



The effect of 180 °C-annealing on the electrochemical behavior of nano-thick zinc-electroplated copper in aqueous solutions with different pH

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Abstract

The anodic polarization and a.c. impedance measurements of 4 nm- and 25 nm-zinc-electroplated copper specimens were conducted in aqueous solutions with four different pH-values. The nano-thick zinc-electroplated copper was tested after electroplating and annealing at 180 °C for 1, 2 and 3 h, respectively. The results showed that the open-circuit potential (OCP) of 25 nm-zinc electroplated copper shifted toward noble potential after annealing. A more noble OCP of 25 nm zinc-electroplated copper could be achieved when zinc plated copper was annealed at 180 °C up to 1 h. Similar change was found for 4 nm-zinc electroplated copper only in neutral and alkaline solutions. The a.c. impedance response of all nano-thick zinc-electroplated copper corresponded to two Randle's circuits in series, in which the circuit measured in a high frequency region of their Nyquist diagrams revealed the electrochemical behavior of nano-thick zinc deposits. The charge transfer resistance of the nano-thick zinc electroplated copper was significantly raised after annealing at 180 °C when tested in pH 9.5 solution. Microstructures of the aforementioned nano-thick zinc electroplated copper were examined with cross-sectional TEM specimens. A distinct phase interface between zinc and

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copper was observed for as plated specimens, while alloying of zinc and copper at the interface was detected after annealing at 180 °C for 1 h. Electroplated zinc diffused into the copper foil during the 180 °C-annealing and the corrosion potential of the anodic polarization curve indicated the condition of the alloy surface. The annealing effect of 4 nm- and 25 nm-zinc electroplated copper specimens could be related to the results of electrochemical measurement.

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1. Introduction

It is well known that zinc electroplating is one of the most economical and effective surface protection methods for corrosion resistance of iron, copper and their alloys [1–3]. Recently copper used for the integrated circuit (IC) devices, such as copper foil and copper lead-frame, is in great demand. Nano-thick zinc-electroplating could be one of the useful methods in improving corrosion and oxidation resistance without reducing their electric property and performance [4–6]. The sacrificial anode of zinc coating is widely used in the industry for a long time and a large number of studies of the electrochemical behavior of zinc-coated steel or copper in different environments have been reported [7–11]. Although nano-thick zinc coating is commonly utilized to improve corrosion resistance of copper products used in the IC devices, electrochemical measurement of the coating is still absent in literature. Jimenez et al. [12] measured the electrochemical behavior of the copper surface implanted with nitrogen in 200 nm depth and reported that the corrosion resistance of copper could be significantly raised. Thus it is of interest to study the electrochemical behavior of nano-thick zinc-electroplated copper, especially, the behavior of nano-thick zinc-electroplated copper after annealing at 180 °C, at which the copper material would be annealed together with packaging polymer materials and be applied to electronic devices.

The objective of this study is to measure the anodic polarization curves and a.c. impedance responses of 4 nm- and 25 nm-zinc electroplated copper specimens in aqueous solutions with four different pH values. Especially electrochemical behavior was studied for specimens as-electroplated and annealed at 180 °C for 1, 2 and 3 h, respectively. Microstructures of aforementioned nano-thick zinc-electroplated copper were examined with high-resolution transmission electron microscope (HRTEM) equipped with an energy-dispersive X-ray spectrometer (EDS). The results of microstructure observation of the four zinc-plated copper specimens were compared with their corresponding electrochemical behavior, and its relationship was discussed.

2. Material treatment and experiment procedure

Zinc electroplating on copper foil was conducted in a zinc sulfate bath consisting of 10 g/L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 20 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and 75 g/L $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

A pure electroformed copper foil (99.99 wt%) in a thickness of 35 μm was used as the cathode. The plating temperature was kept constant at 30 °C and the plating current density was 1.5 A/dm². The thickness of deposits was controlled to 4 and 25 nm with a coulometer, with which the plating time was evaluated based on the law of Faraday's current efficiency. Thus, kinds of four specimens (i.e. as-plated and annealed at 180 °C for 1, 2 and 3 h) with 4 nm and 25 nm zinc-plating were prepared for electrochemical measurement and microstructure examination.

