become apparent in a higher XPS Ni coverage of the alumina surface of the sample annealed at 450°C.

According to the XPS measurements, the Ni coverage of the alumina fracture surfaces is similar to the Al coverage, although the SEM micrographs show a metal particle coverage of only a few percent at most, as visually estimated; see Fig. 5. This confirms the assignment of the Ni and P XPS coverage to the interfacial layer a few nanometers thick, observed with TEM. The crack proceeds through this interfacial layer, leaving behind an Ni containing surface layer all over the alumina fracture surface, which layer is far too thin to be observed with SEM. Only the small amount of P which is assigned to Ni(P) in the multiscan XPS measurements of the alumina surface can be explained by the metal particles. Hence, the fracture for the samples with rough-type alumina proceeds mainly through the interfacial layer and passes through the metal only at interlocking sites. The crack does not enter the ceramic. Because of a stronger intrinsic adhesion for the samples annealed at the higher temperature, it is more difficult to pull out metal from interlocking sites, and this may explain the higher density of metal particles.

The changes in relative coverage of Ni and P containing species with annealing temperature, measured by static-SIMS on the alumina fracture surfaces of samples with smooth-type substrates, are different from those measured with XPS on rough-type substrates as discussed above. With static-SIMS an increasing Ni and P coverage was found with increasing annealing temperature, whereas with XPS this coverage was constant. The cause of this

difference between both substrate types is not understood. To avoid possible uncertainties in the interpretation of the relative static-SIMS intensities, the smooth-type alumina fracture surfaces were therefore also measured with EDX and the increasing coverage was confirmed. For the samples on which Ni was found with EDX, it proved to be present all over the smooth-type substrates, not on interlocking sites because such sites could not be discovered on the smooth-type substrates. A possible explanation might have been that more Ni particles remained on the smooth-type alumina at higher annealing temperature. Such pieces were not found with SEM up to the highest magnification of 40,000 times. It is therefore more probable that the remaining Ni and P on the smooth-type substrates originate from the interfacial layer discussed before. This means that an increasing fraction of the interfacial layer remains on these substrate with increasing temperature. Because of the high surface sensitivity of the static-SIMS technique, an Ni and P surface layer with a mean thickness of 1 or 2 nm can dominate the spectrum.

For samples which have not been annealed, the larger part of the nucleation material was detected on the metal side, too, as for the samples annealed at 150°C, as described in more detail in Ref. 11. In that case also, Ni and P ions and other compounds of the metallization bath were found on the substrate fracture surface. Therefore, in this respect the situation after annealing is similar to the one before annealing, implying that diffusion probably did not play a role here. We believe that a liquid film penetrates underneath the metal film as soon as the Ni(P) nuclei, including the nucleation material, have grown out and form a continuous but still porous film. After drying the sample, the bath compounds remain present at the interface, located underneath the metal film and thus underneath the nucleation material. Only for the sample annealed at 450°C and analyzed with XPS, evidence has been obtained for diffusion of nucleation material into the metal bulk, due to the decreased coverage.¹

The stress which caused the extensive microfracture in the Ni(P) layer which was observed with TEM, may have arisen as a consequence of lateral shrinkage of the Ni(P) material during crystallization. During annealing the adhesion of the Ni(P) layer both to the substrate and to the electrodeposited layer was apparently stronger than the cohesion because cracks along the interface were not observed. Moreover, the brittleness of the Ni(P) material increases during crystallization thereby promoting microcracking. Additional stress is probably introduced into the Ni(P) layer during annealing owing to thermal-expansion differences between the electrodeposited Ni layer and the substrate. Despite the increased brittleness of the Ni(P) phase and despite the microcracks in this layer, the fracture

Table IV. Relative intensities in static-SIMS spectra from alumina fracture surfaces as a function of annealing temperature for samples with a smooth-type substrate.

Rel. Int.	Temperature (°C)			
	As prep.	200	450	580
Ni ⁺ /Al ⁺	0.157	0.219	1.026	8.338
Ni ⁺ /Al ⁺	0.162	0.2802	1.2417	4.095
Na ⁺ /Al ⁺	0.0690	0.0626	1.014	14.389
Na ⁺ /Al ⁺	0.0857	0.0521	1.161	4.762
PO ₄ ⁻ /O ⁻	0.095	0.0979	0.2018	0.489
PO ₄ ⁻ /O ⁻	0.0709	0.0852	0.166	—
PO ₃ ⁻ /O ⁻	0.096	0.0788	0.1736	0.592
PO ₃ ⁻ /O ⁻	0.0775	0.0731	0.146	—
F ⁻ /O ⁻	0.1814	0.0658	0.0406	0.035
F ⁻ /O ⁻	0.0973	0.0568	0.0400	—
Cl ⁻ /O ⁻	0.0166	0.0172	0.0746	0.109
Cl ⁻ /O ⁻	0.0172	0.0153	0.0546	—

Fig. 7. Static-SIMS spectra of the alumina fracture surfaces of samples with rough-type substrates and acetate-type Ni(P) before and after annealing. Peeling was done in the vacuum of the analyzer. A linear intensity scale is used. A, Positive-ion spectrum of an as-prepared sample; B, positive-ion spectrum of a sample annealed at 450°C; C, negative-ion spectrum of an as-prepared sample; and D, negative-ion spectrum of a sample annealed at 450°C.

is found to proceed through the interfacial layer at the metal-ceramic interface.

