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Double Zincate Pretreatment of Sputter-Deposited Al Films

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The characteristics of double zincate pretreatment of thin Al films deposited on glass plates using magnetron sputtering and ion-beam sputtering were investigated. Traces of Zn deposition and immersion potential as well as surface observations using scanning electron microscopy and atomic force microscopy showed that continuous dissolution of an Al film during the double zincate pretreatment occurred in the case of a magnetron sputter deposited film, resulting in Al film failure from the substrate. On the other hand, the substitution reaction of Al dissolution and Zn deposition occurring on the ion-beam sputter-deposited film ceased during the first and the second zincate treatment processes. The difference between the behaviors of the double zincate treatments for the two kinds of sputter-deposited films is related to the film structure. A magnetron sputter-deposited film has a columnar structure, resulting in higher susceptibility to the dissolution reaction in a concentrated alkaline zincate solution. On the other hand, an ion-beam sputter-deposited film has a fine microcrystalline structure with a low density of defects, resulting in lower susceptibility to the dissolution reaction.

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Zincate pretreatment has been used for metal plating on Al to remove the surface oxide film which prevents the plating of metals on it due to its electric insulator property. In this pretreatment, an Al oxide layer and then a metallic Al substrate are dissolved in a concentrated alkaline zincate solution, and then the Al surface is covered with Zn deposition. However, single zincate pretreatment results in a granular Zn deposition, and such a surface is not suitable for a subsequent plating process such as electroless Ni plating. Using double zincate pretreatment in which the first zincate treatment is followed by Zn stripping in a concentrated HNO₃ solution and then by a second zincate treatment, a smooth and uniform Zn deposition layer that is suitable for plating is obtained. This double zincate treatment process is, therefore, widely used in the plating industry, and its mechanism has been investigated by many researchers.¹⁻¹⁰

A demand has recently arisen for electroless nickel plating for an Al film deposited on a substrate such as glass or Si in order to construct an electronic circuit on it. The thickness of the Al film is often less than 1 μm, and Al dissolution reaction during the zincate pretreatment process may, therefore, cause degradation of the circuit and sometimes results in failure of electric contact due to complete dissolution of the Al film. Therefore, suppression of Al film dissolution is very important for such a process. In this study, characterization of double zincate pretreatment of an Al film deposited on a glass plate was investigated. Two kinds of Al film, a magnetron sputter-deposited film and an ion-beam sputter-deposited film, were used. These films have different structures. A pure Al film was used in this study in order to determine the difference in pretreatment characteristics dependent on film structure and to compare the results with previously reported results for a bulk Al plate. A zincate solution containing no additive was also used for the same reason, although commercial solutions contain various additives.

Experimental

The specimens used were two kinds of Al films of 0.5 μm in thickness deposited on glass plates of 2 mm in thickness prepared by magnetron sputtering (MS) and ion-beam sputtering (IB) techniques. An MS-Al film was prepared using a Shimadzu Co. model SP-2C dc magnetron sputtering facility under the following conditions: prepurge pressure reached at 9×10^{-5} Pa, Ar gas pressure was 0.4 Pa, and a 99.999% Al target was sputtered at 0.5 A and 350 V. An IB-Al film was prepared using a Kaufman-type ion-beam gun (Ion Tech Co.) under the following conditions: a 99.99% Al target was sputtered at an Ar gas pressure of 1.3×10^{-2} Pa for 10.8 ks, 40 mA

beam current, and 1000 V acceleration voltage, after prepurge had reached 6×10^{-6} Pa. Before experiments, the specimens were rinsed in acetone using an ultrasonic cleaner. The zincate solution used was a mixture of 230 kg m^{-3} NaOH and 50 kg m^{-3} ZnO prepared from analytical grade chemicals and doubly distilled water followed by milli-Q filtering. For Zn stripping, 50 vol % HNO₃ solution was used. Immersion potential was traced using a Zn reference electrode (RE), a digital voltmeter (Keithly Co., model 2000) and a desktop computer (Apple Computer Co., Macintosh model SE30). Zn RE was used because the Al surface was gradually substituted by Zn deposition. All experiments were conducted at room temperature (*ca.* 296 K). Weight change during the zincate treat-