For electrochemical measurements, four electrolytes were regulated to different pH values, which were prepared by adding a small amount of analytical grade H₂SO₄ (pH 2.2), NaCl (pH 7.5), Na₂HPO₄ (pH 9.5) and NaOH (pH 12.5) to de-ionized water. Anodic polarization curves were measured potentiodynamically with a scan rate of 5 mV/s starting from –250 mV (vs. E_{corr}) to anodic potential of 1200 mV (vs. Ag/AgCl_{sat.}) with a Potentiostat/Galvanostat (EG&G Model 273A) in a flat cell (EG&G Model K0235). Testing temperature was kept at 27 ± 0.5 °C and the exposed area was 1 cm². Prior to anodic polarization scanning, all specimens were immersed in the testing electrolytes for 10 min.

A.C. impedance test was conducted under the same pretreatment of the specimens as that for anodic polarization measurement. The potential amplitude was 5 mV with the frequency range varying from 0.01 Hz to 1 MHz. Results of the a.c. impedance response on the electrode–electrolyte interface were expressed with Nyquist diagrams. The charge transfer resistance was measured and the equivalent circuits were estimated.

Microstructures of the cross-sectional zinc-electroplated copper were examined with a high resolution transmission electron microscope (HRTEM, Jeol 2010EX) with an energy-dispersive X-ray spectrometer (EDS; Links-EDAS system) for chemical composition analysis. The cross-sectional TEM specimens were prepared as follows: First two zinc-electroplated copper specimens of ca. 1.5 × 1.5 × 0.035 mm were bonded face to face tightly with M-Bond 610. Mounted in a copper ring 3 mm in diameter with G1 bond (Gatan company) together with BaTiO₃. Next the specimens were mechanically grounded to 100 μm thick with centers dimpled to 20 μm in thickness.

At last the dimpled specimens were milled with 4 keV-Ar⁺ ion using Ion Miller (VCR XL 2000) until a tiny hole was produced at the center region of the struck faces, where the thickness was so thin that the interfacial microstructures between electroplated zinc and copper foil could be directly examined and analyzed with HRTEM/EDS.

3. Results and discussion

3.1. Electrochemical tests

3.1.1. Anodic polarization measurement

The anodic polarization curves of pure copper foil, 25 nm zinc-plated and annealed specimens were measured in pH 2.2 and 12.5 electrolytes and present in

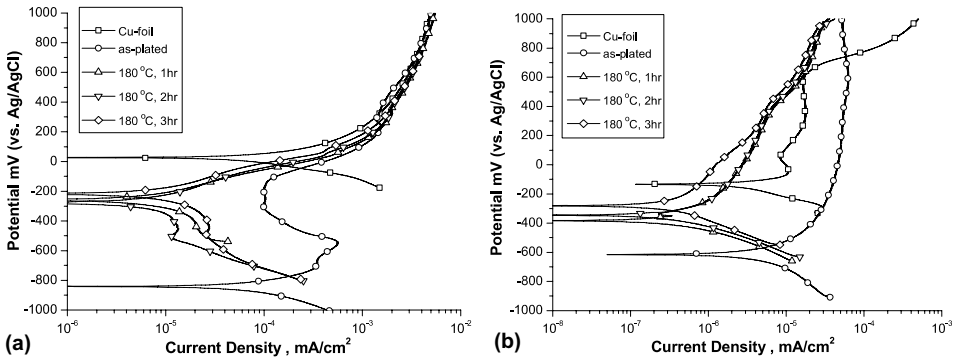


Fig. 1. Anodic polarization curves of pure copper foil, 25 nm Zn-plated and annealed at 180 °C for various periods measured in (a) pH 2.2 and (b) pH 12.5 solutions.

Fig. 1. The open-circuit potential (OCP) of the pure copper foil was ca. 22 mV (vs. Ag/AgCl_{sat.}) in the pH 2.2 electrolyte, and was ca. -134 mV in pH 12.5 electrolyte. From Fig. 1a, it is also apparent that the OCP of the zinc-plated specimens are much more active than those of the annealed specimens. The OCP of 25 nm zinc-plated copper is -859 mV but it shifts to -310 mV after annealing at 180 °C for 1 h in pH 2.2 solution (Fig. 1a). In the pH 12.5 electrolyte, a similar shift of OCP from ca. -620 mV to ca. -270 mV (Fig. 1b) is observed. Therefore, it is concluded that, all the OCPs of 25 nm zinc-plated specimens are more active than that of pure copper foil. Undoubtedly, the OCP has the capability to show the difference between the four types of specimens in both pH electrolytes.

