Copper Electrodeposition onto Aluminum from a Copper Acid Baths In The Presence Of Poly Ethylene Glycol (PEG)

Ferry Budhi Susetyo^{1,4}, Evi M.H. Situmorang^{1,3}, Syifa Luthfiya², Bambang Soegijono^{2,*}

¹Graduate Program, Department of Physics, Universitas Indonesia, Jakarta Indonesia

²Department of Physics, Universitas Indonesia, Jakarta Indonesia

³School of Medicine and Health Sciences, Atmajaya Chatolic University of Indonesia

⁴Mechanical Engineering, Universitas Negeri Jakarta, Jakarta Indonesia

Abstract. Many hydrophobic metal coatings onto Aluminum have been studied in recent years because of their significant potential applications. Unfortunately, most of them lost the original metallic luster due to the micro/nano binary structures. In this paper, a facile method was developed to prepare a hydrophobic and high-glossy copper coating onto aluminum substrates. The wettability and gloss could be tuned by the value of current density. With the increase of current density, the surface roughness raised, thus resulting in increase of contact angle and decrease of glossiness. When the current density was less than 1 mA/cm², the coating exhibited good luster and preferred orientation. Lowering the Current density the coating showed different corrosion resistance and good water repellence.

1 Introduction

In semiconductor manufacturing, like using copper (Cu) technology, metal lines are defined first by lithography and etching processes, and are then filled up with metal for metallization. The electrochemical plating (ECP) method is widely used for the preparation of metallization, such as Cu, and Ni layers. Before the Cu-metal is deposited into the patterns by ECP, other method such as physical-vapor-deposition (PVD) is widely used to form a tantalum (Ta) base diffusion barrier between the dielectric and Cu films [1–4]. Plating techniques also have the advantages of low processing temperature, low tool cost, and good via/trench_filling capability. However, electroplating method needs an external current source and a seed layer of uniform thickness. Furthermore, the electrical uniformity of electrodeposited films and via/trench_filling capability depend on the current distribution for electroplating thorough out the specimens. Usually, stabilizer and surfactant were also added to the plating bath to decrease the surface tension of the solution and for increase the bath stability. Surfactant has a favorable effect on the surface roughness and

* Corresponding author : naufal@ui.ac.id

crystal orientation of electroless deposits [5-7]. These factors influence the electrical characteristic of metal films such as resistance to electro migration and conductivity.

Literature showed that the sheet stress and resistance of Cu films change as a function of time, and are closely related with the grain size growth describe as self annealing. This phenomenon depend on several factors, such as plating current density, thickness, plating method and the additives in the plating solution [8–12].

Therefore, Electrochemical Plating were used to deposit Cu on Aluminum substrate. Effects of Polyethylene Glycol (PEG) and current on the properties of copper deposit films using such as morphology, crystal structure and corrosion resistance were investigated.

2 Experimental Procedures

DC electroplating process of the Cu films was performed at room temperature on the Aluminum substrate with diameter 23.37 mm. A virgin make-up solution (VMS) consisting of 0.25-mol/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 50-ppm chloride ions was used as the standard solutions. Organic additives polyethylene glycol (PEG), were added to the standard solution.

The Cu film was electroplated under galvanostatic control at room temperature with a constant plating current 0.245 A, 0.174 A and 0.124 A. The thickness of Cu film was almost 500 μm . The crystalline structure of the Cu films was identified by X-ray diffraction (Rigaku RINT 2000 with CuK_α radiation). The XRD pattern scans from 20 to 90 degrees with the resolution of 0.01 degree. The surface morphology of Cu were observed by using optical microscope. Highscore plus software were used to refined the XRD pattern to obtained crystal parameter.

3 Results and Discussion

3.1 Optical Microscope

Figure 1 show surface morphology taken using optical microscope of the three samples. Samples with different current show different morphology. Surface roughness decrease as current plating decrease. Plating with higher current density will form a higher dislocation loops and increase the total energy stored in the Cu films lead to increasing in surface roughness.

Fig. 1. Surface morphology taken by optical microscope of the three samples Cu- $I=0.245 \text{ A}$, Cu- $I=0.174 \text{ A}$ and Cu- $I=0.124 \text{ A}$

3.2 X-ray Diffraction

X-ray diffraction were used to investigate the phase and structure of the three samples Cu-I=0.245 A, Cu-I=0.174 A and Cu-I=0.124 A. The pattern obtained were refined using Rietveld Analysis. The evolution of the crystal parameter were tabulated in Table 1.

