Suppression of Defect Formation in Electroless Plated Film by Supercritical Carbon Dioxide

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ABSTRACT
We have developed a novel thin film formation technology that combines the merits of conventional electroless plating and supercritical carbon dioxide (sc-CO$_2$) techniques. Our proposed method is carried out in an emulsion of sc-CO$_2$ and an electroless plating solution with surfactant and has an excellent covering power. The Ni-P film obtained by our proposed technique was extremely uniform and conformal. This film has no pinholes that form from the hydrogen bubbles produced by the electrolysis of water, and moreover no nodules that form from the nuclear growth on the electroless plating reaction. The effects of defect suppression were studied. Various reaction experiments showed that the dissolution of the hydrogen bubbles in the dense CO$_2$ particles of the emulsion prevented the pinholes from forming. The formation of nodules was prevented by the stronger acidic solution by dissolution of CO$_2$ and the transport properties of the emulsion with the diffusive dense CO$_2$.

1 INTRODUCTION
Recent years have witnessed worldwide research and development on micro-electro-mechanical systems (MEMS) undertaken in both academia and industry. MEMS is the integration of mechanical elements, sensor, actuators, and electronics on a common silicon substrate through microfabrication and a smaller nanofabrication technology. And it is certain that the thin-film formation technology is a very important technological element in these fields. However, the increasing complexity and decreasing dimensions of devices for microelectronics are placing stringent demands on thin-film formation technologies that, to date, have not been fully satisfied [1-2].

In our previous report, we have developed a new technique based on the criteria mentioned above [3]. The technique is a new electroless plating method using a supercritical carbon dioxide (sc-CO$_2$) as a solvent. Sc-CO$_2$ has excellent characteristics of intermolecular interaction control due to the changeability of its density and its ability to convey materials to a nano scale area because of its high density and high diffusivity. The Ni-P film obtained by our proposed technique was extremely uniform and conformal. Especially, this film has neither pinholes nor nodules. These defects become a serious problem when the thin film was made on a complex 3-D microstructure.

The aim of this work is to clarify the effect of sc-CO$_2$ in our novel electroless plating on the point of suppression of defect formation.

2 Experimental details
2.1 Materials
Carbon dioxide with a minimum purity of 99.99% was purchased from Nippon tansan Co. Ltd. In our experiments, we employed a nonionic surfactant polyoxyethylene lauryl ether (C$_{12}$H$_{25}$O($CH$_{2}$CH$_2$)$_{15}$OH, CAS No.9002-92-0) supplied by Toshin Yuka Kogyo. The chemical composition of electroless Ni-P plating solution used nickel chloride (9%), sodium hypophosphite (12%), complexing agent (12%) and ion-exchanged water (67%) (Okuno...
Chemical Industries Co. Ltd.). The substrate was 99.99% purity copper with a size of 10×20 mm² (Mitsubishi shindoh Co. Ltd). Before a reaction, the substrate was washed with acetone and rinsed in deionized water. The cleaned sample was degreased by dipping successively in a 10 wt. % NaOH and a 10 wt. % HCl and rinsed in deionized water. The sample was added to the activator solution consisting of hydrogen chloride (18%), palladium chloride (0.04%), ion-exchanged water (81.96%) (Okuno Chemical Industries Co. Ltd.) at 30°C and rinsed in deionized water. This pretreatment was applied to all copper substrates regardless of the condition of the electroless plating reaction.

2.2 Experimental apparatus
A high-pressure experimental apparatus (Japan Spectra Company) for electroless plating is shown in Fig.1. The temperature variation of each run was observed to be less than 1.0 K. The maximum working temperature and the maximum pressure were 424 K and 50 MPa, respectively. The reaction cell that had a volume of 50 ml was a stainless steel 316 vessel in a temperature-controlled air bath with a magnetic agitator. An agitation was performed using a cross-magnetic stirrer bar. The substrate was attached using stainless wires to the reactor.

A typical electroless plating reaction was performed in a constantly agitated ternary system of dense CO₂, the electroless plating solution and a surfactant. The electroless Ni-P plating solution and the surfactant were both put in a high-pressure cell. Liquid CO₂ was introduced to the high-pressure cell using a HPLC pump and pressurized to a predetermined pressure. The ternary system was then constantly agitated at a speed of 500 rev./min under 353K, and the electroless plating reaction started at the same time as the agitation beginning.

