A study on the nucleation behavior of zinc particles on aluminum substrate

Sung-Ki Lee, Jeong-Gi Jin, Young-Ho Kim, Jae-Ho Lee*
Dept. of Materials Engineering, Hanyang Univ., Seoul, 133-791, Korea
*Dept. of Met. Engr. & Mat. Sci, Hongik Univ., Seoul, 121-791, Korea
E-mail: package@empal.com, Phone: 82-2-2290-0405, Fax: 82-2-2293-7445

Abstract

The nucleation and growth behavior of zinc particles deposited from the zincate solution on aluminum substrates were investigated. The zinc particles initially nucleated on the peak or edge of the aluminum surface where was exposed to the zincate solution, and preferentially grew with {0001} plane of hexagonal platelets. In case of zincate treatment on Al alloy substrate, substrate is fully covered by a thin layer of small zinc particles. At high temperature, zinc particles grew with [1100]-oriented hexagonal structure and were appeared a starfish-like shape like the coalescence of hexagonal structure.

Introduction

The flip-chip technology gained an important role in electronic assembly. An increasing number of products contain flip-chip due to size reduction, increase electrical performance and cost saving potential. [10] This flip chip process employs solder bump to electrically and mechanically connect an integrated circuit device to a substrate in a facedown configuration. Manufacturing of solder bumps on aluminum pads needs to introduce an intermediate layer to avoid the direct interaction between aluminum and the solder contents. The solder bumps are usually deposited onto the chip terminal pads, which are coated with an interface or under bump metallurgy (UBM). One of the major functions of the UBM is to promote and maintain adhesion of the solder bumps to the underlying aluminum terminal pads. Many different methods have been employed to fabricate the UBM and solder bumps, including conventional sputtering, evaporation and electroplating techniques. Among these studies, electroless plating has the highest potential for cost reduction of the bumping process in flip chip applications. It provides a selective autocatalytic metal deposition directly on the aluminum pads, and therefore lithography and etching processes are not required. However, due to the high affinity of aluminum to oxygen, aluminum pads exposed to air or to aqueous solution are always covered with thin layer of aluminum oxide or hydroxide. [1] Zincate treatment of aluminum pads is an essential step to make aluminum pads actives for subsequent electroless nickel plating. Major aims of the zincate treatment are to provide an intermediate layer that can initiate electroless nickel deposition. It was recognized that morphology of zinc layer has a direct impact on the quality of electroless nickel layer. [2] A uniform and smooth zinc layer certainly enhances the uniform growth of the subsequent electroless nickel deposit. [11] Many different methods have been investigated to provide better zinc deposit. For example, multiple zincate process, [11] control of bath chemistry, [2] and The influence of Al alloy substrate [6] etc. These methods will provide a uniform and smooth zinc deposit. However, most of this research has been focused on industrial application. Although this research results in a more uniform layer with finer Zn grains, if we will gain the basic understanding of the nucleation behavior of zinc particles, we will control the morphology of zinc particle. Therefore, this study is focused on observation of the initial behavior and growth of zinc particles, which is hardly available in open papers.

In this paper, the zincating process is conducted by immersing the aluminum substrates into an alkaline zincating bath. The alkaline zincating bath containing ZnO and NaOH etch aluminum. Aluminum is dissolved into the solution as anodic reaction to release electrons for the Zn reduction as cathodic reaction. To increase the nucleation sites of zinc deposition, the zincating processes were conducted on Al alloy. [6] Also the zincating processes were conducted at high temperature to increase of growth rate.

Experimental Section

The P-type Si wafer was cleaned sequentially in trichloroethylene, acetone and methanol for 10 min in ultrasonic bath. Aluminum was deposited by DC magnetron sputtering method. All Substrates were initially cleaned in alkaline solution for 10 s followed by acidic cleansing for 10 s. The alkaline solution and the acidic solution were, respectively, 10% NaOH and 30 % nitric acid. The zincating process was conducted in 120 g/l NaOH, 4 g/l ZnO, 1 g/l $NaNO_3$ and 50 g/l $C_4H_4NaO_64H_2O$.

Section 1. Nucleation and Growth of zinc particles

The aluminum deposits were preparation by D.C magnetron sputter deposition using targets of 99.99% Al. Zincating process is carried out at room temperature by dipping the pretreated aluminum specimen into zincate solution.

Section 2. The increase of growth rate

The aluminum deposits were preparation by D.C magnetron sputter deposition using targets of 99.99% Al. Zincating process is carried out at 50 ℃ by dipping the pretreated aluminum specimen into zincate solution.