Table 1. Crystall parameter of Cu-I=0.245 A, Cu-I=0.174 A and Cu-I=0.124 A

Parameter	Sample		
	Cu-I-0.124	Cu-I-0.174	Cu-I=0.245
$a=b=c(\text{\AA})$	3.6234	3.6259	3.62383
$V(\text{\AA}^3)$	47.5741	47.6711	47.5885
$\rho(\text{g cm}^{-3})$	8.87	8.85	8.87
$D(\text{nm})$	1501.0	929.3	987.3
Micro strain (%)	0.022	0.035	0.040
$R_{wp}(\%)$	9.775	9.595	14.155
GOF	4.68	4.04	2.78

Higher current during plating, the unit cell volume increase due to higher number of defect. Arrangement of atom during depositions will be more perfect if the current decrease. Furthermore, microstrain differ markedly when the current become higher.

Figure 2 showed the XRD pattern of the samples Cu-I=0.245 A, Cu-I=0.174 A and Cu-I=0.124 A. The intensity of the peak around $2\theta = 74.75$ increase as the current decrease. It seem that the samples exhibit preferred orientation. From XRD pattern, crystallinity become better when the current decrease.

Fig. 2. XRD Pattern of the three samples Cu-I=0.245 A, Cu-I=0.174 A and Cu-I=0.124 A .

Fig. 3. Peak shifting around $2\theta = 74.75$

Figure 3 showed peak shifting around $2\theta = 74.75$ when the current plating decrease. The crystal become denser and less defect.

3.3 Corrosion Test

Figure 4 showed Corrosion test of the substrat Aluminum, $Cu-I=0.124$ A and $Cu-I= 0.245$ A. Alumunium is more resistance in corrosion than Copper because of alumunium oxide . It seems that decreasing the current, the corrosion resistance decrease because the crystall become more perfect and less dislocation formed

Fig. 4. Corrosion test of the substrat (Al), $Cu-I=0.124$ A and $Cu-I=0.245$ A.

4 Conclusions

Electrochemical plating of Copper on aluminum have been taken successfully. Surface roughness decrease as the plating current decrease. It exhibit highly preferred orientation when the current decrease. The single phase copper have been obtained. The unit cell parameter change as the current decrease. Decreasing current, the crystal become denser.

5 Acknowledgment

The authors acknowledge with gratitude the financial supports from the Universitas Indonesia under grant Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa (PITTA), No. 2239/UN2.R3.1/HKPO5.00/2018

References

1. C. C. Chang, J. S. Chen, and W. S. Hsu, *J. Electrochem. Soc.* 151 **11**, 746 (2004).
2. Y. L. Chin, B. S. Chiou, and W. F. Wu, *Jpn. J. Appl. Phys.* **41**, 3057 (2002).
3. A. Istratov and E. R. Weber, *J. Electrochem. Soc.* 149 **1**, G21 (2002).
4. Stavrev, D. Fischer, A. Preub, C. Wenzel, and N. Mattern, *Microelectr. Eng.* **33**, 269(1997).
5. Valery M. Dubin and Yosi Shacham-Diamand, *J. Electrochem. Soc.* 144, 898 (1997).
6. H-K. Kang, J. S. H. Cho and S. S. Wong, *Elec. Dev. Lett.* 13, 448 (1992).
7. J. Tao, N. W. Cheung, C. Hu, H-K. Kang and S. S. Wong, *Elec. Dev. Lett.* 13, 175 (1992).
8. R. Junginger and G. Elsner, *J. Electrochem. Soc.* 135, 2304 (1988).
9. S. C. Chang, J. M. Shieh, B. T. Dai, M. S. Feng, and Y. H. Li, *J. Electrochem. Soc.* **149**, G535 (2002).
10. J. Koike, M. Wada, M. Sanada, and K. Maruyama, *Appl. Phys. Lett.* **81**, 1017 (2002).
11. C. Detavernier, S. Rossnagel, C. Noyan, S. Guha, C. Cabral, and C. Lavoie, *J. Appl. Phys.* **95**, 2874 (2003).
12. H. Lee, W. D. Nix, and S. S. Wong, *J. Vac. Sci. Technol. B* **22**, 2369 (2004).