We discuss the properties of the plated film by our method in comparison with properties of a plated film fabricated by a conventional method of electroless plating. The experimental conditions of conventional method were performed at 353 K, atmospheric pressure, and used the plating solution of the same chemical composition as the novel electroless method.

2.3 Analysis
For studying the surface of plated Ni-P film, Optical microscope (OM, Digital Microscope VHX-500, KEYENCE. Co. Ltd.) and scanning electron microscopy (FE-SEM, S-4500, Hitachi High-Technologies Co. Ltd.) were used. Average surface roughness values (Ra) were
measured using surface texture measuring instruments (SURFCOM 480A, TOKYO SEIMITSU Co. Ltd.). This measuring instrument in which the minimum resolutions of height measurement are 1nm (For height measurement range is 80μm), and supports ISO, DIN, ASME and CNOMO standards in addition to new and old JIS. The detector is made of a diamond, and the tip radius is 2μm. The surface roughness value (Ra) measured in five places or more on the plated film, and calculated those values on an average. Focused ion beam system (FIB, FB-2100, Hitachi High-Technologies Co. Ltd.) was used to fabricate precise cross section of plated Ni-P film. And then the plated film thickness measurement obtained directly from the SEM image on the screen.

3 RESULTS AND DISCUSSION

3.1 Surface features
The Ni-P film obtained by our proposed technique was extremely uniform and conformal as shown in figure 2. Clear differences were confirmed to the surface morphology of both plating films by SEM observation. Nodules were observed on the Ni-P film made by conventional method in the early stage of the reaction as shown in Fig.2 (b). The nodules are generated because the reaction of the nickel concentrates locally. This is because the nickel extracts centered around the palladium nucleus that adsorbed the surface [4-6]. The size of nodules grew from several hundreds of nm to several μm as reaction time increased, and the number of nodules increased, too. On the other hand, our method did not have the nodules that existed in the conventional method (Fig.2 (a)). This film has no pinholes that form from the hydrogen bubbles produced by the electrolysis of water. As a result, our method has the effect of suppressing the defect of electroless plated film.

The conventional method was Ra=0.048μm, and it roughened more than the value of the activated substrate. From other researches, it was confirmed that the surface morphology and the deposition state of electroless Ni-P film can change because of the activation processing [4-6]. However, smoothness has improved though our method is Ra=0.030μm, and the same activation processing as the conventional method. In addition, the film thickness influences the surface roughness easily, and the thickness of the thin film made with our method is very smooth though it is twice more than the thickness of the thin film made by conventional method.

Figure 2. SEM images of Ni-P films plated from (a) our electroless plating at 353 K and 15 MPa for 180 min (with a film thickness of 0.8 μm and Ra = 0.030 μm), (b) conventional electroless plating at 353 K and atmospheric pressure for 2 min (with a film thickness of 0.3 μm and Ra = 0.048 μm).
3.2 Suppression of defect formation on electroless plated film by our method

The reaction mechanisms of electroless deposition have extensively studied. Four principal reaction mechanisms have been proposed to account for the reduction with hypophosphite in both alkaline and acid media. Each mechanism was successively supported by several authors. However, a conclusive result has not been obtained yet [7].

We studied the defect suppression mechanism on the electroless plating film by our method based on the electrochemical mechanism from among the above-mentioned reaction mechanisms. Table 1 shows the electrochemical mechanism. The autocatalytic deposition is a mixed process which results from anodic reactions (oxidation of hypophosphite) and cathodic processes (reduction of the metallic species, hypophosphite and protons).

We focused attention on the generation reaction of the hydrogen gas of formula (3) as a cause to which nodule formed on the plating film by our method was suppressed. As for our method, sc-CO\textsubscript{2} phase diffuses in the plating solution, and the pH of the plating solution decreases as shown in formula (5) [8]. As a result, the frequency of the hydrogen gas generation reaction increases, and the deposition of Ni decreases.