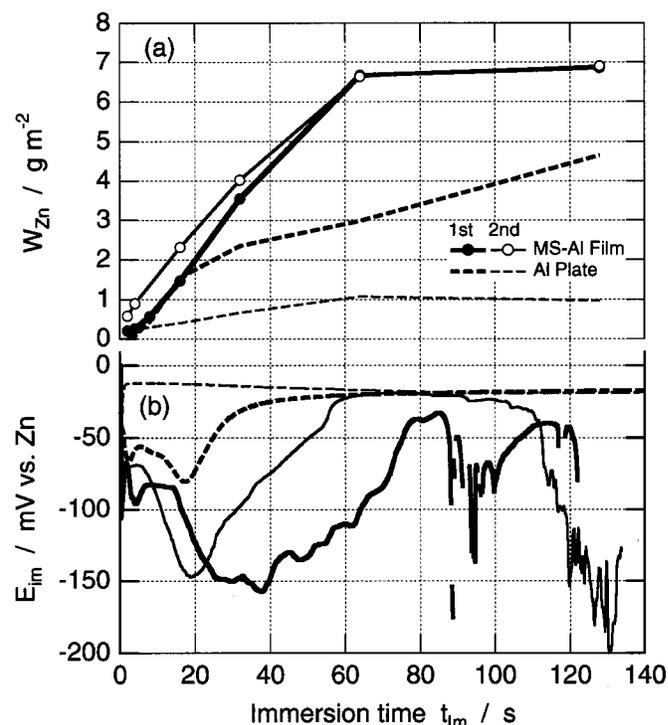


Figure 1. Traces of Zn deposition (a) and immersion potential (b) of an MS-Al film measured during the first zincate treatment and the second zincate treatment in 230 g dm^{-3} NaOH + 50 g zincate solutions following the first zincate treatment for 10 s and Zn stripping.

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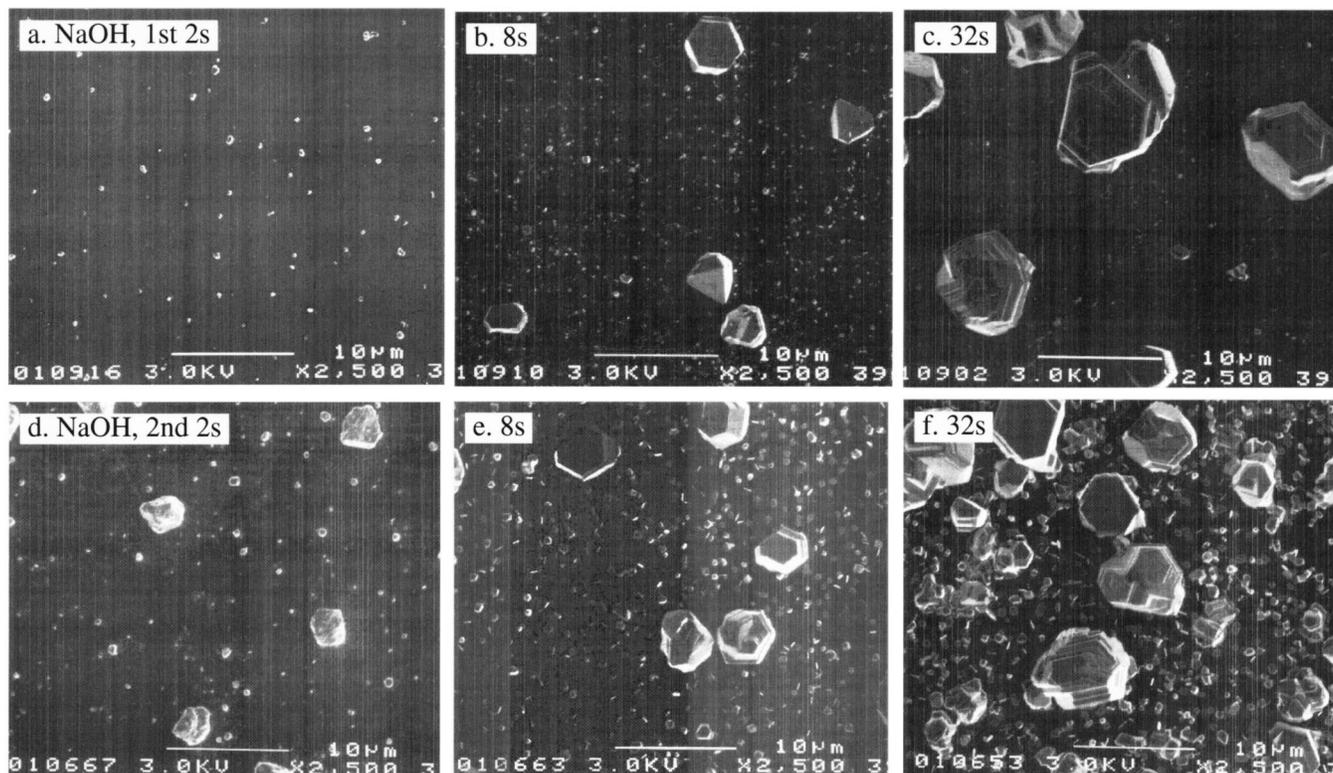