The OCPs of the copper foil and the 25 nm zinc-plated specimens in four solutions with different pH values are summarized in Fig. 2. The OCPs of the copper foil

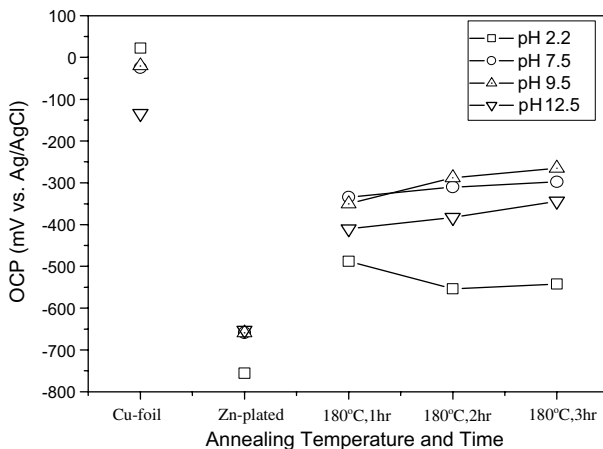


Fig. 2. OCPs of pure copper foil, 25 nm Zn-plated and annealed at 180 °C for various times measured in the electrolytes with different pH.

specimen in four electrolytes were noticeably different; the higher the solution pH, the lower the OCP. The OCP at pH 2.2 is 22 mV but shifts to ca. -134 mV at pH 12.5. The OCPs of the 180°C -annealed 25 nm zinc-plated copper are more active than those of pure copper specimen, but the change in OCP among specimens annealed at 180°C for 1, 2 and 3 h is relatively small.

The anodic current density is often used as a complementary parameter to evaluate the corrosion resistance. Higher corrosion rate could be expected when its anodic current density is higher than the other one under the same polarized potential. As shown in Fig. 1 the anodic current densities of as-plated specimens measured at pH 2.2 and 12.5 are significantly higher than those of 180°C -annealed specimens. The anodic polarization behavior was almost the same for the three types of annealed specimens. The above experimental data suggest that the corrosion resistance of as-plated specimens could be enhanced as they were annealed at 180°C for 1 h.

Fig. 3 shows the anodic polarization curves of 4 nm zinc-plated copper and 180°C -annealed specimens measured in pH 2.2 and 12.5 solutions. The anodic polarization behavior was almost similar for all 4 nm specimens in pH 2.2 solution, but in pH 12.5 solution the OCP shifted toward more noble potential and anodic current densities of the specimen decreased after annealing at 180°C . As shown in Fig. 4, the OCPs of the 4 nm zinc-plated copper specimens measured in the four selected solutions were summarized. The OCPs of 4 nm zinc-plated and 180°C -annealed specimens are almost the same in pH 2.2 solutions. However, the OCPs were raised and anodic current densities decreased with increasing annealing time in neutral and alkaline solutions. Thus the effect of annealing on the electrochemical behavior of 4 nm zinc-plated copper specimens can be seen only in neutral and alkaline solutions and no difference appears in the electrochemical behavior between as-zinc-plated and annealed specimens in the acid solution.

3.1.2. A.C. impedance measurement

Fig. 5 shows the a.c. impedance responses presented with Nyquist diagrams of 4 nm and 25 nm zinc-plated specimens in pH 12.5 solution. Two Randle's circuits

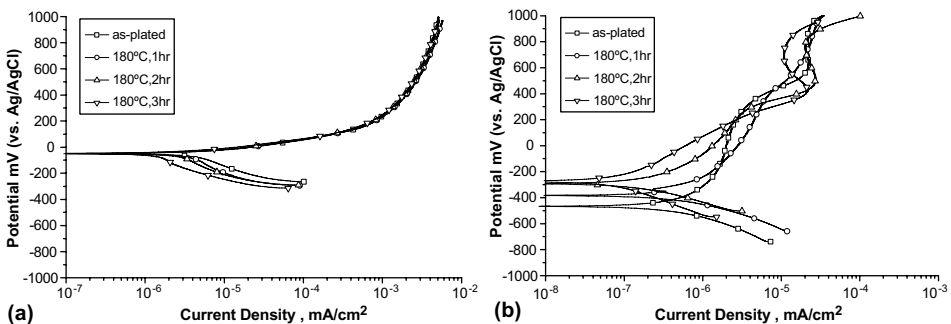


Fig. 3. Anodic polarization curves of specimens as 4 nm Zn-plated and 180°C -annealed measured in (a) pH 2.2 and (b) pH 12.5 solutions.

