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Author(s)	Azumi, Kazuhisa; Yugiri, Takuma; Kurihara, Toshiyuki et al.
Citation	Journal of The Electrochemical Society, 150(7), C461-C464 https://doi.org/10.1149/1.1576770
Issue Date	2003-07
Doc URL	https://hdl.handle.net/2115/22022
Type	journal article
File Information	JECS150-7.pdf





Direct Plating of Electroless Ni-P Layers on Sputter-Deposited Al-Ni Alloy Films

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Direct plating of electroless Ni-P layers on Al-Ni alloy films formed on glass substrates was performed using magnetron-sputtered deposition and ion beam-assisted deposition methods. Dissolution of Al from the alloy films occurred in the initial stage of the plating process and resulted in enrichment of Ni on the surface. Since Ni acts as a catalyst for the Ni-P deposition reaction, Ni-P deposition occurs on the alloy surface without zincate pretreatment. In the case of an Al-10Ni alloy film, however, Ni clusters dropped from the Al-Ni alloy surface, and Ni-P particles grew in the plating bath, causing dissipation of chemicals in the bath. Such particles also readhered to the surface, resulting in a nonuniform plating layer. A lower concentration of Ni in an alloy such as an Al-3Ni or Al-1Ni alloy resulted in a rather smooth plating surface. In the case of a neutral plating bath containing a low concentration of P, cone structures were formed in the plating layer. Such structures seem to form at the nucleation sites of Ni deposition in the initial stage of the plating process.

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Manuscript submitted June 24, 2002; revised manuscript received January 24, 2003. Available electronically May 12, 2003.

Electroless Ni-P plating on an Al film deposited on a substrate, such as a glass plate, has been required for manufacturing circuits used in electric devices. In some cases, wiring patterns have first been produced using an Al deposition method and then an Ni-P plating layer has been deposited to form a strong and thick electric-conducting layer. Since direct plating of metals on a substrate of Al is difficult due to the existence of an electrically insulating surface oxide film, zincate pretreatment has been used to replace the Al surface with a Zn layer. To initiate the plating process, the substrate surface must be activated to mediate charge transfer, oxidation of H_2PO_2^- , and deposition of Ni and P. It has been reported that Al, aluminum oxide or Zn formed by zincate pretreatment is not active for such reactions.¹ The initial deposition of Ni, therefore, occurs as a substitution reaction by Zn dissolution. However, the zincate pretreatment includes a dissolution reaction of the Al substrate in a concentrated alkaline zincate solution and sometimes results in serious damage to the Al film.² The usefulness of various additives to eliminate the dissolution of substrate Al in the zincate pretreatment has been examined. Direct plating of metals on Al films has also recently been attempted to overcome these drawbacks in plating processes. In these works, pre-electrodeposition of metals in the porous anodic oxide films on Al was carried out to create a seed for the subsequent plating^{3,4} and the effectiveness of reducing agents added to the plating solution for the activation of Ni deposition on the Al surface has been examined.^{5,6} Once Ni has settled on the surface, it acts as an efficient self-catalyst for the electroless plating reaction, and an Ni-P layer thus grows rapidly. However, since the initial deposition of Ni is not rapid enough for Ni to cover the entire surface within a short time period, the substrate Al may be dissolved at the initial stage of immersion.⁷ Such dissolution can cause a fatal failure in the case of thin Al-deposited films. Direct plating of an electroless Ni-P layer on an Al-deposited film would thus be useful for not only preventing degradation of the substrate but also for simplifying the plating process in order to reduce the treatment load of chemical waste. In this paper, an alternative approach for direct plating is proposed. The concept of this study is very simple, *i.e.*, an Al-deposited film is alloyed with a small amount of Ni, which is expected to initiate rapid Ni-P deposition without any pretreatment or additives to the plating bath.