Figure 2. SEM images of an MS-Al film after the first zincate treatment for (s) (a) 2, (b) 8, (c) 32, and after the second zincate treatment for (s) (d) 2, (e) 8, and (f) 32 following the first zincate treatment for 16 s in $230 \text{ g dm}^{-3} \text{ NaOH} + 50 \text{ g dm}^{-3} \text{ ZnO}$ solution and Zn stripping in 50 vol % HNO_3 solution.

ment process was traced by using a conventional microbalance with a resolution of 0.1 mg. Surface morphology was observed by using a field emission scanning electron microscope (FE-SEM, JEOL Co., model JSM-6300F) and atomic force microscope (AFM, Digital Instruments Co., model Nanoscope-IIIa).

Results and Discussion

Double zincate treatment of a magnetron sputter-deposited Al film.—Figure 1 shows the traces of Zn deposition and immersion potential measured for an MS-Al film during the first and second zincate treatment processes. In the figure, the results for an Al plate are also shown for comparison. In the first zincate treatment, Zn deposition showed some delay for several seconds after immersion and then increased almost linearly with immersion time, reaching a plateau after *ca.* 60 s. In the second treatment, Zn deposition began immediately after immersion. The delay in the first treatment was explained as a period of dissolution of an Al oxide layer preformed on the Al surface.⁷ In the second zincate treatment, a small delay in the initial stage of Zn deposition indicates that only a very thin air-formed oxide layer exists on Al before the second treatment. The plateau in Zn deposition indicates that the MS-Al film was almost dissolved and that the Zn deposition reaction was therefore terminated. A comparison with the results for an Al plate showed that the deposition rate of Zn on an MS-Al film is considerably faster than that on an Al plate. The trace of the immersion potential during the first treatment in Fig. 1b shows that the potential shifts in a less-noble direction in the range between -70 and -150 mV against Zn RE as the substitution reaction proceeds. This value is larger than that for the Al plate, which is less than -80 mV. The potential shift during the double zincate treatment could be explained by the mixed potential of the Al dissolution reaction on a bare Al surface with a smaller area (anode area) and the Zn deposition reaction occurring on Al and Zn surfaces with a larger area (cathode area).⁷ The area of the cathode is considerably larger than that of the anode because the bare Al surface is immediately covered by Zn deposition. The larger

potential shift of the MS-Al film than of the Al plate means that the dissolution area of the MS-Al film was larger than that of the Al plate. The immersion potential moves toward the potential of Zn RE as the substitution of the Al surface by Zn proceeds. In the case of MS-Al, however, the potential shows a large fluctuation after 80 s because electric contact was disconnected due to complete dissolution of the Al film. In the second zincate treatment, the potential shift occurs faster than that in the first zincate treatment, indicating that the surface in the second treatment is covered by Zn faster than it is in the first treatment, although ohmic contact failed after 100 s.

Figure 2 shows SEM images of an MS-Al film during the double zincate treatment. In the first treatment, the Al film surface is gradually covered by Zn deposition composed of very small particles and sparsely grown larger particles. In the case of an Al plate, the surface is fully covered by Zn particles of almost the same sizes.⁷⁻⁹ Nonuniform Zn deposition on an MS-Al film may be related to the columnar structure of an Al film, as discussed later. In the SEM images obtained after the second treatment, the surface is still covered by small Zn particles and larger-sized particles, as was the surface in the first treatment. Therefore, it is clear that the double zincate pretreatment does not provide a uniform Zn deposition on an MS-Al film that is suitable for a subsequent plating process. The growth of large Zn particles originates from the continuous dissolution of the Al film that is not covered by Zn deposition. In the case of an Al plate, it has been reported that the surface is almost or fully covered by a thin Zn layer in the second treatment.⁷ Therefore, suppression of such Al dissolution is important, especially for an MS-Al film. For this purpose, direct plating of metals on an Al film has been proposed^{11,12} and some additional agents may be contained in some commercial zincate solutions.

To investigate the initial stage of Zn deposition on an MS-Al surface during the double zincate treatment, AFM observation was performed as shown in Fig. 3. The initial surface of the MS-Al film before zincate treatment (Fig. 3a) shows some unevenness. Each convex part probably corresponds to the top of a column formed by