Section 3. The increase of nucleation sites

The Al-Cu-Si deposits were preparation by D.C magnetron sputter deposition using targets of Al (98.5%)-Cu (1%)-Si (0.5%). Zincating process is carried out at room temperature by dipping the pretreated Al alloy specimen into zincate solution.

Results and discussion

Nucleation behaviors of zinc particles

The aluminum substrate generally is formed a columnar structure with holes or boundaries by the magnetron sputtering system as shown in Figure 1. [5]

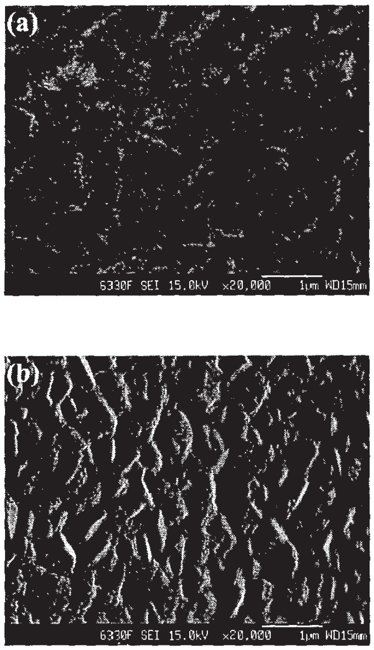

Figure 1. FE-SEM images of as-deposited Al specimen. (a) Plan-view image, (b) tilted image.

When this aluminum with a columnar structure is exposed to the alkaline and acidic solution, the surface of the etched aluminum after pretreatment shows unevenness with holes (Figure 2).

In the Figure 2, when the aluminum is exposed to the alkaline zincating solution, the dissolution rate of each grain varies. Because of the difference in the binding energy of atoms between grain and boundary. Total energy involved in the binding energy and the subsequent dissolution of aluminum is faster for grain boundaries, which have the weak binding energy.

To investigate the an initial stages of zinc deposition on aluminum surface during zincating process, the surface morphologies of aluminum surface just after zincating process were observed by FE-SEM. Figure 3,4 shows the plane and titled image of surface. Dissolution of the aluminum substrate continued along boundaries during the zincating treatment. However, zinc deposition occurs only on the film surface since zinc complex ion cannot reach the inside of holes [5].

The entrance into the holes of zinc particles is suppressed by exchange reaction. Leading to the dissolution of electronegative aluminum and deposition of a more electropositive zinc ion. The deep holes cannot be filled by zinc deposition, even though zincating time was increased to some degree as shown in Figure 5. As a result, after the zincating treatment, zinc ions reduction occurred preferentially on convex part, corresponding to the peaks or edges of aluminum surface etched by zincating solution. Zinc particles form cluster, which were preferentially deposited at high surface energy area of aluminum surface. The above results indicate that zinc nucleation sites correlate to the surface roughness, [7] and electrochemical properties. [2,8]

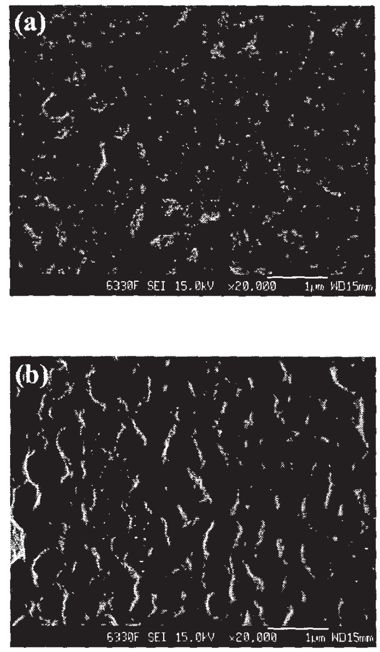

Figure 2. FE-SEM images of alkaline and acidic cleaned Al specimen. (a) Plan-view image, (b) tilted image.

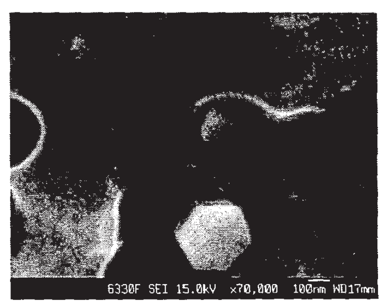

Figure 3. FE-SEM images of first zincated Al specimen for 10 s. (Tilted image with abnormal deposition behavior)

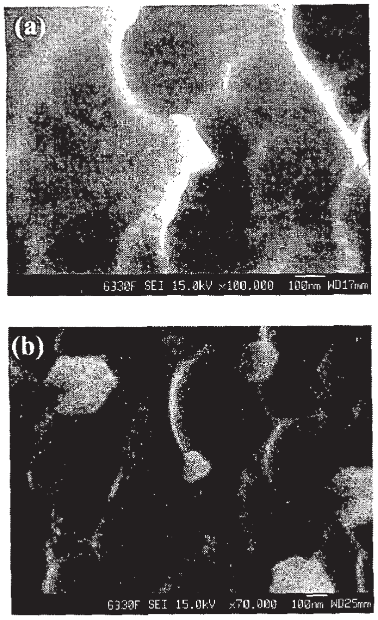

Figure 4.FE-SEM images of first zincated Al specimen after 1 second. (a) Titled image, (b) plan-view image.