Experimental

Al-Ni alloy films, each with a thickness of 0.5 μm , were deposited on glass plates using the magnetron sputter deposition technique

(MS film) and the ion beam-assisted sputter deposition technique (IB film). The equipment and conditions used for deposition are described in our previous paper.² In the case of an MS film, a small Ni plate was placed on an Al target for co-sputtering and co-deposition. The concentration of Ni in the Al-Ni alloy was changed by changing the size of the Ni plate. The specimens were rinsed in ethanol using an ultrasonic cleaner and subjected directly to electroless Ni-P plating. Two kinds of plating baths were used. One was an acidic bath with pH adjusted to 4.6 (Melplate NI-422, Meltex Co.). The plating layer deposited in this bath has an amorphous structure with a P content of *ca.* 11% in weight ratio.^{7,8} The other was a neutral bath with pH adjusted to 6.4 (Melplate NI-426, Meltex Co.). The plating layer deposited in this bath has a crystalline structure with a P content of *ca.* 2% in weight ratio. The plating temperature was 358 K. Surfaces and cross sections of the specimens were observed by using a field emission scanning electron microscope (FE-SEM, model JSM-6300F, Jeol Co.) after plating. Cross-sectional images were observed by cracking a glass specimen after plating. By fluorescence X-ray spectroscopy analysis, the concentrations of Ni in the films were determined to be about 1% (Al-1Ni), 3% (Al-3Ni), and 10% (Al-10Ni) in atomic ratios for the MS films and about 3% for the IB films.

Results and Discussion

Figure 1 shows SEM images of an Al-10Ni film after direct Ni-P plating in an acidic bath for 3.6 ks. The thickness of the plating layer was about 3 μm , considerably less than the thickness of about 10 μm predicted from the plating conditions. A magnified image of the cross section is shown in Fig. 1c. It can be seen that the plating layer is composed of a granular structure in the upper part and a uniform layer in the bottom part. The surface is covered not only by a plating layer but also by spherical particles. Fluorescent X-ray analysis showed that the composition of these particles was the same as that of the Ni-P plating layer. The diameters of these particles ranged from 1 to 10 μm . Some of the particles were attached to the surface, while others were embedded in the plating layer. As is described later, the particles were also found to be formed during the plating process in the bath.

Figure 2 shows the results for a neutral bath. As seen in Fig. 1, many particles were observed on the surface of the plating layer. Most of the particles were about 2 μm in diameter. A magnified image of the cross section (Fig. 2c) shows that the plating layer was composed of a columnar structure growing in the normal direction from the bottom to the substrate surface. Such a columnar structure contains a small amount of P and is thus rather crystalline compared with the plating layer formed in an acidic bath.¹⁰

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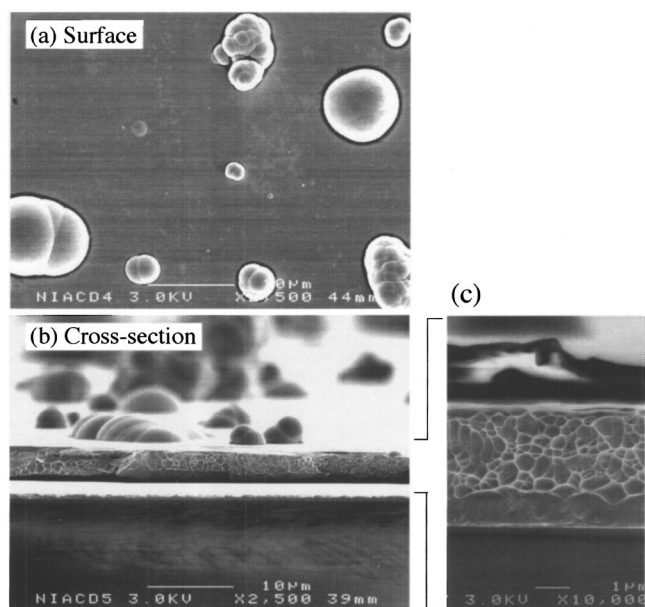


Figure 1. SEM images of an electroless Ni-P layer directly plated on an MS Al-10Ni alloy film in the acidic plating bath: (a) surface, (b) cross section, and (c) magnified image of the cross section.

These results suggest that Ni-P particles grow in the plating bath as illustrated in Fig. 3. In the initial stage of the plating process, dissolution of the surface of an Al substrate continues at least until the surface is covered by an Ni-P plating layer.⁹ In the case of an Al-Ni alloy, however, Ni is not dissolved and is thus enriched on the surface. The resultant Ni-rich surface provides many active sites for catalysis of the Ni-P deposition reaction. Some of the Ni clusters, however, detach from the surface and then float in the plating bath. Ni-P deposition also occurs on these floating Ni clusters, and an Ni-P layer grows. Because the plating bath is stirred, some of these particles adhere to the specimen surface and become embedded in the growing Ni-P layer. The growth of a layer of Ni-P particles in the