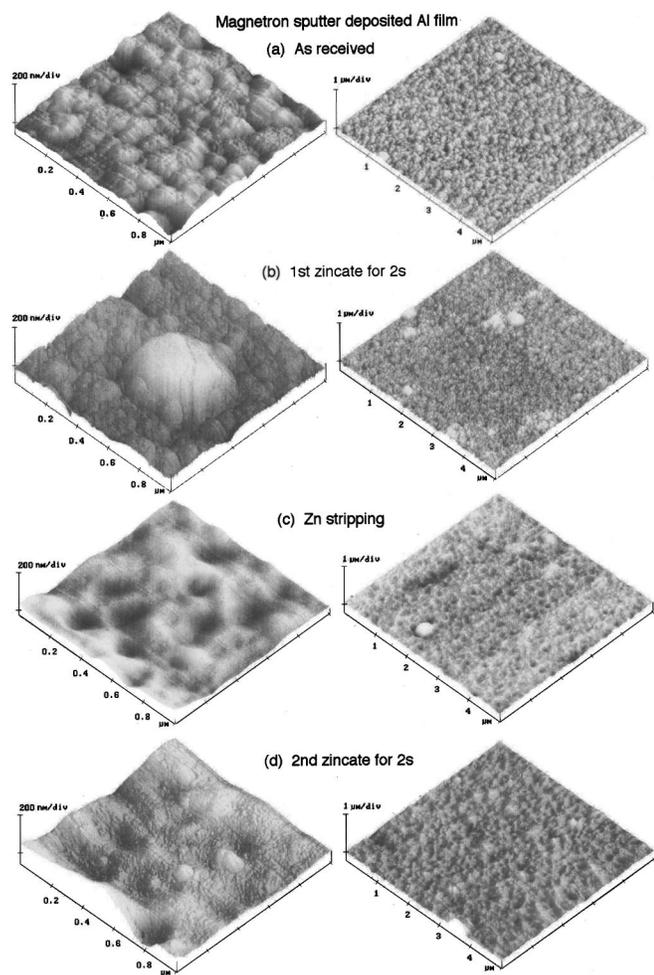


Figure 3. AFM images of an MS-Al film surface deposited on glass. (a) As received, (b) after the first zincate treatment for 2 s in $230 \text{ g dm}^{-3} \text{ NaOH} + 50 \text{ g dm}^{-3} \text{ ZnO}$ solution, (c) after Zn stripping for 30 s in 50 vol % HNO_3 solution, and (d) after the second zincate treatment for 2 s.

magnetron sputter deposition at a low temperature.^{3,14} After the first zincate treatment (Fig. 3b), most of the surface is apparently covered by Zn deposition within 2 s, and initiation of Zn particle growth is also observed. The period for the zincate treatment was limited to 2 s because longer immersion results in a surface that is too rough for AFM observation. After Zn stripping (Fig. 3c), dissolution traces and holes were observed on the surface. After the second zincate treatment for 2 s (Fig. 3d), the surface was covered by Zn deposition again and initiation of larger Zn particle growth was also observed. The deep holes that formed during the first zincate treatment were, however, not covered by the Zn deposition due to the steric effect of Zn deposition, as discussed later. This causes a continuous substitution reaction of the Al surface by Zn on the MS-Al film as seen in Fig. 1.

Figure 4 shows AFM images of an MS-Al surface after Zn stripping for 30 s following the first zincate treatment for 16 s. On the surface shown in Fig. 4a, large Zn particles were not completely dissolved, whereas small Zn particles were completely dissolved. It can be seen that the Al surface around the Zn particles is lower. In Fig. 4b and 4c, shrunken Zn particles and clefts around the Zn particles can be clearly seen. These images indicate that massive dissolution of Al occurred around large Zn particles, or, in other words, Zn particles grew at the location where considerable Al dissolution occurred. After complete dissolution of Zn particles, a mountain-like protrusion of Al remains in the center of the dissolu-

tion hole or a complete dissolution hole is formed as seen in Fig. 4d. Although the depth of the hole in this image appears to be *ca.* 100 nm, the actual depth could be greater because of the limitation in AFM measurement due to the curvature of the tip of the AFM probe. Figure 4e is a high contrast image of an MS-Al surface showing how the formation of large Zn particles affect the Al dissolution around them. In the figure, the area of dissolution (dark area) extends around Zn particles (light particles). These results suggest that massive Al dissolution continues at locations where large Zn particles grow during the first and second zincate treatment.

Double zincate treatment of an ion-beam sputter-deposited Al film.—Figure 5 shows the traces of Zn deposition and immersion potential of an IB-Al film measured during the double zincate treatment. A comparison with Fig. 1a shows that Zn deposition on an IB-Al film is considerably smaller than that on an MS-Al film and that it is suppressed after 10 s in the first treatment and after a few seconds in the second treatment. A comparison also shows that the initial stage of Zn deposition on an IB-Al film is faster than that on an MS-Al film. The small amount of Zn deposition and its suppression suggest that the IB-Al film is fully covered by a thin layer of Zn. From the value of Zn deposition, the average thickness of Zn deposition in the second treatment was estimated to be about 40 nm, using the density of a bulk Zn crystal. The immersion potential during the substitution reaction shows a smaller potential shift of less than 60 mV in a less-noble direction, indicating that the area of the dissolving surface on an IB-Al film is considerably smaller than that on an MS-Al film.

