Chemical Mechanical Polishing for Copper in Hydrogen Peroxide-based Slurries

Tzu-Hsuan Tsai and Shi-Chern Yen
Department of Chemical Engineering,
National Taiwan University, Taipei, Taiwan 106

Abstract

Chemical mechanical polishing (CMP) is a promising method of delineating copper patterns in this process [1-2]. However, the slurry composition and electrochemical mechanisms of copper during CMP may be more complicated. Therefore, more thoroughly understanding the electrochemical effects on removal rates and surface finishing is critical to achieving copper metallization.

This study investigated the electrochemical characteristics of copper in H_2O_2-based slurries during CMP. Electrochemical OCP measurements were performed in accurately predicting CMP performance. In this study we prepared various chemical compositions of CMP slurries dependent mainly on the Kaufman's model [3]. 5 w% 50 nm- Al_2O_3 was chosen to be abrasives. H_2O_2 and urea-H_2O_2 (U-H_2O_2) were selected to be oxidants in slurry solutions. Moreover, NH_4OH was also added to enhance the complex reaction of Cu. We took advantage of the electrochemical methods to investigate the effect of reactants and additives in the Cu CMP process. The experimental results show that the H_2O_2-based slurry displayed a good removal rate and planarized surface. Furthermore H_2O_2 is always unstable, especially adding NH_4OH. Therefore we also choose U-H_2O_2 as an oxidizer. The electrochemical measurements of copper CMP in U-H_2O_2 system are presented.

Fig. 1 depicts XRD patterns recorded from 10 to 60 2Θ degrees for the copper films. The XRD patterns for the copper before polishing only shows the reflections d_{111} (2Θ=43.32°) and d_{200} (2Θ=50.47°) corresponding to metallic copper. For copper dipped in 5 v% U-H_2O_2 + 0.1 w% BTA + 1 v% NH_4OH slurry for 5 min, the XRD pattern, in addition to metallic copper peaks, shows the presence of Cu_2O. However, the peak resulted from Cu_2O would disappear after polishing as shown in Fig. 1(c). Moreover, the surface roughness after CMP would be reduced to less than 10 nm, as shown in Fig. 2. In addition, the open circuit potentials (OCP) of various slurries were investigated as shown in Fig. 3. As the polishing pressure was released, the OCP curves of H_2O_2-based slurries would rise rapidly. This increasing in OCP indicates that the passive film forms on the metal surface. However 5 v% U- H_2O_2 shows more oxidation capability to protect copper surface than H_2O_2. As 0.1 w% BTA + 1 v% NH_4OH is added, U-H_2O_2-based solution displays gradual increase after release of polishing pressure, indicating that a gradual thickening of the passive film with time. On the other hand, the H_2O_2 shows an abrupt increasing in OCP, indicating a fast and unstable oxidation takes place. Therefore, U- H_2O_2 displays a better controllability than H_2O_2. Compared with H_2O_2 system, U-H_2O_2 makes better surface properties, and gets more stable slurries as NH_4OH is added. The electrochemical behaviors of copper CMP in H_2O_2-based slurries have been explored in this study.

Reference

1. J. M. Steigerwald, R. Zirpoli, S. P. Murarka, D. Price and R. J. Gutmann, *J. Electrochem. Soc.*, **141**, 10, p2842-2848 (1994).
2. D. T. Price, R. J. Gutmann and S. P. Murarka, *Thin Solid Films*, **308-309**, 523-528 (1997).
3. F. B. Kaufman, D. B. Thompson, R. E. Broadie, M. A. Jaso, W. L. Guthrie, D. J. Pearson and M. B. Small, *J. Electrochem. Soc.*, **138**, 11, 3460-3465 (1991).

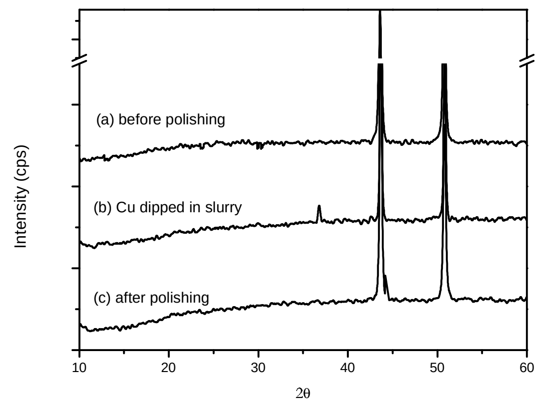

Fig. 1. XRD patterns for copper CMP in the slurry of 5 v% U-H_2O_2 + 0.1 w% BTA + 1 v% NH_4OH.

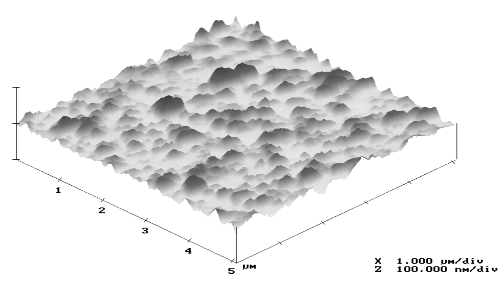

Fig. 2. AFM micrographs show the features of copper surface after polishing in the slurry of 5 v% U-H_2O_2 + 0.1 w% BTA + 1 v% NH_4OH.

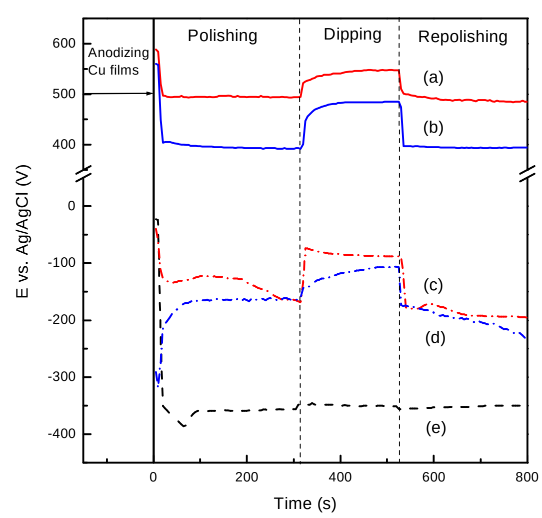

Fig. 3. OCP vs. time curves of anodic copper films: (a) 5 v% H_2O_2; (b) 5 v% U-H_2O_2; (c) 5 v% H_2O_2 + 0.1 w% BTA + 1 v% NH_4OH; (d) 5 v% U-H_2O_2 + 0.1 w% BTA + 1 v% NH_4OH and (e) 1 v% NH_4OH. (Polishing: at 5 psi/100 rpm)