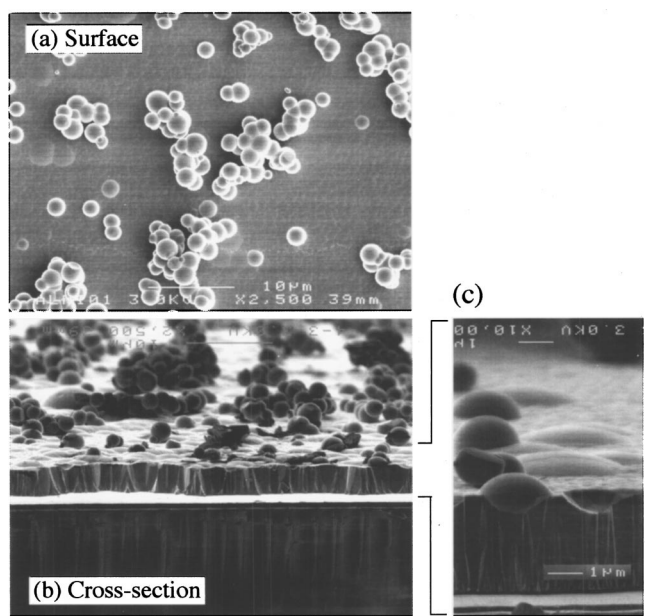


Figure 2. SEM images of an electroless Ni-P layer directly plated on an MS Al-10Ni alloy film in the neutral plating bath: (a) surface, (b) cross section, (c) magnified image of the cross section.

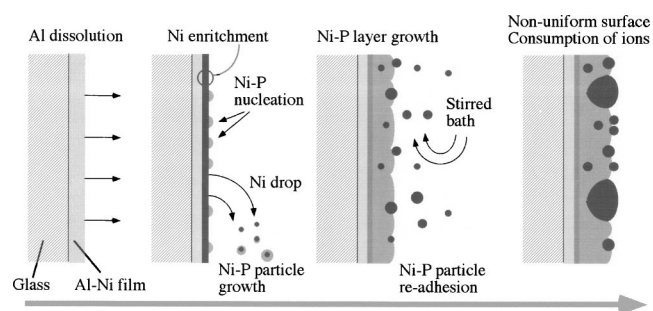


Figure 3. Mechanism of Ni-P particle formation.

plating bath causes dissipation of ions in the bath. Indeed, it was observed that the green color of plating bath caused by the existence of Ni^{2+} ions faded considerably during the plating process of these specimens. Consumption of ions in the bath reduces the efficiency of growth of the plating layer on an Al-Ni film compared with that on a film without particle formation, resulting in a thinner layer as seen in Fig. 1 and 2.

To confirm the formation of Ni-P particles in the plating bath, the solution was sampled during the plating process and filtered using a membrane filter with a pore size of 200 nm. Figure 4 shows SEM images of particles found on the membrane filter. These images show that the particles tend to increase in size and number with prolongation of the plating period. In the magnified image shown in Fig. 4f, it can be seen that some of the particles were broken, indicating that the Ni-P particles grew radially from the center in the neutral bath. This means that an Ni-P plating layer grows in a columnar form on a flat surface of a substrate because the growth in a lateral direction is limited.

As mentioned above, the formation of Ni-P particles should be eliminated to obtain a smooth plating layer and to avoid dissipation of the plating bath. For this purpose, the concentration of Ni in the

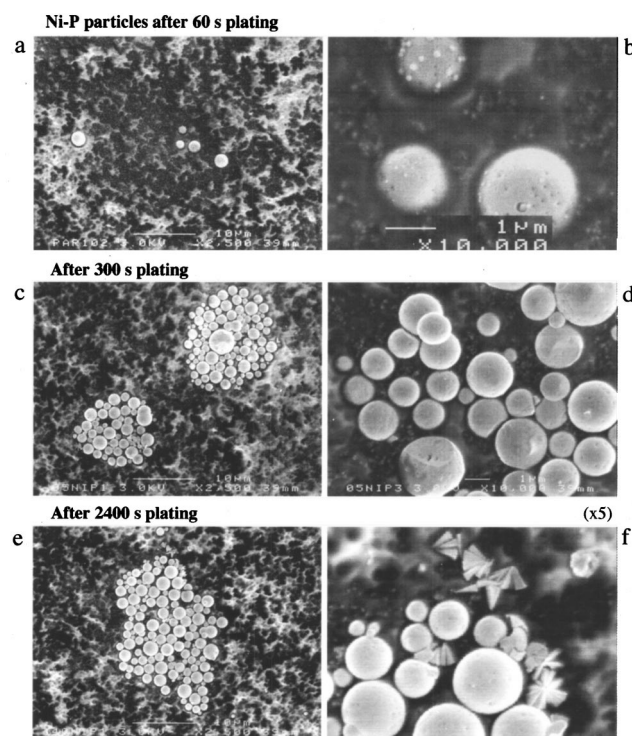


Figure 4. SEM images of Al-Ni particles found in the neutral plating bath sampled after plating periods of (a, b) 60, (c, d) 300, and (e, f) 2400 s.