SEM images of an IB-Al film (Fig. 6) show that the surface is covered by uniform Zn deposition, and large Zn particles are not observed in either the first or second treatment. This is in agreement with the smaller Zn deposition on an IB-Al film shown in Fig. 5. A magnified image of an IB-Al film surface after the second treatment (Fig. 6f) shows that the surface is rather rough and that there are small, submicrometer-sized Zn particles are sparsely observed.

AFM images of an IB-Al film surface during the double zincate treatment are shown in Fig. 7. The initial surface of the MS-Al film before the zincate treatment (Fig. 7a) is composed of a microcrystalline structure with a grain size of about 40 nm, considerably smaller than those of the MS-Al film shown in Fig. 3a. Such a microcrystalline structure of the IB-Al film was formed due to a higher formation temperature.^{8,15} After the first zincate treatment for 2 s (Fig. 7b), the surface is covered by Zn deposition. In a magnified image, the surface shows a mountain-like shape of submicrometer size. This shape is formed by the following process. In the zincate treatment, Zn deposition starts at the point corresponding to the top of the mountain. Then, Zn deposition expands as Al dissolution proceeds, resulting in a larger dissolution depth far from the starting point. The size of the mountain is determined by the density of nucleation of Zn deposition. Such a mountain-like shape was reported in the case of zincate treatment of an Al plate.⁶ After Zn stripping (Fig. 7c), the surface still has a mountain-like shape with a microcrystalline structure, as shown in Fig. 7a. Although the roughness of the IB-Al film surface is apparently greater than that of an MS-Al film surface, dissolution holes on the IB-Al film cannot be seen. After the second treatment (Fig. 7d), the surface is covered by Zn deposition again, and the surface seems to be flattened.

Comparison of MS-Al and IB-Al films.—As described above, the characteristics of the double zincate treatment process of MS-Al and IB-Al films are considerably different. It has been reported that the structure of a sputter-deposited film is dependent on temperature at film formation.¹³ For example, a film grows in a columnar structure with gaps or crevices between columns at a low temperature, and crystalline proceeds, resulting in the formation of a fine crystalline structure without such gaps at a higher temperature. The magnetron sputter technique is generally used for rapid film formation at a relatively low temperature, resulting in the formation of a columnar structure with gaps.¹⁴ If an Al film with such a structure is exposed to a zincate solution of concentrated alkaline, dissolution of the Al