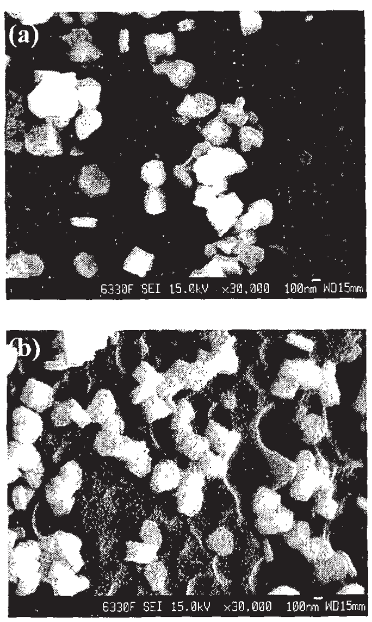

Figure 5. SEM Images of double zincated (10 s-10 s) specimen. (a) Plan-view image, (b) titled image.

Growth mode of zinc particles

Figure 6 shows the morphology of the stacking hexagonal platelets. At the initial growth stage (Figure 4b), Zinc particles form hexagonal platelet and grow with [0001] direction of hexagonal platelet as shown in Figure 6. Dissolution of the aluminum substrate continues along boundaries. Therefore, the displacement reaction between anodic aluminum ions and cathodic zinc ions continues at a considerably fast rate, resulting in the formation of large zinc particles near the dissolution holes, as seen in Figure 4b. This shows that the morphology of hexagonal platelets which represents the basal texture. [9] The close packed planes, or the low index planes are known to be more resistance to dissolution because of the higher binding energy of surface atoms. [9] In hcp metals, The {0001} plane exhibits the best corrosion resistance [9]. In the Figure 6, The {0001} Plane has the most probability to stabilize thermodynamically; because this stack has the lowest energy state.

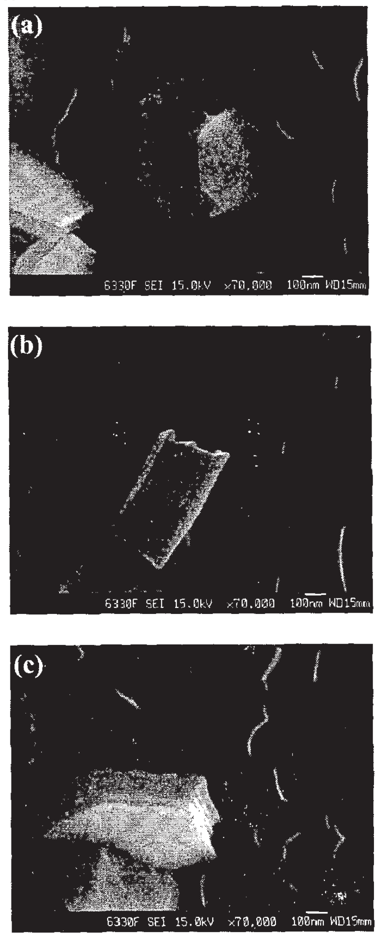

Figure 6. FE-SEM images of first zincated Al specimen for 10 s.
(a) Titled image with normal stacking behavior,
(b) Titled image with lateral stacking behavior,
and (c) titled image with lateral stacking behavior.

Figure 7 show the SEM images that illustrate the microstructure of zinc growth deposited.

The zincate reaction occurs sporadically on the aluminum surface. The groups of hexagonal phase at isolated area were formed locally as islands (Figure 7a).