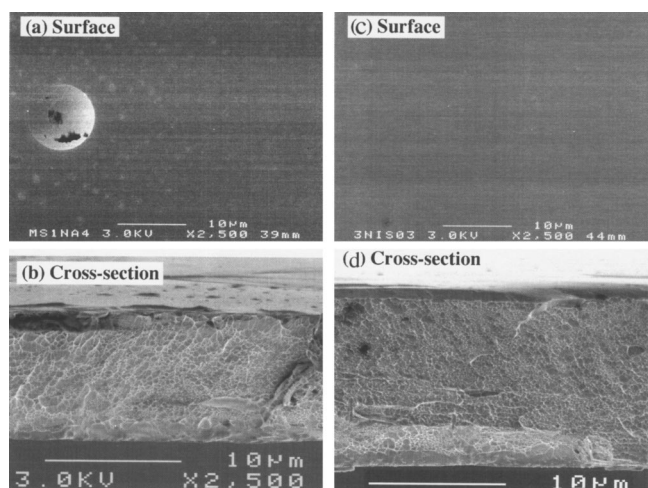


Figure 5. SEM images of electroless Ni-P layers directly plated on MS Al-3Ni (a, b) and Al-1Ni (c, d) alloy films in the acidic plating bath: (a, c) surface, (b, d) cross section.

Al-Ni alloy film was reduced. Figure 5 shows SEM images of Al-3Ni and Al-1Ni films after plating in the acidic bath for 7.2 ks. It was confirmed that an almost flat surface was obtained. Small spherical-shaped projections were rarely observed on the surface, indicating that embedding of Ni-P particles was still possible but would rarely occur. Ni-P particles were rarely found in the plating bath after plating. Suppression of the formation of Ni-P particles enabled the Ni-P plating layer to grow efficiently on these alloy films. The thickness of the plating layer was about 15 μm , which is considerably larger than that obtained on an Al-10Ni alloy film.

Figure 6 shows SEM images of an Ni-P layer plated on an Al-3Ni alloy in a neutral bath. The surface is relatively flat compared with the plating layer formed on an Al-10Ni alloy film. Ni-P particles could not be found in the plating bath. On the plating layer surface, however, many convex parts with small heights were observed. In the cross-sectional images shown in Fig. 6c and d, it can be seen that each convex part was the top of a cone-like structure that had formed in the plating layer. This structure started at the substrate surface, grew not only normally but also laterally as the plating layer became thicker, and ended at the surface with a semi-

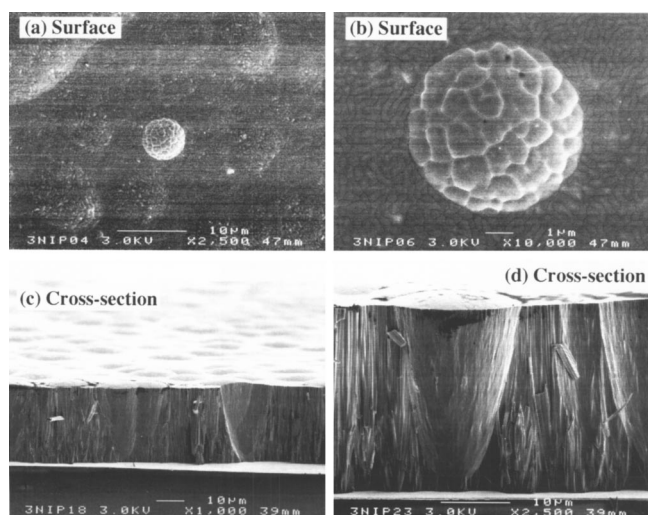


Figure 6. SEM images of an electroless Ni-P layer directly plated on an MS Al-3Ni alloy film in the neutral plating bath: (a, b) surface, (c, d) cross section.

