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A Study on Changes in Surface Chemistry during the Initial Stages of Electroless Ni(P) Deposition on Alumina

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ABSTRACT

The formation of the interface between electrolessly deposited Ni(P) and an alumina substrate is investigated. Prior to metallization, the substrate is cleaned, etched, and activated with Sn, Ag, and Pd-containing solutions. Changes in surface chemistry due to these pretreatments are analyzed with XRF and static-SIMS. TEM plan-view micrographs visualize the changes in surface structure during the pretreatments. The initial stages of metallization are measured on Si$_3$N$_4$ membrane substrates. Cross-sectional TEM micrographs are made of a thin Ni(P) film on the alumina ceramic, showing a columnar Ni(P) structure, a thin interfacial layer, and an intimate interfacial contact. Possible consequences for initiation and adhesion are discussed.

The metallization of alumina ceramic surfaces with electroless Ni(P) is often used in the electronics industry, among other things for IC packaging, printed circuit, and sensor applications. The use of alumina offers the advantage of a relatively high substrate thermal conductivity compared to other insulators, combined with a low cost price. To reach the required properties of the Ni(P) layer, besides the bulk composition and properties of the Ni(P) material, the processes that occur at the substrate surface before deposition are also important. The cleanliness, the chemical composition of the substrate surface, and the nucleation all influence the initiation and the subsequent adhesion both during and after deposition.

Generally, three different goals can be distinguished for the pretreatments. First, adsorbed organic contaminations and particles are removed in a cleaning step. Second, by etching the substrate, the surface roughness is increased and possible sites for mechanical interlocking are created to improve adhesion. Third, by the nucleation procedure the substrate surface is made catalytic for electroless deposition.

Many aspects of nucleation on the substrate surface have been investigated. For the nucleation procedures a one-step and a two-step process have been distinguished. For the one-step nucleation, samples are immersed in a SnCl$_2$-PdCl$_2$ colloidal solution. In the two-step procedure, substrates are sensitized by immersion in a SnCl$_2$ containing solution and activated with a PdCl$_2$ solution. According to Svendsen et al., the one-step nucleation procedure is not suitable for alumina substrates. This is confirmed by Honma and Kanemitsu who reported that with a two-step procedure the adhesion of Ni(P) on alumina is 30% to 50% stronger than with a one-step procedure, as measured by the direct pull-off technique.

Here, a two-step procedure is studied including an intermediate immersion in an Ag-containing solution between the Sn and Pd steps. Therefore, this nucleation procedure henceforth is referred to as three-step nucleation. This three-step procedure on glass substrates has many advantages that high (3000-5000 in the mass range from 20 to 150 amu) mass resolution of the spectra, m/Am at half peak height, is expected that the relevant properties are sufficiently similar. The changes in surface structure during these process steps are analyzed on nanometer scale with TEM. Since plan-view TEM micrographs cannot be made using ceramic substrates, Si$_3$N$_4$ membranes are considered to be the best alternatives and are therefore used as model substrates. It is reasonable to expect that the relevant properties are sufficiently similar for the purposes of this study: Cross-sectional TEM micrographs are made of Ni(P) layers on the alumina ceramic after deposition of 50 to 100 nm Ni(P).

Experimental Procedures

Polycrystalline 95% alumina substrates were used with 4% glass phase, mainly present at grain boundaries (Hoechst Rubalit 708). As shown by chemical analysis these substrates contained 441 wt ppm Na, 231 wt ppm K, 1.23 weight percent (w/o) Si, 0.55 w/o Mg, ±0.3 w/o Ca, and 0.2 w/o Fe. The Si$_3$N$_4$ model substrates were prepared as given in the literature. Prior to metallization, the substrates were cleaned, etched, and nucleated successively in the aqueous solutions listed in Table I. After each step the samples were rinsed in demineralized water. All immersion times were 2 min except for the metallization step, where samples were immersed for 6 and 30 s. The Si$_3$N$_4$ model substrates were not etched because the membranes are attacked by HF solutions. A commercially available electroless Ni(P) metallization bath (Enlyte 512 from OMI) was used. The conditions under which it was operated are listed in Table I. The bath contained NiCl$_2$, NaH$_2$PO$_2$, acetate, and lactate complexing agents.