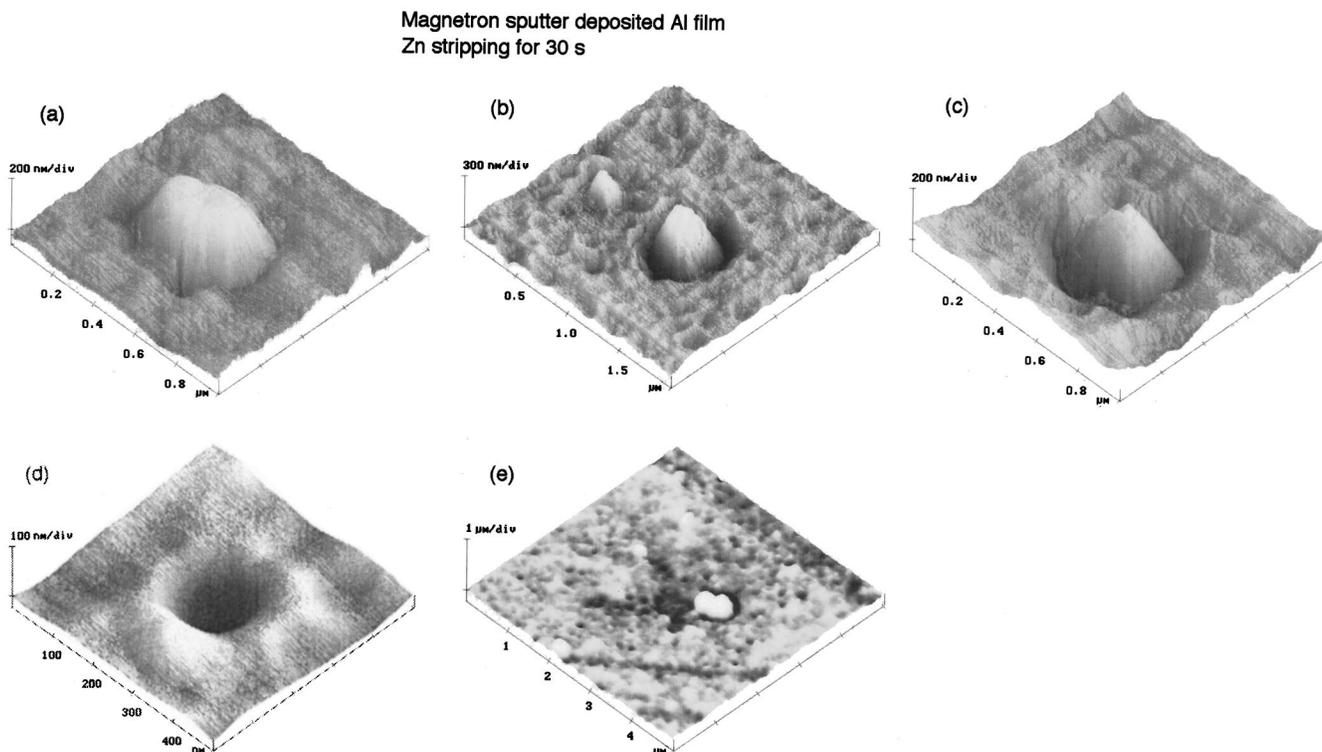


Figure 4. AFM images of an MS-Al film surface deposited on glass after Zn stripping for 30 s in 50 vol % HNO₃ solution following the first zincate treatment for 16 s in 230 g dm⁻³ NaOH + 50 g dm⁻³ ZnO solution.

substrate may continue within the gaps during the zincate treatment process. Zn deposition occurs only on the film surface because Zn(OH)₄²⁻ ions cannot reach the inside of a gap due to a steric effect, *i.e.*, Zn(OH)₄²⁻ ions are preferentially captured on the film surface or edges of the gaps where Zn was deposited previously, and thus the entrances of the gaps are hidden by Zn deposition. As a result, dissolution continues under Zn deposition and widens the gap to form large dissolution holes, as seen in Fig. 4. This situation resembles that of pitting corrosion, as schematically shown in Fig. 8a. Because the deep holes are not filled by Zn deposition even in the second zincate treatment, the substitution reaction continues at a considerably fast rate, resulting in the formation of large Zn particles near the dissolution holes, as seen in Fig. 2b. The dissolution of Al within the gaps could be suppressed by using a zincate solution with high viscosity or by pore-filling pretreatment of an MS-Al film specimen, although the results are not shown here.

In the case of an IB-Al film, the amount of Zn deposition is considerably lower than that of an MS-Al film and the substitution reaction is terminated during the first and second zincate treatment processes. This means that the film does not have defects such as gaps or holes that are susceptible to continuous dissolution. Therefore, the characteristics of the substitution reaction resemble those of a metal plate without any defects, as schematically shown in Fig. 8b. In the case of both the first and second zincate treatments, the surface is completely covered by a Zn deposition layer. Because large Zn particles do not grow on an IB-Al surface during either the first or second zincate treatment, electroless Ni plating may be applicable to an IB-Al film not only after the second treatment but also after the first treatment, although the former surface is less smooth. In conclusion, an IB-Al film provides a better quality Zn-substituted surface in the zincate pretreatment for the plating process than does an MS-Al film.

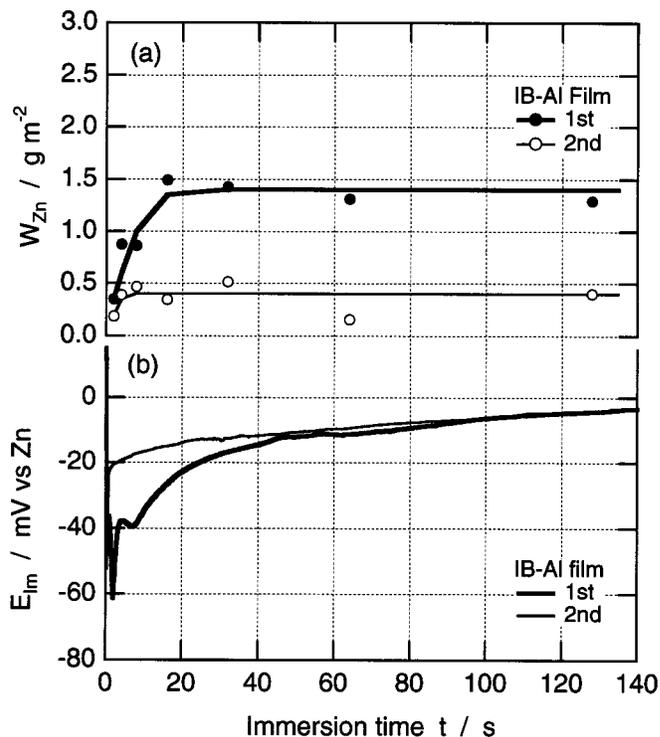


Figure 5. Traces of Zn deposition (a) and immersion potential (b) of an IB-Al film measured during the first zincate treatment and the second zincate treatment in 230 g dm⁻³ NaOH + 50 g zincate solutions following the first zincate treatment for 10 s and Zn stripping.