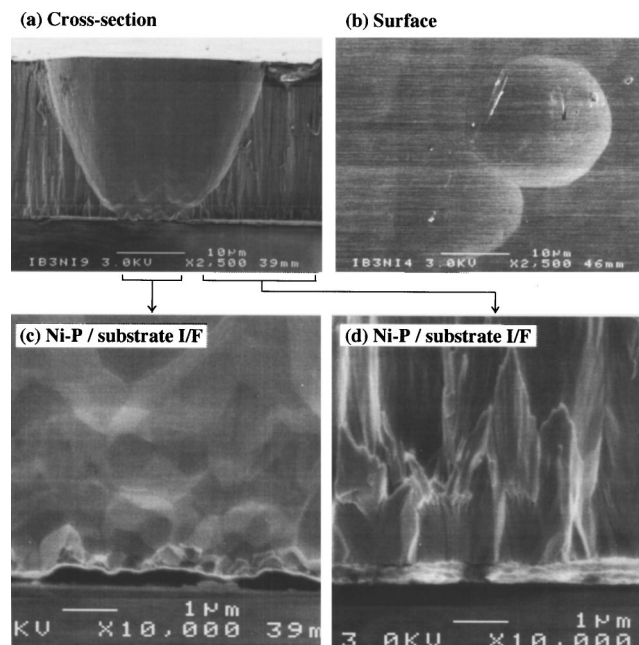


Figure 7. SEM images of an electroless Ni-P layer directly plated on an IB Al-3Ni alloy film in the neutral plating bath: (a, c, d) cross section, (b) surface.

spherical plane having a large radius. The plating layer was composed of a thin columnar structure of Ni-P crystalline. The cone structure was also a bundle of such thin columnar structures. The small undulations found in the plane part and in a semispherical part of the surface shown in Fig. 6b were terminals of columnar structures.

Figure 7 shows SEM images of the bottom part of the plating layer formed on an Al-3Ni alloy film. Figure 7c shows a magnified image of the bottom of the cone structure, and Fig. 7d shows a magnified image of the other part. The substrate of an Al-Ni film with a thickness of 0.5 μm is clearly observed in the latter image. However, the substrate film in the former image was distorted, and crystalline particles of Ni deposition were observed at the interface. Such Ni deposition has been reported to occur in the initial stage of Ni-P electroless deposition.⁷ These results suggest that the cone structure formed at the nucleation point of plating, where Al was dissolved, and that Ni particles were thus concentrated to provide effective catalytic sites for the electroless plating reaction. Deposition and growth of Ni-P occurred preferentially in these parts, resulting in an expansion of the cross-sectional area of the cone structure during plating layer growth. The density of the cone structure was dependent on the concentration of Ni in the Al-Ni alloy film. For example, in the case of Al-10Ni shown in Fig. 2, the plating layer was mostly composed of cone structures. The density of cone structures in the case of Al-1Ni was considerably less than that in the case of Al-3Ni.

Figure 8 shows a possible mechanism for the formation of an Ni-P layer containing cone structures in a neutral plating bath. At the initial stage of the plating process, Al on the surface of the Al-Ni alloy film is dissolved, resulting in the formation of an Ni-enriched surface. The distribution of the Ni concentration on the surface is probably not uniform, resulting in nonuniform nucleation of Ni deposition followed by electroless Ni-P deposition. As seen in Fig. 7c, it seems reasonable that the sites at which Ni was initially deposited preferentially became the bottom of the cone structure. At a certain stage during Ni-P growth, a thin columnar structure of Ni-P crystalline became distinguishable, as can be seen in Fig. 7d. The reason for the formation of such a thin columnar structure and the factors determining its thickness are not known at present. Since