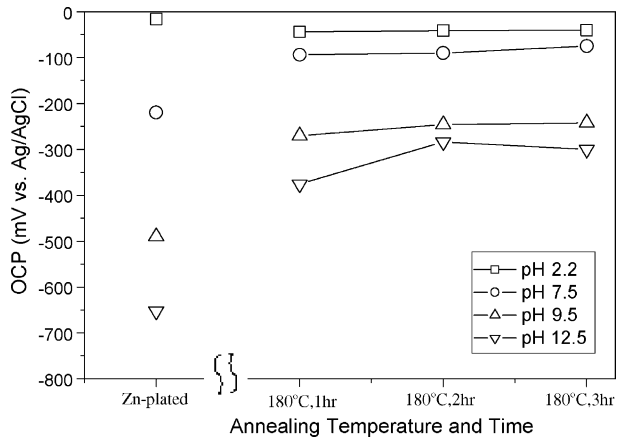


Fig. 4. The OCPs of anodic polarization curves, of 4 nm Zn-plated specimens and annealed at 180 °C for various periods, measured in various pH solutions.

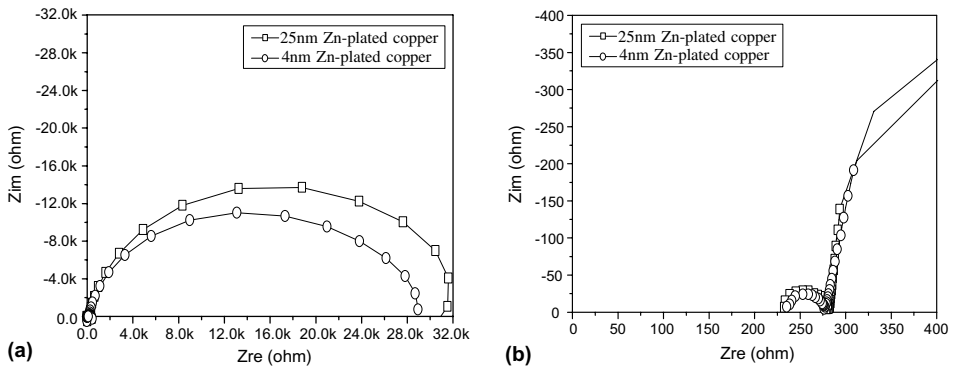


Fig. 5. Nyquist diagrams of nano-thick Zn-electroplated copper in pH 12.5 solution, (a) the frequency ranging from 1 M Hz to 0.01 Hz, and (b) magnified curves in the higher frequency portion of curve (a).

in series can be detected; namely, the first circuit with very small charge-transfer resistance (~ 50 ohm) in high frequency portion and a second circuit with relatively high charge-transfer resistance (~ 3000 ohm) in low frequency portion. The former circuit can be regarded as electrochemical responding to the nano-thick zinc-deposit and the latter to that of the copper foil. The presence of two Randle's circuits of a.c. impedance response can also be found in other pH solutions (pH 2.2, 7.5 and 9.5) but with different charge transfer resistances. The same equivalent circuit for a.c. impedance response of all nano-thick zinc-deposits is given in Fig. 6.

Fig. 7 shows the effect of 180 °C-annealing on the a.c. impedance response in magnified high frequency portion of two nano-thick zinc specimens in pH 12.5 solution. As can be seen clearly in Fig. 6, the charge-transfer resistance of the nano-thick zinc-deposit was affected by the annealing treatment. Interestingly, the solution resistance

