Effect of Slurry Temperature on Cu Chemical Mechanical Polishing with Different Oxidizing Agents

Subrahmanya Mudhivarthi[1, 2] and Ashok Kumar[1, 2]

[1]Department of Mechanical Engineering,
[2]Nanomaterials and Nanomanufacturing Research Center,
University of South Florida, Tampa, Florida-33620.

ABSTRACT

Chemical Mechanical Planarization (CMP) has evolved as one of the most critical and significant process in the manufacturing of semiconductor devices. Copper has become the material of choice for the interconnect wiring. The effect of heat generation at the interface is realized to be significant on copper CMP process. The increase in the oxidation rate of the chemical reaction and viscoelastic properties of polishing pads due to increase in temperature at the surface results in increased removal rates and change in planarization performance. In this research, the effect of temperature on the CMP performance using two most common oxidizing agents, KIO_3 and H_2O_2 has been investigated using the CETR^{TM} bench-top CMP tester. The coefficient of friction at the interface of polishing using both the oxidizers at different temperatures was monitored. The generated surface roughness post CMP was evaluated for samples polished using different oxidizing agents at different slurry temperatures. The AFM study was carried out using Digital Instruments^{TM} D3100 instrument. This study is aimed at understanding the effect of temperature on the CMP process performance and the relative sensitivity of two most common oxidizers used in copper CMP towards temperature.

INTRODUCTION

Copper has replaced aluminum as an interconnect wiring material for the damascene structures to be used in ultra large scale integration of microelectronic devices. Copper has superior electromigration resistance and much lower resistivity when compared to Aluminum. As the device sizes shrink and the prominence of Multilevel Metallization structures increase, CMP process has evolved into a crucial process step during device fabrication [1, 2]. Copper CMP has gained prominence as the metal overburden is planarized and removed extensively to achieve damascene structure. Copper CMP process involves chemical modification of the soft copper surface followed by mechanical abrasion and subsequent dissolution of the removed copper debris into the slurry [3-5]. Process of reaction of copper with slurry has high activation energy of about 0.5 eV compared to approximately 0.06 eV activation energy of dielectric CMP process [6]. Thus, copper CMP process is estimated to be highly sensitive to the temperature. Heat is generated at the interface of polishing due to friction and interaction of the asperities of wafer, pad and the abrasive particles. Thus generated heat is transferred from the interface through conduction and convection heat transfer modes to wafer, polishing pad and to the slurry. Slurry acting as a cooling agent and thermally more conducting copper surface take majority of the heat generated at the interface. As a result, copper surface interacts with the slurry at various temperatures throughout the polishing process. As mentioned earlier, the copper interaction with the slurry is highly sensitive to temperature. Thus, it is absolutely necessary to understand the interactions of copper surface at various temperatures and also, the effect of softening of the polishing pad needs to be studied in detail. In the recent past, both theoretical and experimental studies to estimate the wafer and pad temperatures at the interface during CMP have been attempted [7, 8]. Also, many investigations involving changing the chemistry of slurry used for copper polishing have been carried out [9, 10]. In this study, the effect of temperature on different kinds of oxidizers is being researched. Two most common oxidizers being used in copper CMP are hydrogen peroxide (H_2O_2) and potassium iodate (KIO_3). The relative sensitivity of the oxidizers that are used to modify the copper surface, towards temperature is investigated in this study. The alterations of the removal rates during copper CMP and changes in evolution of a smooth planarized surface due to the change in slurry temperature and hence temperature at the interface are explored to better understand and optimize the process of copper CMP.

EXPERIMENTAL

CMP experiments are carried out on the bench-top tester manufactured by CETR Inc., (see Fig. 1) which has in-situ coefficient of friction (COF) and Acoustic Emission (AE) signal data acquisition capabilities. Copper blanket samples of 1"X 1" are polished under exactly same process conditions including the down pressure, platen rotation, carrier rotation and the slurry flow rate in presence of two oxidizers. The only varying parameter is the temperature of the slurry.

Figure. 1 CMP bench-top tester manufactured by CETR Inc.