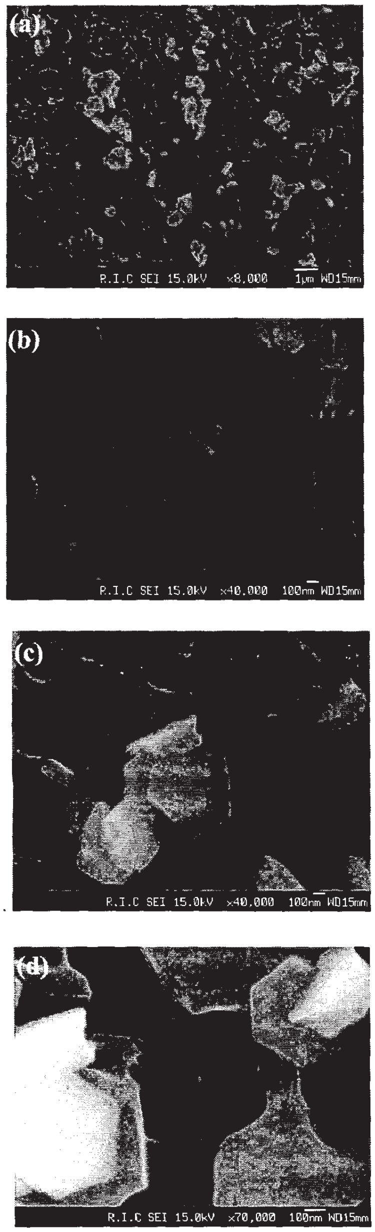

Figure 7. FE-SEM images of first zincated on same Al surface for 5 s.
(a) Low magnification, (b) plan-view image with parent zinc particle, (c) plan-view image and (d) Plan-view image of parent zinc and groups of hexagonal platelets.

The increase of growth rate

When zincating process were conducted at 50℃, zinc particles grew with [1100]-oriented hexagonal structure and were appeared a starfish-like shape, due to thermally activated migration of boundary at high temperature (Figure 8).

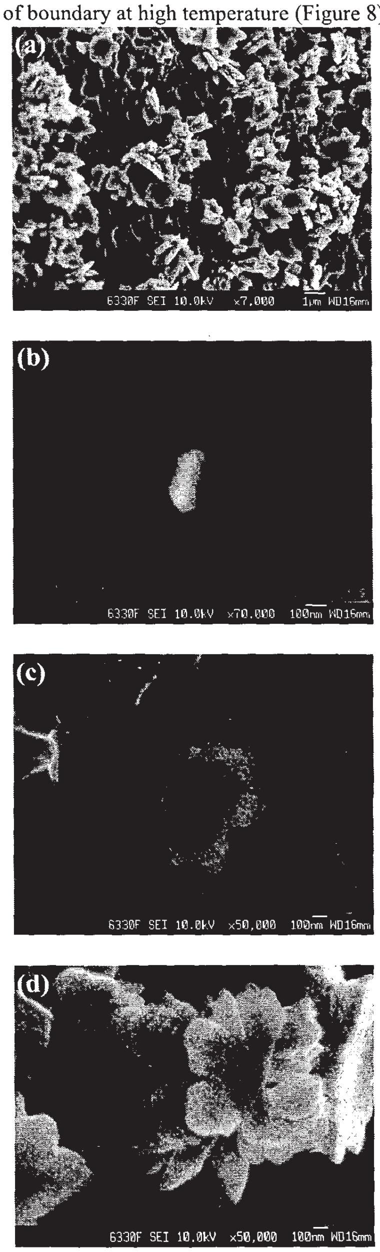

Figure 8. FE-SEM images of first zincated Al specimen for 10 s in 50℃ zincate solution.
(a) Low magnification, (b) titled image of hexagonal platelet, (c) titled image and (d) titled image with a starfish-like shape.

Comparison on Pure Al and Al alloy substrates

Figure 9 show SEI (secondary electron image) and BSE (back scattered electron) during zincating treatment for 1s on pure Al and Al-Cu-Si substrate.