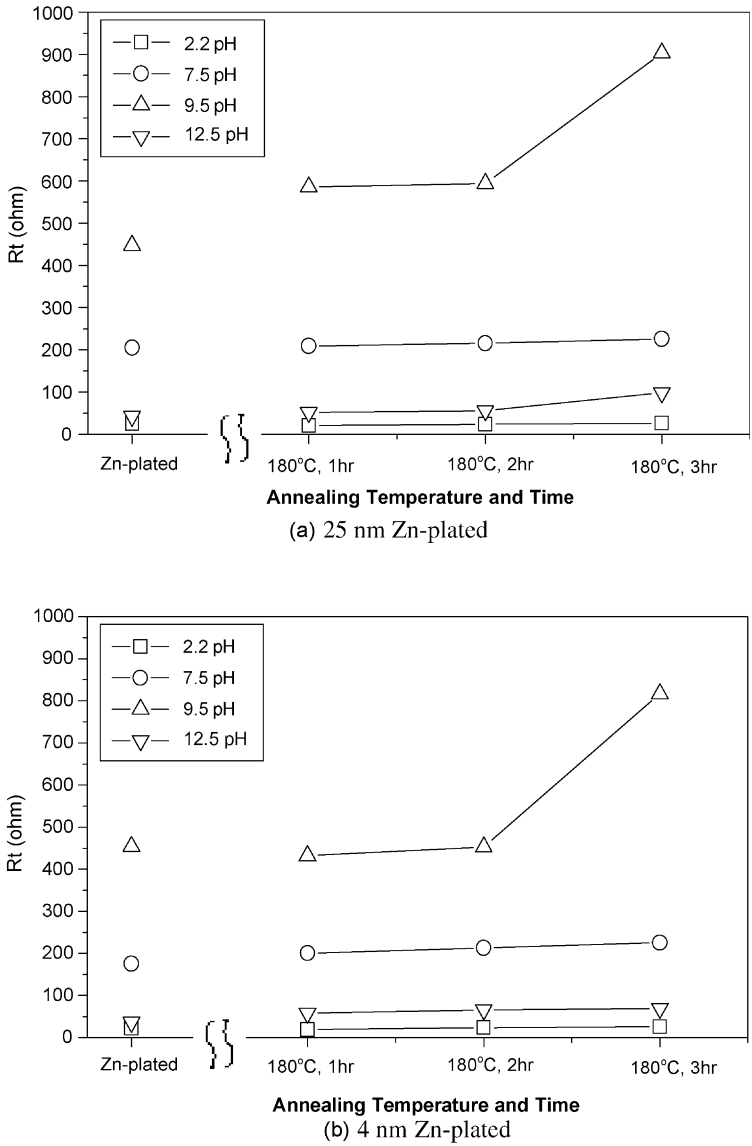


Fig. 6. Charge transfer resistance of nano-thick Zn-electroplated copper specimens and those annealed at 180 °C for different periods measured in different pH solutions.

of as-plated specimen was lower, ca. 15–20 ohm, than those of annealed specimens. It could be assumed that some dissolution from annealed specimens into the test solution occurs during a.c. impedance test.

The charge-transfer resistances of nano-thick zinc-plated and those then annealed specimens were also measured in four solutions, and the results are summarized in

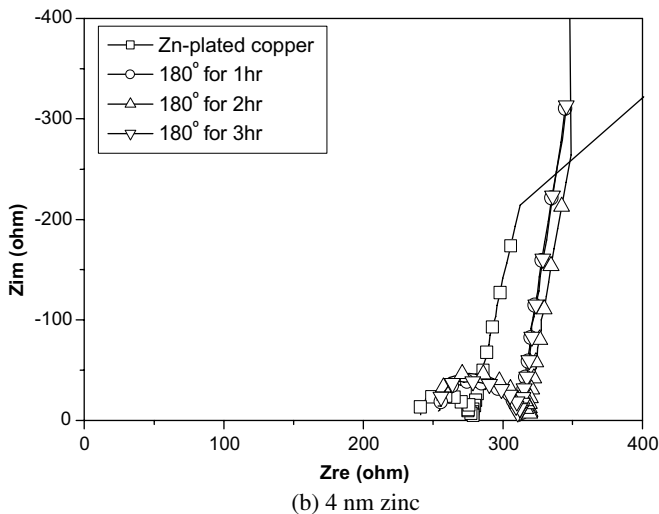
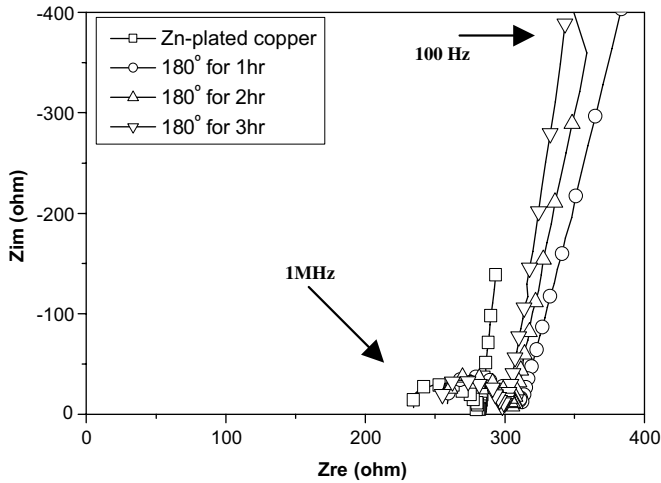


Fig. 7. Nyquist diagrams of nano-thick Zn-electroplated copper specimens and 180 °C-annealed specimens measured in pH 12.5 solution.