Down pressure of 3 Psi and platen/carrier rotation of 100/95 RPM respectively with a constant slurry flow rate of 75 cc/min constitute the experimental parameters. Oxidizer concentration of 5 % by volume was used for both H_2O_2 and KIO_3 oxidizers. Electroplated copper samples of 1100 nm thick were polished for 3 minutes with slurry fed at five different temperatures. To vary the slurry feed temperature, the slurry container was heated with continuous stirring of the slurry contents to ensure uniform temperature rise of the slurry. The slurry was maintained at each individual temperature for 5 minutes for stabilization. The slurry was passed onto the polishing pad and pad was soaked in the heated slurry for 2 minutes to achieve steady state temperature of the pad before starting the actual experiment. The container carrying hot slurry was placed in a thermally insulated casing to avoid any thermal losses. A temperature fluctuation of 1^oC occurred over the period of 3 minutes of actual polishing experiment. Post CMP metrology was performed on the samples polished at different temperatures in presence of two oxidizers using Digital Instruments D3000 Atomic Force Microscope (AFM).

RESULTS AND DISCUSSION

Tribological Characterization

The coefficient of friction data for the polishing of samples with varying slurry temperature is obtained from the bench top tester data acquisition with the help of a load sensor, which measures both the normal and lateral forces equipped directly above the carrier holder assembly. The removal rate for these experiments was determined using weight measurements with the help of a precision balance (Sartorius R200D research model) with a sensitivity of 0.01 mg. Equation. [1] was used for estimation of removal rate.

$$\text{Material Removal Rate} = \frac{(\text{Mass}_{\text{initial}} - \text{Mass}_{\text{final}})}{\rho * A * t} \quad [1]$$

Where ρ = Density of copper
A = Area of the sample coupon
t = Time of polish

Removal rate change with varying slurry temperature for both oxidizers is estimated and plotted as shown in Fig. 2. From the figure it can be seen that the removal rate increases exponentially with temperature of the slurry containing hydrogen peroxide whereas for slurry containing KIO_3, the removal rate first decreases and then increases with temperature. This could be due to the formation of a thick passivating layer which prevents further oxidation of the copper surface reducing the removal rate. The passivating layer gets dissolved into the slurry at high temperatures exposing fresh copper surface for further oxidation and hence high removal rates. The difference in the numerical range of removal rates for the slurry that contains hydrogen peroxide and for the slurry that contains potassium iodate is because the slurry used for hydrogen peroxide was commercial slurry, which was not compatible with potassium iodate. The slurry used for potassium iodate chemistry is the laboratory made slurry under development. COF data with varying temperatures of slurries containing both peroxide and iodate oxidizers is plotted as shown in Fig. 3. Coefficient of friction data for both the slurries show similar trend with temperature. Same slope of the COF graph for both oxidizers implies that the coefficient of friction is more dominated by pad conformality and the number of slurry particles trapped at the interface. The effect of change in chemistry is minimal on the coefficient of friction at the interface.

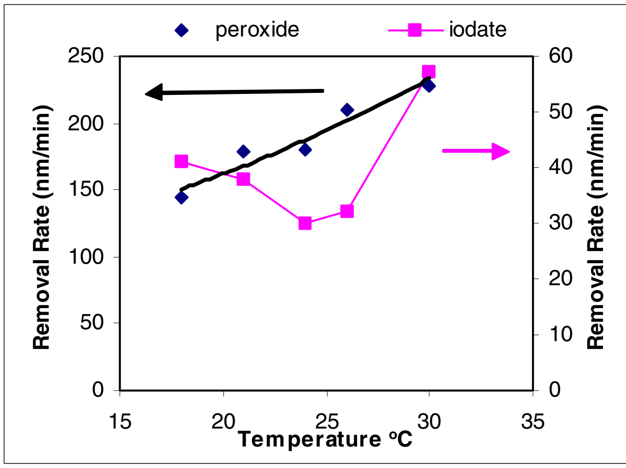

Figure. 2 Removal Rates versus slurry temperature.

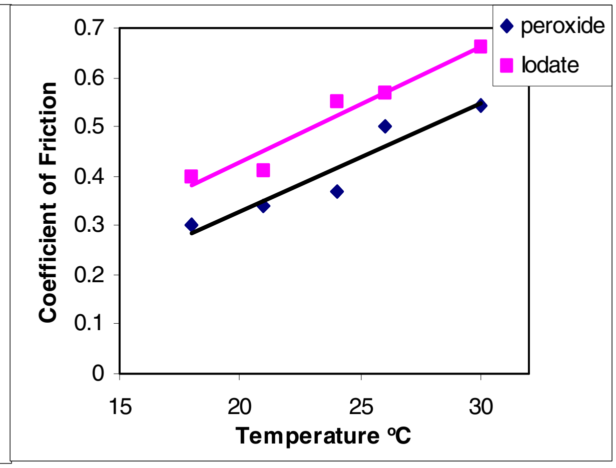

Figure. 3 Coefficient of friction versus slurry temperature

Surface Characterization

The copper samples polished with two oxidizers at different temperatures are characterized for their surface topography using an Atomic Force Microscope (AFM). Figures 4 and 5 present the surface plots of the samples polished with slurry containing hydrogen peroxide and slurry containing potassium iodate respectively