We experimented with the verification of this hypothesis. HCl (10 wt.%) was added to original plating solution (pH=5.3) to become adjusted to pH=4.0, and we made the plating film by conventional method (Fig.3). As for the SEM image of the plating film made in the original plating solution shown in Figure 3(a), the surface was rough though it was the same film thickness as the plating film made by our method in Figure 2(a), and a lot of nodules were observed. On the other hand, the plating film made in the plating solution with pH 4.0 at the same reaction time as Fig.3(a) slowed the growth speed, and decreased the size and the number of nodules (Fig.3(b)). The growth speed of the plating film generally decreases by the decrease of the pH of the plating solution [9]. Reaction time was lengthened with the plating solution to verify the influence of the density of hydrogen bubbles on the surface of the plating film (Fig.3(c)). In Fig.3(c), the Ra value near that of Fig.2(a) is indicated that the size and the number of nodules have decreased greatly in comparison with Fig.3(a). There is an effect of suppressing the formation of nodule when the density of hydrogen ion in the plating solution increases from these results.

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<th>Table 1. Electrochemical mechanism</th>
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<td>( \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{PO}_3^- + 2\text{H}^+ + 2\text{e}^- ) (1)</td>
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<td>( \text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni} \downarrow ) (2)</td>
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<td>( 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow ) (3)</td>
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<tr>
<td>( \text{H}_2\text{PO}_2^- + \text{e}^- \rightarrow \text{P} \downarrow + 2\text{OH}^- ) (4)</td>
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<th>Table 2. Water in contact with carbon dioxide becomes acidic due to the formation and dissociation of carbonic acid</th>
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<td>( \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- ) (5)</td>
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Figure 3. SEM images of Ni-P films plated from conventional electroless plating at 353 K and atmospheric pressure. (a) reaction time is 5 min and pH of plating solution is 5.3 with a film thickness of 0.80 μm and Ra = 0.063 μm, (b) 5 min, pH = 4.0 with a film thickness of 0.17 μm and Ra = 0.023 μm, (c) 20 min, pH = 4.0 with a film thickness of 0.77 μm and Ra = 0.027 μm.

We consider the suppression mechanism of nodule with the hydrogen ion to originate in the concentration of a three-dimensional ion on a minute convex part like nodule. The suppression of the plating film growth by nonlinear diffusion of reactive kinds to such a minute convex part was reported in the effect of the dissolved oxygen in the plating solution of Jacobs [10]. However, the driving force of the diffusion of the dissolved oxygen to a minute convex part is not referred. We consider the driving force of nonlinear diffusion to nodule of the hydrogen ion to be concentration diffusion by the consumption of the hydrogen ion by the hydrogen gas generation reaction of formula (3). In addition, the generation of the pinholes and voids are sure to increase if the generation of the hydrogen gas increases. Actually, the pinholes with the hydrogen gas more than Fig.3(a) were observed in Fig.3(c). On the other hand, the pinholes were absent from the Ni-P film plated by our method since the hydrogen bubbles produced by the electrolysis of the water had dissolved in the sc-CO$_2$ phase distributed in the emulsion [3].

Various reaction experiments showed that the dissolution of the hydrogen bubbles in the dense CO$_2$ particles of the emulsion prevented the pinholes from forming. The formation of nodules was prevented by the acidic solution by dissolution of CO$_2$ and the transport properties of the emulsion with the diffusive dense CO$_2$. Sc-CO$_2$ phase distributed from a viscosity decrease in the ternary system because of emulsification might assist in the above-mentioned effect. More evidence will be needed to formulate a detailed mechanism for these our process.

4 CONCLUSION

In summary, we have developed a new electroless plating method. Our proposed method is carried out in an emulsion of sc-CO$_2$ and an electroless plating solution with surfactant and has an excellent covering power. The Ni-P film obtained by our proposed technique was extremely uniform and conformal. Moreover, defects such as nodules and pinholes generated by conventional electroless plating have been decreased in the surface morphology. The viscosity of the ternary system decreased by emulsification, and the density of the hydrogen ion in the plating solution increased because CO$_2$ dissolved in the plating solution, and the anomalous growth on the plating film was suppressed. At the same time, the increasing hydrogen gas had dissolved in the sc-CO$_2$ phase distributed in the emulsion. Therefore, our method can suppress the nodules, the pinholes and the voids formation that becomes the big
problems because of the plating film formation at the same time.

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REFERENCES