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Citric acid/tartaric acid as complexing agent in sodium carbonate based CMP slurry for tantalum

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In the present work Ta disk was polished using slurry composed of alumina and sodium carbonate (Na_2CO_3) as abrasive and oxidizer respectively, and citric acid ($C_6H_8O_7$) or tartaric acid ($C_4H_6O_6$) as complexing agent. For slurry formulation alumina (2 wt%) and Na_2CO_3 (1 wt%) and various concentrations of citric acid and tartaric acid were chosen for tantalum (Ta) chemical mechanical planarization. The influence of change in pH, complexing agent concentration, pressure and rotational platen speed on Ta removal rate (RR) were inspected and the outcomes are stated. Potentiodynamic polarization curves for tantalum with both the complexing agents were studied and the results are reported. An electrical equivalent circuit is proposed to describe the EIS results.

Keywords: CMP, tantalum, sodium carbonate, complexing agents, electrochemical characterization.

Introduction

Chemical mechanical planarization (CMP) has emerged as one of the most promising technology which has been recognized widely in aiding global planarization. Along with the microelectronic fabrication, planarization is considered to be the prime focus of CMP. For achieving a globally planarized and smooth surface, CMP combines both chemical and mechanical actions exceptionally due to the presence of oxidizer and abrasive[1]. In the field of integrated device manufacturing, CMP of copper (Cu) and its cognate barrier layer has been proven as a promising technology for *meta* planarization[2]. Cu exhibits innate problems including rapid diffusivity and little adhesion with elemental dielectric Si/SiO_2 layer, which are undesirable for an interconnect material in the absence of barrier layer.

Ta/TaN has been effectively employed to subdue the hitches combined with Cu as an interconnect metal. Their ability to promote adhesion and to work as a conductive diffusion barrier layer plays a plausible reason behind this[3]. Planarization of barrier layer after removing Cu is imperative in the manufacturing of sub-micron inlaid Cu interconnect and the barrier layer. For the case of Ta, several abrasives including alumina, ceria and silica have been frequently tried out[4]. But still, investigations on oxidizer are limited to hydrogen peroxide. The putrefaction property of hydrogen peroxide paves way for the addition of a stabilizer for slurry stabilization[5].

This research work highlights the effects of tartaric acid and citric acid as the complexing agents in slurry comprising sodium carbonate and alumina. Alumina and sodium carbonate serves the purpose of abrasive and oxidizer respectively. Electrochemical tests were conducted to validate the CMP results.

Experimental

A 2 wt% alumina, 1 wt% Na_2CO_3 and 1 wt% tartaric acid/citric acid slurry was incorporated for CMP experiments. Labopol-5 and laboforce-3 assembled Struers bench top polisher (Denmark) was employed for conducting CMP experiments. A Ta disk having 2.5 cm diameter, 1.25 cm thickness was used in this research work. All the experiments were conducted with the applied downward pressure of 5.6 N/m^2 except for varied pressure experiments. A platen rotational and metal holder speed of 100 and 250 rpm were maintained constant. The slurry flow rate was upheld 100 ml/min using a peristaltic pump. 2 wt% alumina and 1 wt% Na_2CO_3 dispersed in distilled water were used to formulate

polishing slurry. The preferred pH of the polishing slurry was attained by employing potassium hydroxide (KOH) or nitric acid (HNO_3). The slurry container was constantly agitated by employing a magnetic stirrer, to ensure even dispersion throughout the polishing experiment. SUBA IV (Eminess, USA) polishing pad was employed for polishing purpose.

Electrochemical tests were executed using electrochemical workstation (PARSTAT MC 1000-AMETEK, USA). 1 wt% Na_2CO_3 and 1 wt% citric acid/tartaric acid at 11 pH was used as electrolytic solution. Open circuit potential (OCP) analysis was carried out for 3 min prior to all the electrochemical runs to ensure stability of electrochemical system. Tafel analysis was performed with respect to acquired potential from OCP, –250 mV to +250 mV potential range and at a scan rate of 1 mV/s. EIS was done at a frequency range of 0.1 Hz to 100 kHz.

Results and discussion

CMP experiments:

CMP experiments were performed with 2 wt% alumina and 1 wt% Na_2CO_3 at varied pH and Fig. 1 shows the obtained results. It is observed that as the pH slides from acidic to basic region, the Ta RR further surges from ~18 nm/min to 44 nm/min. The resulted enhancement in Ta RR can be due to the softening of oxide film formed[6]. As maximum removal is seen at pH 11, all the further experiments were performed at 11 pH.

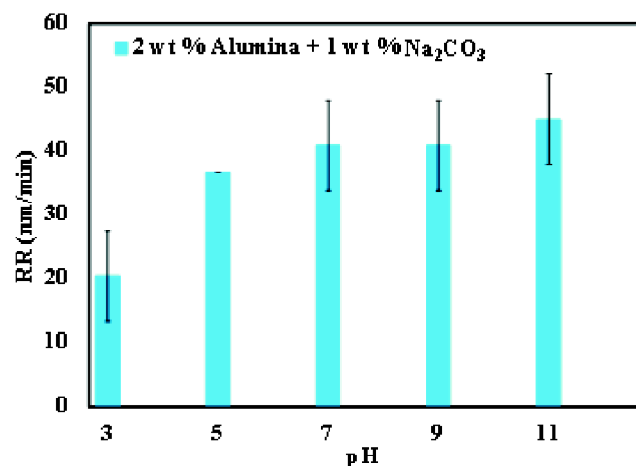

Fig. 1. Effect of pH on Ta RR.