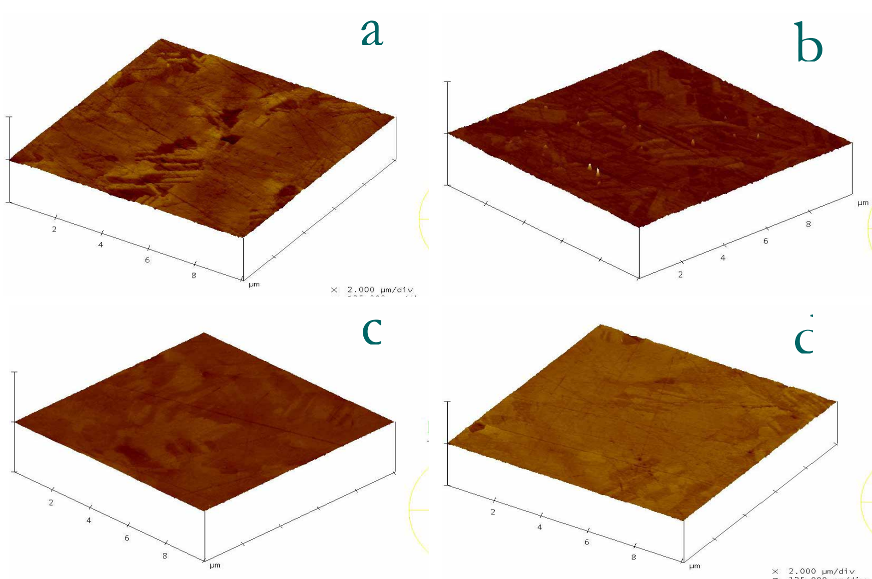

Figure. 4 Surface plots of samples polished at a) 18°C b) 21°C c) 26°C d) 30°C using hydrogen peroxide as oxidizer

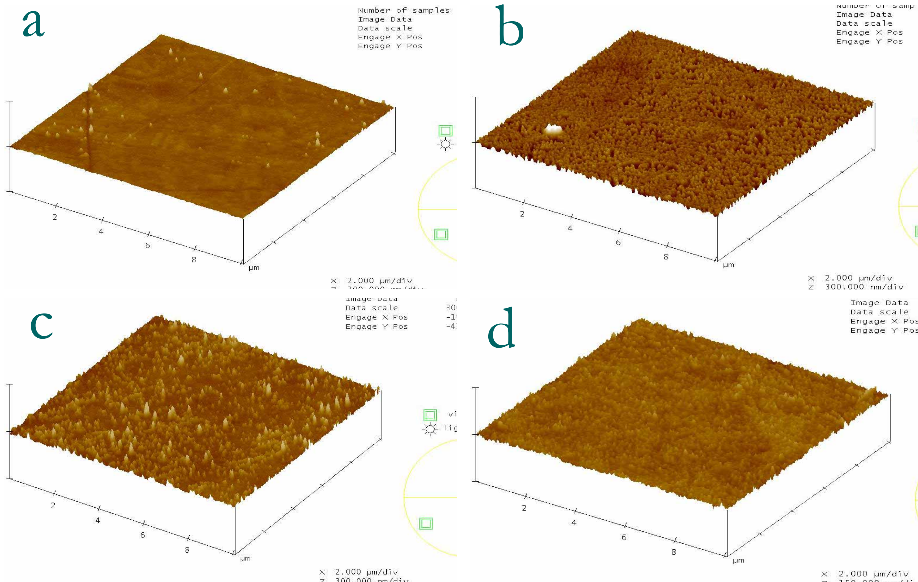

Figure. 5 Surface plots of samples polished at a) 18^{o}C b) 21^{o}C c) 26^{o}C d) 30^{o}C using potassium iodate as oxidizer