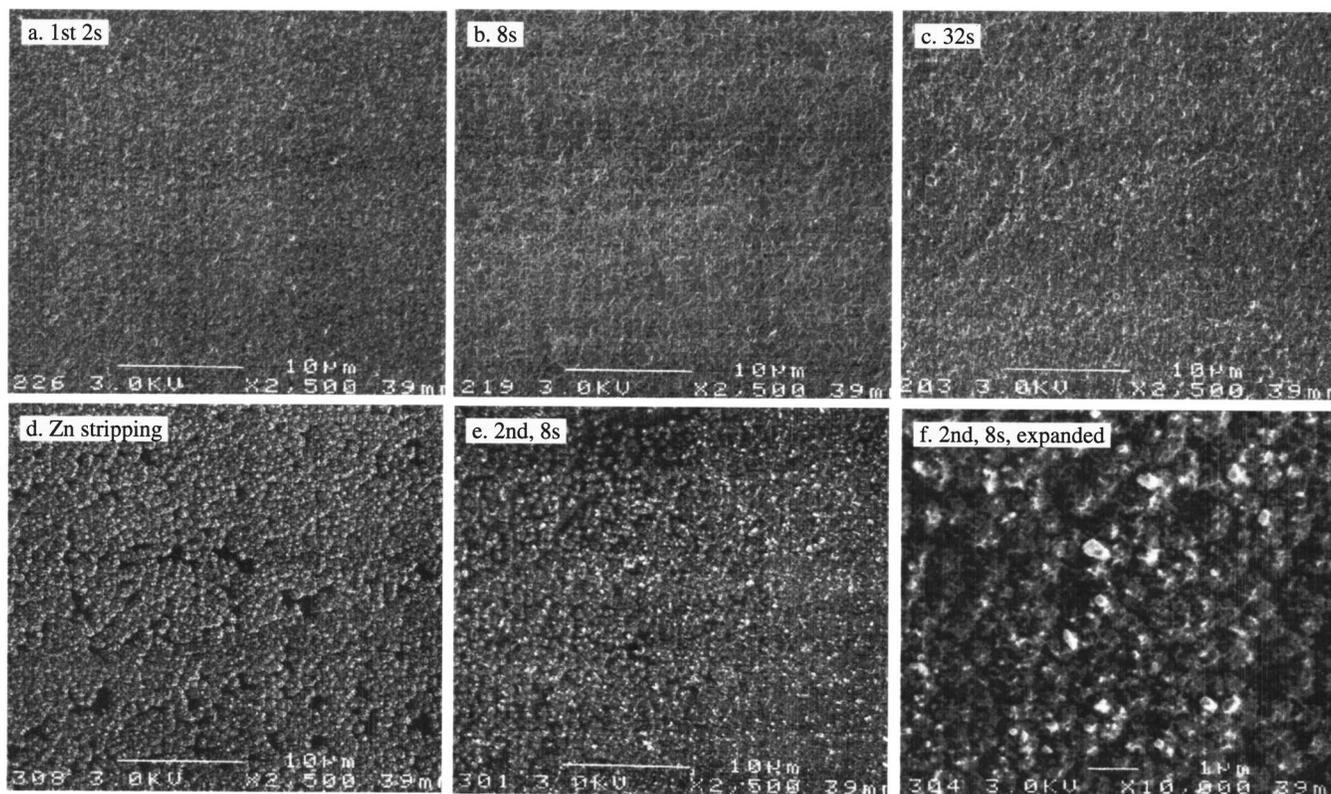


Figure 6. SEM images of an IB-Al film surface after the first zincate treatment for (a) 2, (b) 8, and (c) 32 s, after (d) Zn stripping, and (e,f) after the second zincate treatment for 8 s following the first zincate treatment for 16 s in $230 \text{ g dm}^{-3} \text{ NaOH} + 50 \text{ g dm}^{-3} \text{ ZnO}$ solution.

Conclusions

Double zincate pretreatment of Al films deposited on glass using MS and IB was characterized and compared with each other. It is clear that an IB-Al film gives a better surface suitable for subsequent electroless Ni plating, and it is achieved by the formation of a microcrystalline structure without defects in the film. In industry, however, the MS method is widely used because of its lower operational cost and faster production rate. Therefore, further research to improve the zincate pretreatment such as composition of a zincate solution or additional agents that will suppress Al dissolution is required.