The equipment and experimental conditions for the XRF and static-SIMS analyses are described in Ref. 20 and 22, respectively. A reflection-type time-of-flight static-SIMS apparatus (JonTOF Münster) is used for the surface analysis of the first monomolecular layers of the surfaces. The mass resolution of the spectra, m/Am at half peak height, is that high (3000-5000 in the mass range from 20 to 150 amu).

<table>
<thead>
<tr>
<th>Step</th>
<th>Function</th>
<th>Solution</th>
<th>T (°C)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cleaning</td>
<td>Surfactant</td>
<td>40</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>Etching</td>
<td>Diluted HF</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Sensitization</td>
<td>SnCl$_2$</td>
<td>20</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4</td>
<td>Intermediate</td>
<td>AgNO$_3$</td>
<td>20</td>
<td>~10</td>
</tr>
<tr>
<td>5</td>
<td>Activation</td>
<td>PdCl$_2$</td>
<td>20</td>
<td>&lt;2</td>
</tr>
<tr>
<td>6</td>
<td>Metallization</td>
<td>Electroless bath</td>
<td>65</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table I. Process steps in sample preparation with bath temperature and pH.
Table II. Coverage (10^15 atom/cm^2) of alumina substrates after various pretreatment steps for electroless metallization.

<table>
<thead>
<tr>
<th>Step</th>
<th>Sn</th>
<th>Ag</th>
<th>Pd</th>
<th>Cl</th>
<th>Si</th>
<th>Cu</th>
<th>K</th>
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<td></td>
<td></td>
<td>17</td>
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<tr>
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<td>14</td>
<td>4.2</td>
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<tr>
<td>2</td>
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<td></td>
<td></td>
<td></td>
<td>19</td>
<td>2.8</td>
<td>0.6</td>
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<tr>
<td>3</td>
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<tr>
<td>3</td>
<td>0.71</td>
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<td>4</td>
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<tr>
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<td>1.4</td>
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</tr>
<tr>
<td>5</td>
<td>0.71</td>
<td>1.3</td>
<td>0.6</td>
<td>1.7</td>
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</tbody>
</table>

When the coverage was below the detection limit this is indicated with —; the asterisk is explained in the text.

Fig. 1. SEM micrograph of alumina surface (a, top) before; and (b, bottom) after etching in HF solution.

that peaks from the metal ions can be separated from those of the hydrocarbon ions of the same nominal mass.

Plan-view TEM micrographs were taken on a Philips EM 300 transmission electron microscope at an electron energy of 100 keV. Cross-section TEM micrographs of the metal-ceramic interface were taken using a Philips EM 400 transmission electron microscope at an electron energy of 120 keV. Samples were prepared by grinding, polishing, and ion milling as described in Ref. 23.

Measurement Results

**SEM results.**—Before and after etching in the HF solution, SEM micrographs were made from the alumina surfaces (Fig. 1a and b). In these micrographs two effects can be seen from the etching treatment: the first is that the grain surfaces become less smooth and the second that gaps appear between the grains. This is caused by the removal of the glass second phase during etching.1,3

**XRF results.**—With XRF, the surface composition was measured quantitatively after each subsequent process step as listed in Table I. For each step three samples were measured. The analyzed surface was about 20 × 30 mm^2. The results are given in Table II. The coverages are expressed in 10^15 atom/cm^2 which is of the order of a monolayer of solid material. The detection limits are 0.02 for Sn, 0.1 for Ag, 0.1 for Pd, 0.1 for Cl, and 1 for Na, respectively. The relative accuracy is estimated to be within 10%. The surface coverage of the glass phase elements Si, K, Ca, and Na in Table II was obtained from the difference in the absolute amounts measured before and after etching in HF solution. The values indicated with step 1 therefore represent the original surface coverage and in the subsequent steps these values are taken to be zero, indicated by *