Conclusion

An improvement by a factor of two to three in the adhesion of electroless Ni(P) to alumina is observed with both peel tests and DPO tests after annealing at temperatures above 250°C. Fracture surface analyses with SEM/EDX, XPS, and static-SIMS show that, irrespective of the annealing treatment, fracture occurs through an interfacial layer of a few nanometers thickness, observed with cross-sectional TEM. It is therefore concluded that the adhesion improvement is due to stronger cohesion within this interfacial layer. With TEM, indications were obtained for densification of the interfacial layer by annealing. With static-SIMS and XPS, changes were observed in the chemical composition of the fracture surfaces.

The contribution of mechanical interlocking for the rough-type substrate cannot be changed with heat-treatment of the metallized samples. Therefore, the adhesion improvement is entirely ascribed to a larger contribution by chemical interactions. The same holds for the smooth-type substrates, for which evidence for mechanical interlocking was not obtained at all. The greater effect of water on the fracture energy of samples annealed at the higher temperatures is consistent with this explanation.

Since only DPO results are reported in the literature, a comparison between the present results and literature data must be made using the strength results only. The strong dependence of the DPO strength on temperature in the range between 200 and 300°C (Fig. 3), may explain the divergent results reported in the literature, as summarized in the introduction. Thus, small changes in processing may lead to large changes in DPO strength, at temperatures of about 250°C. The fact that the sharp decrease in DPO strength observed after annealing at 500°C is approxi-

mately equal to those observed after annealing at 100 to 200°C, is consistent with literature reports. However, at about 400°C, where we have measured the highest DPO strengths, literature reports have not been found.

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Chemical Vapor Deposition of Silicon from Disilane under Reduced Pressure in a Circular Impinging Jet Reactor

Simulation and Experiments

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ABSTRACT

The chemical vapor deposition of silicon from disilane under reduced pressure in an impinging jet reactor has been studied experimentally and simulated numerically by a 2D model. The measured deposition rate and profile have been compared to the results of the calculations performed with various hypotheses concerning both gas-phase and surface reactions. The influence of the number of species considered, of the kinetic rate constants, and of the models used for the reactive sticking coefficient of silane and disilane were investigated. Among the 17 species that may be present in the gas phase, a mechanism including 8 silicon-carrier species has been determined to represent satisfactorily the deposition rate and profile experimentally observed.

Chemical vapor deposition (CVD) is a method widely used to deposit a large diversity of materials such as pure elements, compounds, solid solutions, and composites.¹ Further improvement and comprehension of the CVD processing technology is largely dependent on our ability to develop reliable predictive modeling. These simulation models provide reliable predictions of the growth rate profiles. Recent publications have shown relatively successful modeling of carbon incorporation,² microscopic step-coverage,³ self-limiting growth inhibition,⁴ and selectivity.⁵ Other properties such as microstructure or surface morphology are studied experimentally. Any significant progress in this field seems far away.

Here, we look at the influence of both homogeneous and heterogeneous chemistry on the growth rate of silicon deposits.

It is well known that a deposition process involves three basic transport phenomena (*i.e.*, motion, energy, and mass) governed by a set of coupled partial differential equations, together with gas-phase and surface-reaction kinetics. Since Eversteyn *et al.*,⁶ boundary layer models were used extensively to describe the flow field for a long time in the CVD process.⁷⁻¹⁰ In the early 1980s, real progress was achieved in solving the complete set of governing equations. After detailed analysis of flow structures with 2D or 3D models, the increasing power of supercomputers allows an increasingly accurate description of all coupled phenomena including chemical reactions.

It is common to use simplifications for modeling either the chemical mechanisms involved or the flow fields. A schematic chemical model of only one species, one surface reaction, and no gas-phase reaction was considered by Wahl¹¹ for the 2D modeling of a stagnation point flow reac-

tor. Such a model was used recently by Snyder *et al.* for CdTe deposition.¹²

In contrast, complicated chemical reaction systems were taken into account by Michaelidis and Pollard,¹³ Rebenne and Pollard^{14,15} approaching the flow by the 1D similarity equations, and Coltrin *et al.*^{16,17} using a 2D flow model with boundary layer simplifications, or the 1D similarity equations applied to the rotating disk flow.¹⁸ It is only since 1984 that real improvement in modeling CVD reactors have been observed. 2D and even 3D geometry now is treated together with a realistic gas-phase and surface chemical mechanism. We may quote the works of Moffat and Jensen,^{19,20} who have used a fully parabolic flow approximation in axial direction for a 3D horizontal reactor. In a similar reactor geometry, Gokoglu *et al.*²¹ have studied the silicon deposition with a more detailed 3D flow treatment. In a confined 2D axisymmetrical reactor, Fotiadis *et al.*²² have carried out a detailed study of the velocity profiles for various reactor shapes. Kleijn *et al.*^{23,24} studied silicon deposition with a 2D model including multicomponent diffusion.

Axisymmetrical reactors present attractive features. It is the only configuration that can be treated as two-dimensional. It can be assumed even one-dimensional in the vicinity of the axis by suitable transformations. The assumptions required for such a 1D treatment have been discussed for stagnation point flow²⁵ and for rotating disk²⁶: flow field can be treated as 1D only when the border effects can be neglected and the buoyancy is absent, otherwise 2D models must be used.

With better master of flow treatment, the main difficulty remains our ignorance of the chemical mechanism or the reaction kinetic rates. The Si-H system is one of the most studied because of silicon applications to the electronics-