Table 1. From the results shown in Table 1, nano-thick zinc plated specimens have a relatively low charge-transfer resistance in low and high pH solutions. Furthermore, the charge-transfer resistances of as-plated and annealed nano-thick zinc-plated specimens are almost the same in these solutions. The annealing effect of nano-thick deposits on their a.c. impedance responses can be detected with the variation of charge-transfer resistance in pH 7.5 and 9.5 solutions. That is, the charge-transfer resistance increases as the specimens were annealed at 180 °C; especially, this variation tendency can be easily observed in the solution at pH 9.5. This behavior was

Table 1

Charge-transfer resistance of nano-thick zinc-plated and annealed specimens from a.c. impedance measurements

	R_t (ohm)			
	pH 2.2	pH 7.5	pH 9.5	pH 12.5
<i>25 nm-zinc electroplated</i>				
As-plated	25.7	275.1	447.3	42.3
180 °C, 1 h	20.4	209.2	585.6	51.5
180 °C, 2 h	23.8	215.5	594.0	55.3
180 °C, 3 h	26.0	225.9	903.0	98.2
<i>4 nm-zinc electroplated</i>				
As-plated	22.5	175.3	454.1	36.3
180 °C, 1 h	18.7	200.7	432.1	57.5
180 °C, 2 h	23.5	212.9	452.9	65.7
180 °C, 3 h	25.6	223.7	816.5	69.2

attributed to the fact that annealing tends to enhance alloy formation, which in turn retards corrosion rate.

In general, zinc coating is widely utilized as a sacrificial anode for protection of some constructional materials, such as steel, copper and their alloys. The electrochemical behavior of nano-thick zinc coating is still not reported in public literatures. In this study, we confirmed that better corrosion resistance of nano-thick zinc electroplated copper could be achieved when being annealed at 180 °C up to 1 h; however, the 4 nm zinc coated specimen seems to dissolve immediately in the pH 2.2-solution but be relatively stable in neutral and alkaline solutions. The results of electrochemical tests on nano-thick zinc-deposits can be also recognized from the Pourbaix diagram of zinc, in which pure zinc dissolves in lower pH solution and can be passivated in higher pH solution under the thermodynamically stable potential of ca. -110 mV [13]. It has been also reported [8,14,15] that an oxide and/or hydroxide film could be developed on the zinc surface when pure zinc was immersed in neutral and alkaline solutions.

3.2. Microstructure examination

Figs. 8 and 9 show the HRTEM cross-sectional views of 25 nm and 4 nm specimens. A distinctive and sharp interface between zinc deposit and copper foil can be observed. The EDS analysis was conducted by using 4 nm electron beams to analyze the chemical composition on a specific position of the specimen. Fig. 8b illustrates the results of EDS-analyses on the positions A and B located in Fig. 8a. As expected, pure zinc can be detected merely on the upper side of the sharp interface (see EDS-spectra on A and B in Figs. 8b and 9b).

Figs. 10 and 11 show the HRTEM cross-sectional views of 4 nm and 25 nm specimens after 180 °C-annealing for 1 h and their EDS analyses. It shows prominently the distinctive and sharp interface of two nano-thick zinc-plated copper disappeared after annealing at 180 °C for 1 h. This indicates clearly that interfacial diffusion