The Sn, Ag, Pd, and Cl coverages measured with XRF range from 0.5 to 2 × 10^15 cm^-2 using the present experimental procedures. Cl was present only after the Pd step. The coverages vary by up to 50% of the maximum values in Table II using identical procedures and solutions, with samples prepared immediately after one another. A similar spread in coverages also was reported by Meek using high-energy ion-scattering surface analysis.

**Static-SIMS results.**—Static-SIMS was used to analyze the Al_2O_3 samples, also before and after the treatments listed in Table I. Figures 2a and b show, as typical examples, positive-ion static-SIMS spectra of the surface before the cleaning step (Fig. 2a) and after activation step 5 with a PdCl_2-containing solution (Fig. 2b). An overview of the most relevant static-SIMS results from both the positive and the negative-ion spectra is given in Table III.

Due to the high sensitivity of the static-SIMS technique, many peaks are measured of which only the most intense

Fig. 2. Positive-ion static-SIMS spectra of the alumina surface (a, top) before the cleaning step; and (b, bottom) after the activation (Pd) step.
After deposition of about 0.1 μm electroless Ni(P) (step 6), no signals originating from Al, Sn, Ag, or Pd were found due to the static-SIMS information depth of about 1 to 2 nm. The strongest peaks in these spectra were those from the native oxide on a closed Ni(P) layer (Ni²⁺, PO₃⁻, and PO₄⁻). TEM results.—Figure 3a shows a plan-view TEM micrograph of a Si₃N₄ membrane after cleaning and sensitization (step 3). A structure of chains and islands of particles of a few nanometers in size was observed. The background shows the structure as observed on a blank sample. A similar structure was observed after subsequent immersion in an ammoniacal AgNO₃ solution. As shown in Fig. 3b, also after the subsequent activation with a PdCl₂ solution, no significant changes were observed. The larger particles which appear in Fig. 3c (after 6 s metallization) are interpreted as the first Ni(P) nuclei. As can be seen in this figure, these nuclei started to grow from the clusters of primary activator particles. This micrograph was made at the earliest possible stage of growth, since at the bottom righthand-side the growth had not yet started. As observed in Fig. 3d, larger particles were formed from the nuclei, covering the whole surface after 30 s of metallization.

In Fig. 4 a cross-sectional TEM micrograph is shown of a thin Ni(P) film on an alumina substrate. Between both phases a layer of 1 to 2 nm thickness with an amorphous structure is observed. Good interfacial contact is observed on all micrographs, no voids or interface gaps are discernible within the resolution of these micrographs (about 0.5 nm). The structure of the material close to the interface also can be observed. On the micrographs the diffraction lines of the crystalline alumina grains are visible. In addition, a branching structure of Ni(P) columns indicates the coalescence of the initially formed small primary particles to fewer broader columns during the growth process. The Ni(P) layer thickness of this sample was of the order of 50 to 100 nm.

Discussion

In spite of many studies devoted to the nucleation of surfaces for electroless deposition, no consensus has been reached on the chemical processes that take place during this process. 17,25,26,28-33 This study is not aimed primarily at providing a decisive explanation for the experimental observations in the nucleation processes. Rather, the experimental results on the alumina surface are discussed and compared with data found by other researchers, who used glass or polymer substrates and employed different experimental conditions.