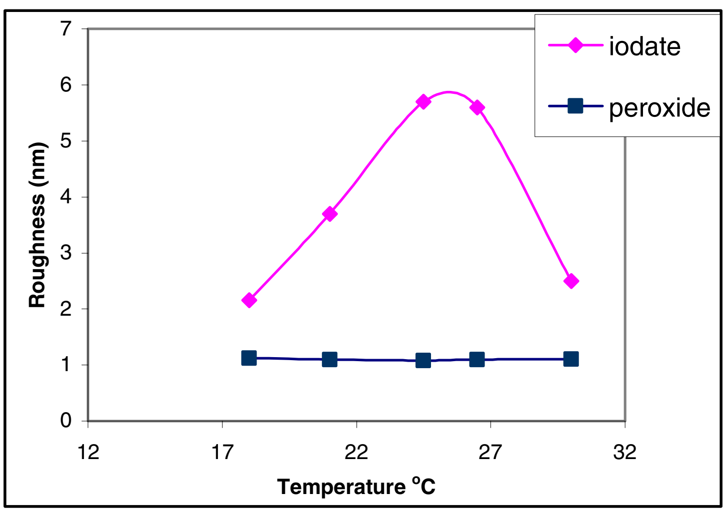

Figure. 6 Surface roughness variation for samples polished at various slurry temperatures

The variation of the generated surface roughness during CMP using both the oxidizers is plotted against slurry temperature as shown in Fig. 6. From the graph it can be seen that the roughness of the samples polished with hydrogen peroxide as oxidizer is not affected by the slurry temperature. Even though the sample polished at 18^{o}C (see fig. 4) does not have a perfectly smooth surface, the uneven ness of the surface did not contribute much to the overall surface roughness. The uneven surface finish could be due to insufficient chemical activity at lower temperatures. From Fig. 6 it can also be seen that the roughness of the samples polished with potassium iodate as oxidizer experienced significant effect of temperature. The formation of a thick layer of passivation over copper surface prevented further oxidation and accordingly planarization of the surface. The passivation layer breaks at higher temperature allowing active oxidation of copper surface resulting in much better surface planarization and removal rate as well.

CONCLUSION

The effect of temperature at the interface is significant on CMP performance. Slurry chemistry and its sensitivity towards temperature are extremely crucial during copper CMP process. Copper appears to be forming a thicker passivation layer with KIO_3 as an oxidizer compared to H_2O_2. The polishing performance at moderately high temperatures decreases with increase in temperature in presence of KIO_3 due to thicker surface (passivation) layer formation preventing further oxidation of copper. The generated surface roughness of copper while polishing using hydrogen peroxide was not affected by the temperature of the slurry whereas the surface roughness of the samples polished using KIO_3 as oxidizer was affected significantly.

ACKNOWLEDGEMENTS

Authors like to acknowledge the financial support by NSF GOALI Grant # DMI 0218141. Authors would also like to acknowledge valuable inputs of Dr. Arun Kumar at University of South Florida and Dr. William Fortino of Cabot Microelectronics, IL, USA

REFERENCES

1. D. Zeidler, Z. Stavreva, M. Plotner, and K.Drescher, *Microelectron. Eng.,* **33**, 259, (1997).
2. P.B. Zantye, A. Kumar, and A.Sikder, *Mater. Sci. Eng. R-Rep.*, **45 (3-6)**, 89, (2004).
3. R. Carpio, J. Farkas, R. Jairath, *Thin Solid Films* **266,** 238,(1995).
4. J.M. Steigerwald, S.P. Murarka, R.J. Gutmann, D.J. Duquette, *Materials Chemistry and Physics,* **41,** 217, (1995).
5. Ronald J. Gutmann, Joseph M. Steigerwald, Lu You, David T. Price, Jan Neirynck, David J. Duquette, Shyam P. Murarka *Thin Solid Films* **270**, 596, (1995).
6. J. Sorooshian, D. DeNardis, L. Charns, Z. Li, F. Shadman, D. Boning, D. Hetherington, and A. Philipossian, *J. Electrochem. Soc.*, **151 (2)**, G85, (2004).
7. Z. Li, L. Borucki, I. Koshiyam, and A. Philipossian, *J. Electrochem. Soc.*, **151 (7)**, G482, (2004).
8. Jesse Cornely, Chris Rogers, Vincent Manno and Ara Philipossian, *Mat. Res. Soc. Symp. Proc*. **767,** F1.6.1, (2003).
9. Q. Luo, D.R. Campbell, S.V. Babu, *Thin Solid Films,* **311**, 177, (1997).
10. Tianbao Du, Arun Vijayakumar, Vimal Desai, *Electrochimica Acta,* **49,** 4505, (2004).