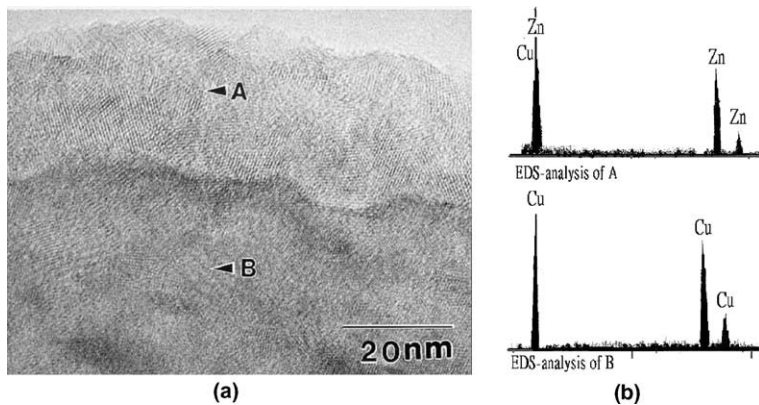


Fig. 8. (a) Cross-section HRTEM-micrograph of 25 nm Zn-electroplated copper, (b) EDS-analysis on points A, B in Fig. 8a.

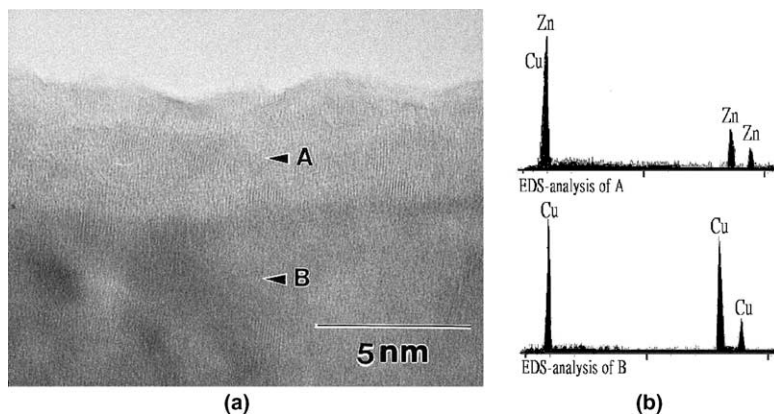


Fig. 9. (a) Cross-section HRTEM-micrograph of 4 nm Zn-electroplated copper, (b) EDS-analysis on points A, B in Fig. 9a.

between nano-thick zinc-deposit and copper foil occurred during annealing. Figs. 10b and 11b present the results of EDS-analyses with a line interval method using 4 nm electron beam from outermost M-bond/zinc interface to zinc/copper interface to detect the chemical composition of nano-thick specimens. The result of EDS analyses from the outermost M-bond/zinc-plated interface to zinc/copper interface, shows clearly the alloying of zinc and copper in the outermost surface of annealed specimens. Furthermore, the interfacial diffusion thickness of the zinc-plated copper became to 75 nm after 180 °C annealing for 1 h (Fig. 10b). EDS-analysis indicated that zinc diffused from the zinc/copper interface dispersed in copper foil during annealing. As shown in Fig. 11b, an interfacial diffusion layer was observed in the outermost M-bond/zinc-plated interface after 180 °C-annealing for 1 h. The layer was composed of zinc and copper and approximately greater than 10 nm in

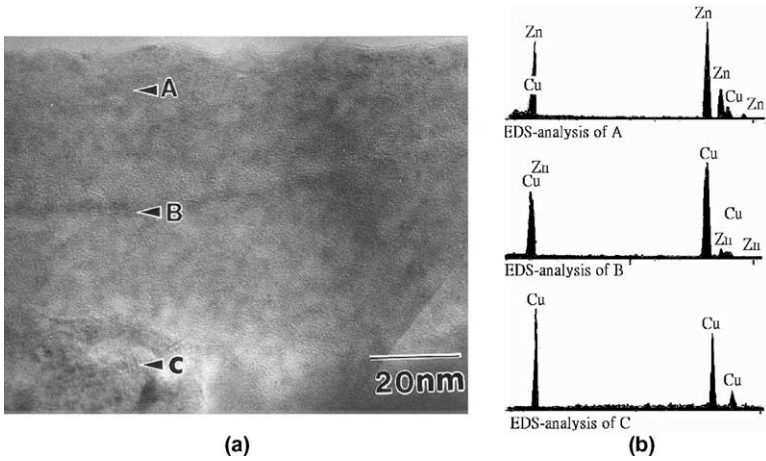


Fig. 10. (a) Cross-section HRTEM-micrograph of 25 nm Zn-electroplated copper annealed at 180 °C for 1 h, (b) EDS-analysis on points A, B and C in Fig. 10a.