To understand the changes in surface chemistry observed with the three-step process as reported in Measurement Results, the two-step process first is discussed briefly on
the basis of literature data. This process has been investigated much more extensively than the three-step process. Essentially, the two-step process consists of the adsorption of Sn\(^+\) ions onto the substrate, followed by deposition of Pd ions or atoms. The Sn\(^+\) ions may either be adsorbed as single ions or as part of colloidal particles. De Minjer et al.\(^{17}\) proposed various types of adsorbed single Sn\(^+\) ions with glass surface groups, for the reason that the average Sn coverage is of the order of a monolayer. Pederson\(^{26}\) followed this ionic adsorption model for the interpretation of XPS spectra of sensitized surfaces. However, a real ionic adsorption is unlikely at a pH value as low as 2. This can be concluded from ion adsorption data as a function of pH for various oxidic surfaces described by Schindler and Stumm.\(^{27}\) However, more evidence has been supplied in various publications for the colloidal adsorption model.

On TEM micrographs taken after sensitization of Formvar polymer substrates a particulate structure has been observed,\(^9\) consisting of primary particles of about 2 nm size, which are agglomerated into clumps of about 5 nm size. Similar observations were made by Sard\(^{28}\) on carbon films. Cohen et al.\(^{29,30}\) studied the chemistry of Sn in the sensitizer solution and after sensitization on substrate surfaces with Mössbauer spectroscopy and concluded that Sn is deposited onto the surface by adsorption of colloidal particles which are already present in the sensitizer solution. They expected that the results obtained on polyimide (Kapton) surfaces apply to other insulating surfaces as well.\(^{31}\) They also found that these particles contained both Sn\(^+\) and Sn\(^4+\), in the solution and after the sensitization step. After the activation step the same amount of Sn was detected, but in a 4+ state only. Similar results were obtained by Meek,\(^9\) who also reported that metallic Pd is present after activation as measured with ESCA. These data support the assumption that reaction 1 describes the deposition of Pd

\[
\text{Sn}^{4+} + \text{Pd}^{2+} \rightarrow \text{Sn}^{4+} + \text{Pd}^{0}
\]  

It is obvious that with an increasing initial Sn\(^+\) content, the apparent efficiency of reaction 1 decreases if this is measured by coverage ratios only. By using aged Sn\(^+\) sensitizer solutions, in which part of the Sn\(^+\) is converted into Sn\(^2+\), the efficiency was 25% or less.\(^31\)

In several studies the chemical composition of the surface after the sensitization and activation steps appeared not to be, or at least not completely to be, in agreement with reaction 1, suggesting that different or additional processes take place.\(^{11,12,18}\) For instance, initiation of electroless metal
The occurrence of Ag\textsubscript{1-x}Cl\textsubscript{x} fragments (x = 1, 2; y = 1, 2) may be explained by the equilibrium between Sn\textsuperscript{4+} and Sn\textsuperscript{2+} during aging.

For the nucleation of the substrate surface by the three-step procedure (following reactions 2 and 3 can be proposed as a model), in analogy to the simple reaction 1 for the two-step Sn-Pd nucleation, in an XPS study for the silver mirror process, Pederson\textsuperscript{8} found experimental evidence that reaction 2 adequately describes the deposition of Ag.

\begin{equation}
\text{Sn}^{2+} + 2\text{Ag}^+ \rightarrow \text{Sn}^{4+} + 2\text{Ag}^0
\end{equation}

\[ 2\text{Ag}^+ + \text{Pd}^{2+} \rightarrow 2\text{Ag}^0 + \text{Pd}^{0} \]