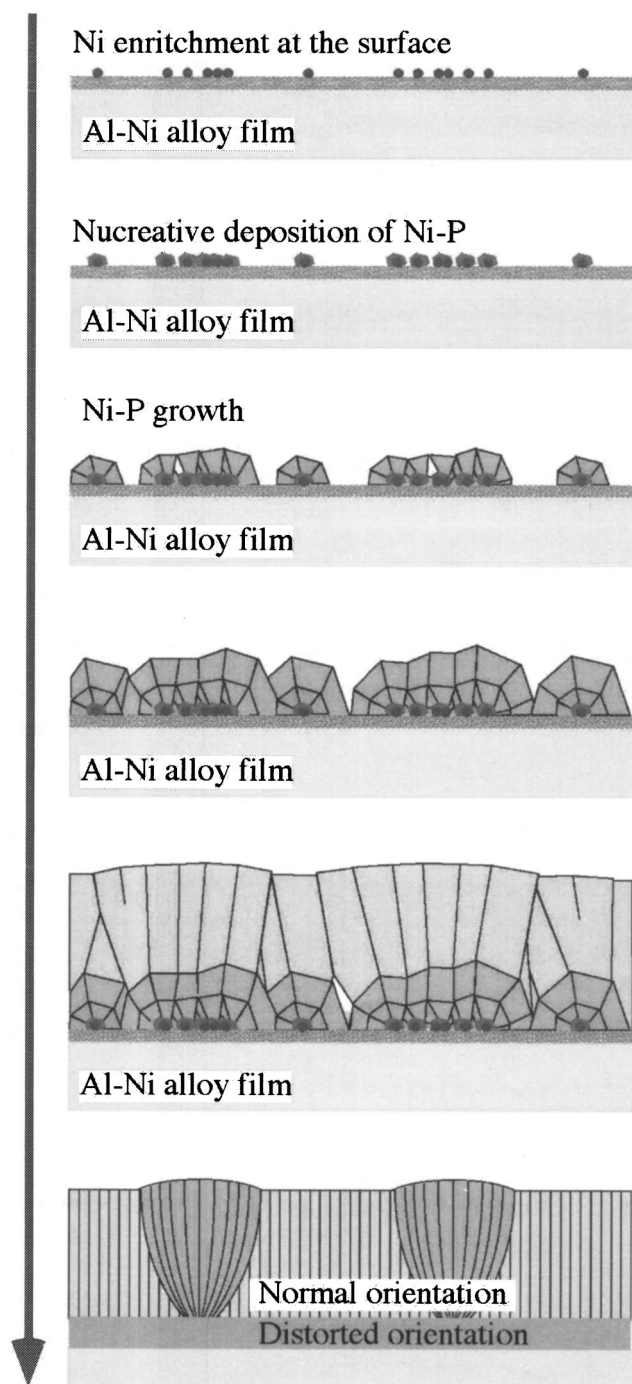


Figure 8. Formation of cone structures in the electroless Ni-P layer plated in the neutral bath.

each thin columnar structure of Ni-P deposition tends to grow not only in a normal direction but also in a lateral direction, as seen in

Fig. 4f, growth of these columnar structures is competitive. It seems reasonable to assume that the thin column growing from the bottom part of the cone structure survives in such competition, resulting in expansion in the lateral direction with its growth. The expansion of thin columns on other parts is thus limited. Such a mechanism seems to be a reasonable explanation for the formation of cone structures in the plating layer in a neutral bath. This process also causes the formation of a distorted orientation of Ni-P crystalline in the bottom of the plating layer and uniform orientation in the upper layer, as seen in Fig. 7d.

A simple test was performed to evaluate the strength of adhesion of the plating layer to the substrate film. A steel rod was glued to the plating surface and was then pushed down. In this case, the plating layer did not peel off from the substrate, and sufficient adhesion thus seems to have been achieved. Once the plating layer had peeled off from the edge of the specimen, however, the plating layer continuously peeled off rather easily. The adhesion of a plating layer formed on an Al alloy film is thus weaker than that of a plating layer formed on an Al alloy plate. This is because no anchor effect is expected in the case of direct plating described in this paper. In the case of an ordinal plating sequence of an Al alloy, double zincate pretreatment roughens the surface and sometimes causes formation of pits. In the subsequent electroless plating process, Ni-P deposition occurs within such pits, thus providing strong adhesion between the plating layer and the substrate.⁹

Conclusions

Direct plating of electroless Ni-P was achieved by using a sputter-deposited film of Al containing a small amount of Ni. To obtain a smooth plating layer, the concentration of Ni in the alloy film should be low. Since Al is dissolved in the initial stage of the plating process, the surface is enriched in Ni, even if the concentration of Ni is low, and thus provides sufficient activity for the plating reaction. If the concentration of Ni is high (10% in atomic fraction), clusters of Ni drop off from the surface during the plating process, resulting in the formation of Ni-P particles of spherical forms. This causes dissipation of chemicals in the bath and redeposition of particles on the plating layer to provide a nonuniform surface. However, this phenomenon may be useful for the production of small particles of Ni-P. If Al-Ni films with low Ni concentrations are used, a smooth plating layer can be obtained.

Hokkaido University assisted in meeting the publication costs of this article.

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