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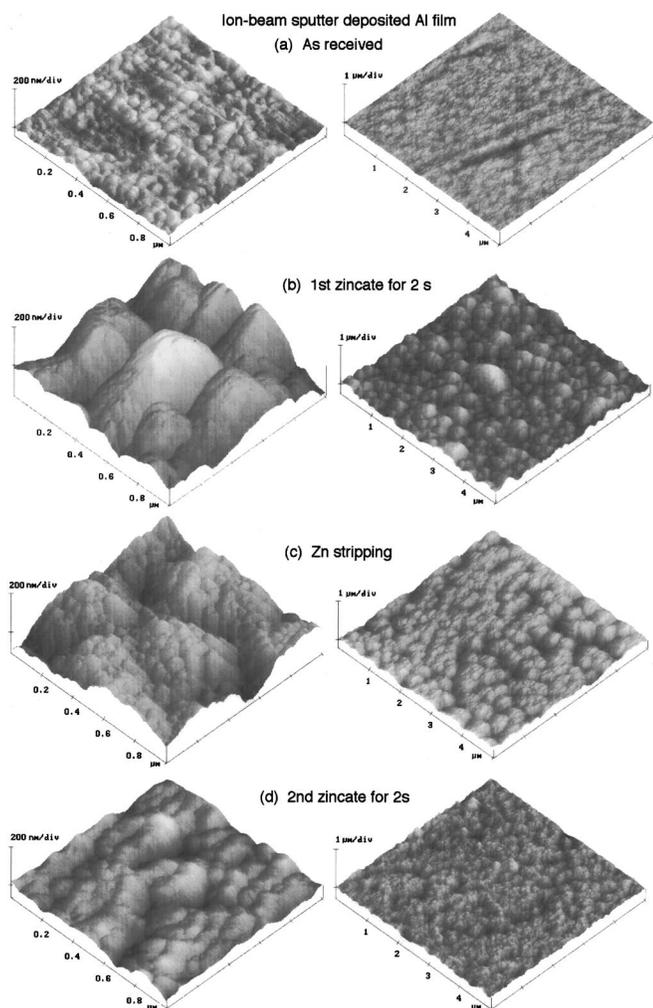


Figure 7. AFM images of an IB-Al film surface deposited on glass. (a) As received, (b) after the first zincate treatment for 2 s in $230 \text{ g dm}^{-3} \text{ NaOH} + 50 \text{ g dm}^{-3} \text{ ZnO}$ solution, (c) after Zn stripping for 30 s in 50 vol % HNO_3 solution, and (d) after the second zincate treatment for 2 s.

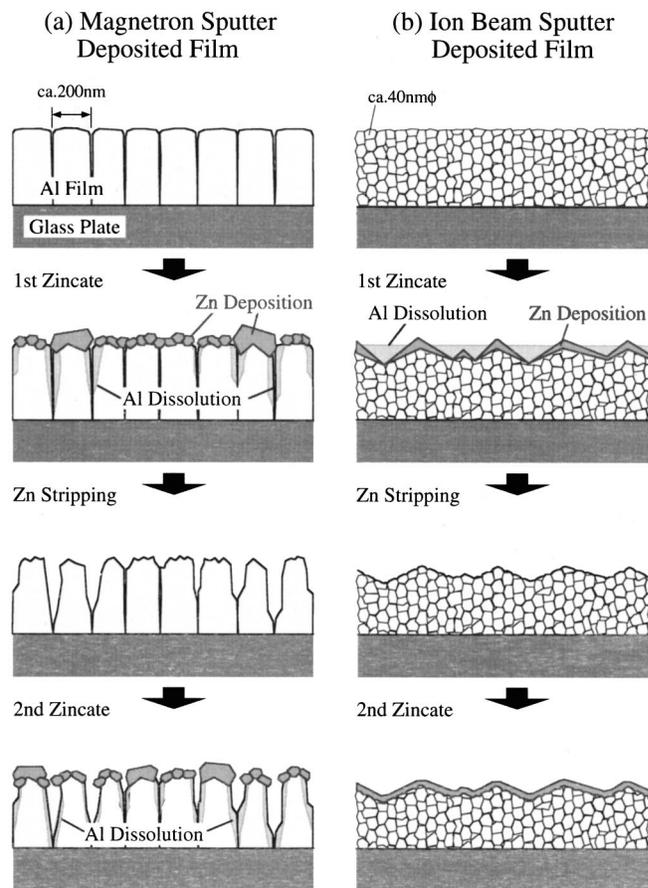


Figure 8. Comparison of Al dissolution and Zn deposition on (a) MS-Al film and (b) IB-Al film during the double zincate pretreatment.