The Sn coverage on alumina after the sensitization step of about 7 \cdot 10^{14} cm\textsuperscript{-2}, see Section on RF results, compares well with the Sn coverage found by de Minjer \textit{et al.} on glass slides (5 \cdot 10^{14} cm\textsuperscript{-2}).\textsuperscript{10} After the intermediate step, the Ag coverage is two times the Sn coverage, within the accuracy of the XRF measurements of about 10\%. This is again in agreement with, but of course no proof for, reaction 2. After the activation step, a higher Ag to Sn ratio is found, which may be caused by partial dissolution of Sn ions in the acidic activation solution. The dissolution of Sn from activated surfaces is a well-known phenomenon and sometimes causes problems due to its poisoning effect when Sn dissolves during initiation in the electroless bath. After activation, the Pd coverage amounts to about 5 \cdot 10^{14} cm\textsuperscript{-2}, which is ten times the coverage minimally required for initiation of electroless deposition.\textsuperscript{29} This Pd coverage amounts to about 70\% of the Sn coverage. This may imply that, if the reaction couple 2 + 3 describes the Pd deposition, these reactions have an overall efficiency of 70\% or lower, depending on the amount of Sn ions dissolved in the activator step. Since an efficiency of 80 to 100\% was found for Cu,\textsuperscript{26} this efficiency decrease must occur after the intermediate step. Probably, this is due to oxidation of Ag, deposited in reaction 2, during the intermediate step or during rinsing. In that case less Ag\textsuperscript{3+} is available for reaction 3.

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Due to the very low solubility of silver chloride, it is probable that Ag\textsuperscript{+}, formed by reaction 3 in the PdCl\textsubscript{2} solution, precipitates with Cl\textsuperscript{-} on the activated substrate surface. Hence, the fact that Ag remains on the surface after activation should not be used as an indication that Ag does not take part in the reactions 2 and 3 as argued by de Minjer \textit{et al.}\textsuperscript{10} The same holds for remaining Sn\textsuperscript{2+}, which is oxidized to the 4\+ state after activation as discussed above.

The species and the intensity changes measured with static-SIMS after the various process steps correlate well with the quantitative XRF results. In a few cases the composition of the fragments may give an indication of surface chemical bonding. For instance, the SnO and SnOH-containing fragments correspond to the hydrolyzed polymer structures proposed for the sensitized colloid particles.\textsuperscript{9} The occurrence of Ag\textsubscript{1-x}Cl\textsubscript{x} fragments (x = 1, 2; y = 1, 2) may support the assumption that an AgCl precipitate is formed. Furthermore, it is probable that F\textsuperscript{-} which also is observed in AIF\textsubscript{3} (x = 2 to 4) fragments is bonded to AI atoms on the substrate surface. However, due to the possibility of recombination reactions in the static-SIMS experiment, the fragments observed should be used as an indication rather than as a proof for the presence of these surface structures.

The TEM micrographs show that the morphology of the surface which arises during the Sn sensitization step is maintained during the Ag or Pd activator steps. The results from the XRF analyses indicate that after the nucleation procedure about 3 \cdot 10^{15} Sn, Ag, Pd, and Cl cm\textsuperscript{-2} are present. From TEM measurements we conclude that the activator material is present as small particles, rather than as a continuous layer. Hence, we conclude that a large part of the surface area, that is to say, between the clusters of activator material is not covered by Sn, Ag, or Pd. This is in agreement with the observation that the growth of Ni(P) starts on these clusters only. The major part of the substrate surface is covered by Ni(P) through lateral growth of nuclei starting from the activator particles. A similar observation has been made with TEM on various dielectric substrates by Marton and Schlesinger\textsuperscript{30} using a two-step nucleation.

They found a linear relation between particle diameter and time of deposition between 15 and 120 nm particle size. By extrapolation of this relation to the moment of initiation, they concluded that then the active sites are smaller than 1 nm: this is the size that we found for the primary particles after activation. The smallest distinguishable Ni(P) particles are about 2 nm in size. Marton and Schlesinger also observed that growth initiated as a continuous film on Ni and Pd substrates, which yielded a strong adhesion.

The gradual increase of the particle size also is demonstrated by the TEM cross-section micrograph shown in Fig. 4. The coalescence of many small columns to fewer thicker columns agrees well with the plan-view images in Fig. 3c, and d. The interfacial layer with a thickness of about 2 nm cannot be explained by the presence of the activator material only. This layer may be of importance for the adhesion between Ni(P) and alumina and is investigated further.