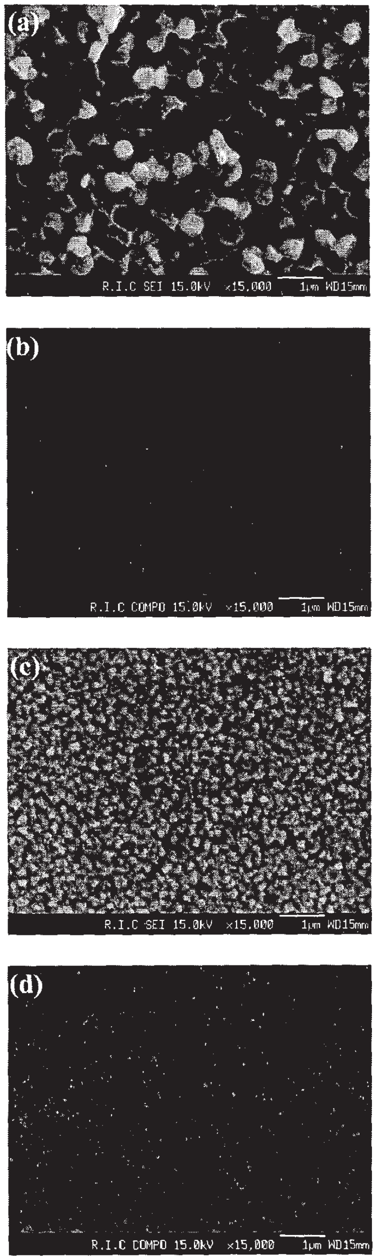

Figure 9. FE-SEM images of zincated pure Al substrate (a: SEI and b: BSE) and Al alloy substrate(c: SEI and d: BSE) for 5 s.

A comparison with Figure 9 shows that zinc particles on Al-Cu-Si substrate is considerably smaller than that on a pure Al substrate. In Figure 9a, most of zinc particles apparently covered sporadically. In Figure 9c, Al-Cu-Si substrate is fully covered by a thin layer of small zinc particles. This comparison indicates that the initial stage of zinc deposition on Al-Cu-Si substrate is faster than that on pure Al substrate. And the zinc nuclei on Al-Cu-Si substrate are more than that on pure Al substrate. These results indicate that zinc nucleation sites directly correlated to the intermetallic particles. Zinc nucleates preferentially on intermetallic precipitates in an Al matrix. [6]

The studies for the various influences of zinc deposition have been investigated by the three focus of (1) electrochemical properties of the cathode materials, (2) the effect ionic impurity in the electrolyte, and (3) the cohesion strength between the deposited metal and its substrate. [6]

Conclusion

During nucleation stage, the parent zinc is created on the peak or edge of Al surface. During the growth stage, zinc particles are migrated into parent zinc, and then hexagonal platelets formed. As a result, localized zinc islands were formed. At 50℃ zincating process, zinc particles were appeared a starfish-like shape by the fast migration of zinc ions. Zinc nuclei on Al-Cu-Si substrate are more than that on pure Al substrate.

Acknowledgments

This wok was supported by Center for Electronic Packaging Materials of Korea Science and Engineering Foundation.

References

1. J. H. Lau, Flip Chip Technologies, McGraw-Hill (New York, 1996), pp. 435-437
2. G. Qi, X. Chen, Z. Shao, Influence of Bath Chemistry on Zincate Morphology of Aluminum Bond Pad, *SEMICON Korea Technical Symposium 2001*, Session 8-3, pp. 1186-1190
3. Kwang-Lung Lin, Shiuh-Yuan Chang, The Morphologies and the chemical states of the Multiple Zicating Deposits on Al Pads of Si Chips, Thin *Solid Films* 288(1996) pp. 36-40.
4. C.J. Chen, K.L. Lin, Internal Stress And Adhesion of Amorphous Ni-Cu-P Alloys on Aluminum, Thin *Solid Films*, 370(2000) 106-113
5. Kazuhisa Azumi, Takuma Yugiri, Masahiro Seo, Shinji Fujimoto, Double Zincate Pretreatment of Sputter Deposited Al Film, *Journal of The Electrochemical Society*, 148(6) C433 C438 (2001)
6. Ping Gu, R. Pascual, M. Shikhanzadeh, S.Saimoto, J.D. Scott, The influence of Al substrate intermetallic precipitates on zinc electrodeposition, *Hydrometallurgy*, 37(1995) pp. 267-281

7. Mihalis Lazaridis, Qystein hov, Kostas Eleftheriadis, Heterogeneous nucleation on rough surfaces: implications to atmospheric aerosols, *Atmospheric Research*, 55(2000) pp. 103-113
8. C.J. Chen, K.L. Lin, A kinetic and electrochemical study of the zincate immersion process for aluminum, *Jounal of Applied Electrochemistry*, 25(1995) pp. 659-666
9. H. Park, J. A. Szpunar, The role of texture and morphology in optimizing the corrosion resistance of zinc-based electrogalvanized coatings Corrosion *Science,* Vol.40, No.4/5,pp.525-545, 1998
10. Anhock. S, Ostmann. A., Aschenbrenner. R., Reichl. H, Qualification of the system electroless nickel bumps and PbSn5 for high temperature applications Advanced *Packaging Materials: Processes, Properties and Interfaces, 2000. Proceedings. International Symposium on 2000*
11. Chung-Daw Young and Jenq-Gong Duh, Adhesion Strength and Microstructural Evaluation in Electroless Ni-P Metallized AlN Substrates, *IEEE Transactions on Components, Packaging, and Manufacturing Technology,* Part A.vol.20, No. 3. September 1997