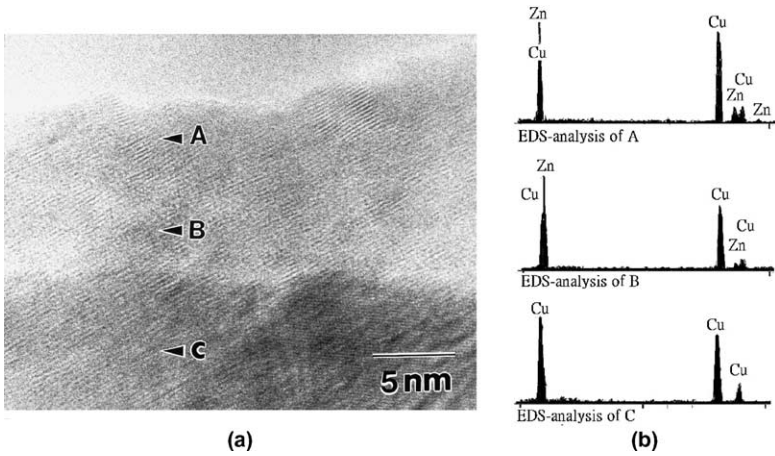


Fig. 11. (a) Cross-section HRTEM-micrograph of 4 nm Zn-electroplated copper annealed at 180 °C for 1 h, (b) EDS-analysis on points A, B and C in Fig. 11a.

thickness. It is reasonable to expect that the electrochemical behavior of annealed specimens would be affected by such surface alloying.

4. Summary and conclusions

Based on the experimental results following conclusions can be drawn:

- (1) The effect of annealing at 180 °C on 25 nm zinc-plated copper was evaluated in four different pH solutions by using anodic polarization curves. Open circuit

potentials of as-plated specimens were more active and their anodic current densities were higher than those of annealed specimens. However, the annealing effect on 4 nm zinc-plated copper was detected only in neutral and alkaline solutions.

- (2) With a.c. impedance test the annealing effect of nano-thick specimens was found by the variation of their charge-transfer resistance in pH 9.5 solution. The charge-transfer resistances of as-plated nano-thick zinc specimens drastically increased when the specimens were annealed at 180 °C up to 1 h.
- (3) Sharp interface between pure zinc deposit and copper foil of the two nano-thick as-plated specimens was observed in cross-sectional TEM images. The sharp interface disappeared and the interfacial diffusion between zinc and copper was found when the specimens were annealed at 180 °C for 1 h. Surface alloying was responsible for the change in their electrochemical behavior.

References

- [1] S. Rajendran, B.V. Apparao, N. Palaniswamy, *Electrochimica Acta* 44 (1998) 533.
- [2] X.G. Zhang, *Corrosion Science Section 55* (1999) 787.
- [3] X.G. Zhang, *Corrosion* 51 (1995) 679.
- [4] E.E. Abd Ei Aal, *Corrosion* 55 (1999) 582.
- [5] J.H.O.J. Wijenberg, J.T. Stevels, J.H.W. De Wit, *Electrochimica Acta* 43 (1997) 649.
- [6] D. Weng, P. Jokiel, A. Uebleis, H. Boehni, *Surface and Coatings Technology* 88 (1996) 147.
- [7] I. Zouari, F. Lapique, *Electrochimica Acta* 37 (1992) 439.
- [8] M.A. Pech-Canul, R. Ramanauskas, L. Maldonado, *Electrochimica Acta* 42 (1997) 255.
- [9] T.E. Graedel, *Journal of the Electrochemical Society* 136 (1989) 193.
- [10] A. Jardy, R. Rosset, *Journal of Applied Electrochemistry* 14 (1984) 537.
- [11] W.A. Badawy, F.M. Al-kharafi, *Corrosion Science Section 55* (1999) 268.
- [12] A. Jimenez-Morales, J.C. Galvan, R. Rodriguez, J.J. De Damborenea, *Journal of Applied Electrochemistry* 27 (1997) 550.
- [13] P. Marcus, J. Oudar, *Corrosion Mechanisms in Theory and Practice* (1995) 5.
- [14] A.R. Suresh Kannan, S. Muralidharan, K.B. Sarangapani, V. Balaramachandran, V. Kapali, *Journal of Power Sources* 57 (1995) 93.
- [15] C. Cachet, F. Ganne, S. Joiret, G. Maurin, J. Petitjean, V. Vivier, R. Wiart, *Electrochimica Acta* 47 (2002) 3409.