Homma \textit{et al.}\textsuperscript{31} explained the superior adhesion strength of Ni(P) on alumina relative to that of electroless Cu by the presence in the initial metal growth mechanism in the first 30 nm, rather than by the surface nucleation procedures. They concluded from a plan-view TEM study on carbon films that Ni(P) makes a more intimate interfacial contact with the substrate than Cu. It is difficult to obtain information on interfacial morphology by plan-view imaging. Nevertheless, our cross-section TEM images confirm that a close interfacial contact between Ni(P) and alumina is present on nanometer scale.

**Conclusion**

The cleaning treatment removes organic contaminants up to the monolayer level. We conclude that the subsequent surface preparation steps such as etching and nucleation do not introduce any organic or other contaminations although all steps are carried out in laboratory air.

A glass layer is removed from ceramic grains by etching in an HF solution, also up to monolayer level. In this step fluoride is deposited onto the surface. Since this is not removed completely in subsequent steps, it is present at the interface, bonded to alumina.

An amount equivalent to about 3 monolayers of activator material is deposited in small particles of a few nanometers in size. An AgCl coverage of 1 to 2 \cdot 10^{15} cm\textsuperscript{-2} remains on the surface. The Sn, Ag, Pd, and Cl coverages can be explained by simple redox reactions. Though other possibilities cannot be excluded definitively, for the present discussion we assume that nucleation is described satisfactorily by these redox reactions.

The activator particles are clustered in islands and chains. Here metallization is first observed. The structure of the activator material on the surface is determined by the sensitization step. A large part of the surface area is not covered by activator material and becomes covered with Ni(P) by lateral growth of initial Ni(P) particles.

The interfacial layer which is observed with cross-section TEM, cannot be explained completely by the presence of activator material. This layer undoubtedly plays a crucial role in adhesion for all cases where interfacial failure is observed.

**Acknowledgment**

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A Room Temperature Chemical Vapor Deposition SiOF Film Formation Technology for the Interlayer in Submicron Multilevel Interconnections

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ABSTRACT

A new interlayer dielectric film formation technology for multilevel interconnection by catalytic chemical vapor deposition has been developed. This technique utilizes fluorotriethoxysilane \([\text{FSi(OC}_2\text{H}_3)_3]\) and water vapor as gas sources. The films deposited at 25°C have remarkably good properties, such as tightly bonded Si-O networks with no OH radicals, low leakage current, and small dielectric constant (3.7), although the film contains residual fluorine and carbon atoms with \(5.3 \times 10^{27}\) and \(2 \times 10^{28}\) atom/cm\(^3\), respectively. Based on the film characterization results, we speculate that the reaction sequence for the film deposition is: hydrolysis of fluorotriethoxysilane monomers, formation of siloxane oligomers with reaction by-product (alcohol), adsorption of the oligomers to the wafer surface, and then polymerization. The electrical conduction mechanism study revealed that the deposition film thickness has no dependence on Al wiring widths, and is completely isotropic with no crack or keyhole in the film.

Interlayer dielectric film formation technology is essential for multilevel interconnection fabrication in ULSI devices. Low temperature deposition has been required for interlayer dielectric films used in multilevel interconnection, because thermal stress degrades device characteristics and wiring reliability.\(^*\)\(^*\)TEOS-ozone APCVD, H\(_2\)-O-TEOS PECVD, and biased ECR CVD techniques, which utilize organic materials as gas sources, have been investigated for this purpose. However, when using these techniques, a fatal drawback is the impossibility of reducing deposition temperature, because a substrate temperature above 300°C is required for polymerization and dehydroxylation. Therefore, deposition at a lower temperature, without residual OH, has been difficult to achieve simultaneously. This residual OH degrades the hot carrier resistance for MOSFETs, and also assists a poisoned-via formation.\(^*\)\(^*\)