Nanoscale Wiring by Cu Electrodeposition in Supercritical Carbon Dioxide Emulsified Electrolyte

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1. Introduction

Copper wiring into nanoscale holes with high aspect ratio by electrodepostion is an important problem for 3-D integration in integrated circuit technology toward miniaturization of electronic devices [1]. However, void and pinhole found in Cu wiring for the integration can cause trouble for miniature device. Cu electroplating method without void and pinhole is needed.

We have proposed novel electroplating methods with supercritical carbon dioxide (sc-CO_2) emulsion (EP-SCE) [2]. The electrochemical reaction is carried out in an emulsion of sc-CO_2 in electrolyte with surfactants. Sc-CO_2 has low viscosity and compatibility of hydrogen. Thus, this method is applicable in fine Cu wiring. The aim of this report is to examine Cu electrodeposition by using sc-CO_2 emulsified electrolyte into nano-scale Cu wiring on the viewpoints of dissolution of Cu seed layer, gap-filling capability into nano-scale holes and contamination in the plated Cu.

2. Experimental apparatus and procedure

Copper-sulfate-based electrolyte was purchased from Okuno Industry. 40 vol.% CO_2 at 313 K and 15 MPa under agitation were used with sc-CO_2 apparatus [3]. Surfactant, polyoxyethylene lauryl ether, was added for formation of emulsion, and the concentration was 1.0 vol.% with respect to the electrolyte. Cu particles (63μm, min. 95%) were added for formation of the suspension. Current density of electroplating was 1.0 A/dm^2. Hole test element group (TEG) had an integrated structure with Cu seed layer on TiN barrier layer sputtered on Si was used for filling in high aspect ratio holes. The holes were 70 nm in diameter, 350 nm in depth. The cross-sectional SEM images of holes filling with electrodeposited copper were observed by a scanning electron microscope (FE-SEM, S-4300SE, Hitachi high technologies Co., Ltd).

3. Results and Discussion

At First, we conducted EP-SCE on the hole TEG, Then Cu seed layer on the substrates was dissolved, and Cu electroplating could not be conducted. It is also reported that Cu dissolved in Cu sulfate plating solution. [4] Moreover, the dissolution of CO_2 into the electrolyte can cause the acidity of the solution to be higher and the Cu seed layer to dissolve into the solution. In Cu plating on Cu substrate, the current efficiency by conventional electroplating (CONV) was 84%, though that by EP-SCE was 61%. This means dissolution of Cu may occur in the emulsion of sc-CO_2. Thus, we concluded that EP-SCE is not adequate for Cu wiring.

In order to inhibit dissolution of Cu, we made sc-CO_2 suspension by addition of Cu particles to sc-CO_2 emulsion. Electroplating method with sc-CO_2 suspension is denoted as EP-SCS [3]. It is interesting that when the Cu particles were added into the emulsion of the electrolyte in supercritical CO_2, the smooth Cu surface was obtained by EP-SCS. It is widely accepted that the electroplating reaction in the suspension with Cu particles gives rough surface of the plated films, because the Cu particles were deposited with plated Cu at the same time. However our results did not show such a phenomenon. Thus, we suggest that Cu particles in the EP-SCS at high pressure suspension could be dissolved into the continuous phase of the Cu electrolyte.

Next, filling experiments were also conducted on TEG holes with 70 nm in diameter and aspect ratio 5 by CONV and EP-SCS. The holes were filled by COV, but there were observed many defects. These voids could come from the surface tension between air and the electrolyte or the viscosity of the electrolyte. On the other hand, Cu can be filled in holes without voids and pinholes by EP-SCS method. Thus, EP-SCS method is effective for filling of Cu into nanoscale holes. These complete gap-filling experiments are because sc-CO_2 has low viscosity enough to fill such fine holes with high aspect ratio and the addition of Cu particles in the sc-CO_2 emulsion suppressed the dissolution of the Cu seed layer.

Recently, Ni film obtained by this technique was found to contain carbon more than by conventional electroplating methods [5]. The reason is suggested that dissolved CO_2 was reduced to carbon and the carbon was codeposited with Ni. It is expected that impurities cause high electric resistance problem in the electrodeposited Cu. Thus, we have to investigate impurity concentration in the film obtained by this electroplating method.Glow discharge optical emission spectroscopic (GDOES) was conducted to measure impurity concentration. Electroplated Cu films obtained by EP-SCE and EP-SCS had a smooth surface without void. GDOES shows that low level of carbon concentrations in the film by EP-SCE and EP-SCS same as by CONV, although high carbon concentration was detected in the film by CONV with surfactant. These results indicate that EP-SCE and EP-SCS are applicable for pure Cu wiring.

4. Conclusion

We examined Cu electrodeposition in sc-CO_2 emulsified electrolyte into nano-scale Cu wiring on the viewpoints of dissolution of Cu seed layer, gap-filling capability into nano-scale holes and contamination in the plated Cu. The addition of Cu particles in the sc-CO_2 emulsion on EP-SCS suppressed the dissolution of the Cu seed layer. The complete gap-filling in EP-SCS experiments are because sc-CO_2 has low viscosity enough to fill such fine holes with high aspect ratio. Moreover, the contamination in EP-SCS did not occur.

References

1.O. Luhn, A. Radisic, C.V. Hoof, W. Ruythooren, J.P. Celis, J. Electrochem. Soc. 157, D242 (2010)
2. T.F. M. Chang, M. Sone, A. Shibata, C. Ishiyama, Y. Higo, *Electrochim. Acta*, **55** (2010) 6469
3. N. Shinoda, T. Shimizu, T.F.M. Chang, A. Shibata, M. Sone, *Thin Solid Films*, **529** (2013) 29
4. N. M. Martyak, P. Ricou, Mater.Sci. Semicon. Process., 6, 225 (2003).
5.T.Nagoshi, T.F.M.Chang, T.Sato, M.Sone *Microelectronic Engineering*, (2013) DOI: 10.1016/j.mee.2013.02.001