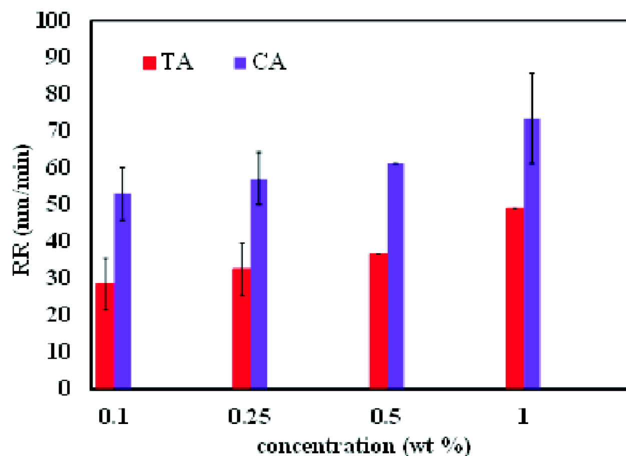

Fig. 2. Effect of complexing agent concentration on Ta RR.

Experiments were executed to know the effect of different complexing agent concentrations on Ta RR. Fig. 2 shows the Ta RR with different concentrations of both the complexing agents. As the concentration is escalated from 0.1 wt% to 1 wt%, the Ta RR also increases for both tartaric acid and citric acid. For former, it increases from ~28 nm/min to ~49 nm/min, and for later from ~53 nm/min to ~73 nm/min. As the maximum removal rate is observed with 1 wt% concentration, all the further experiments are performed with same. The addition of tartaric acid and citric acid increases Ta RR as shown in Fig. 3.

To study the mechanical aspect of CMP, studies were performed using the same slurry composition mentioned earlier with 11 pH. The outcome of which on Ta RR is represented in Fig. 4 and Fig. 5. As the pressure and platen rota-

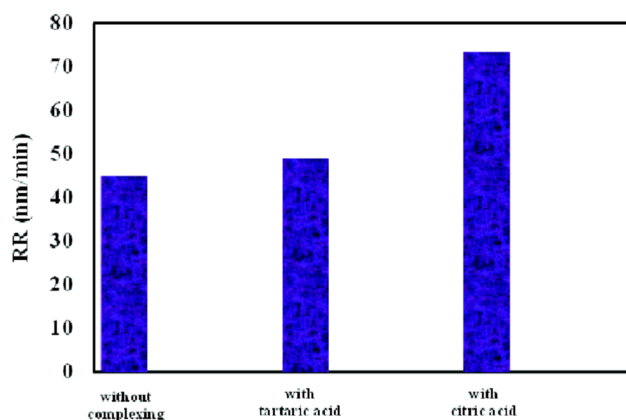

Fig. 3. Effect of complexing agent effect on Ta RR.

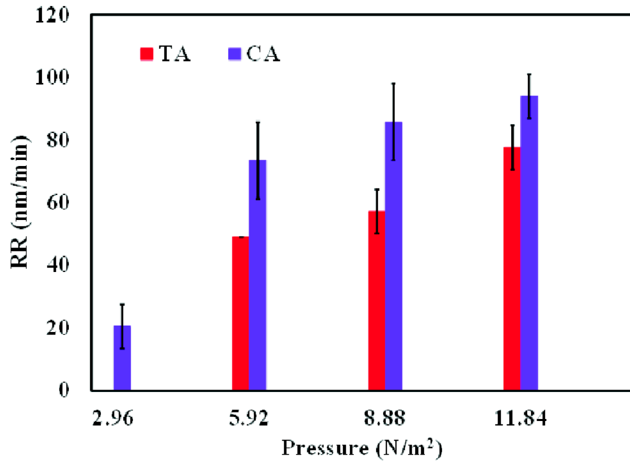

Fig. 4. Effect of pressure on Ta RR.

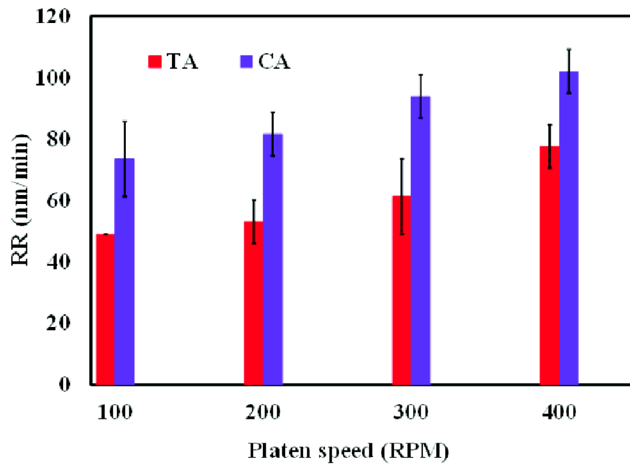

Fig. 5. Effect of platen speed on Ta RR.

tional speed are increased the Ta RR also increases for both the complexing agents. The increase in RR in both cases is due to mechanical abrasion surge.

Electrochemical analysis:

With the addition of tartaric acid, a positive shift in anodic branch is observed, as depicted in Fig. 6. This further shifted more with the addition of citric acid. This behavior explains the hike in Ta RR followed with the introduction of complexing agents[7]. Extrapolation of the cathodic and anodic branches of Tafel plots were performed to procure corrosion current density (I_{corr}). An I_{corr} value of 555.198 nA was calculated in the absence of complexing agents. 1.182 μA and 259.914 μA I_{corr} values were obtained for tartaric and citric acid respectively. The obtained I_{corr} value suggests high Ta removal with citric acid[8]. The results obtained with potentiodynamic polarization matches well with the Ta CMP results.

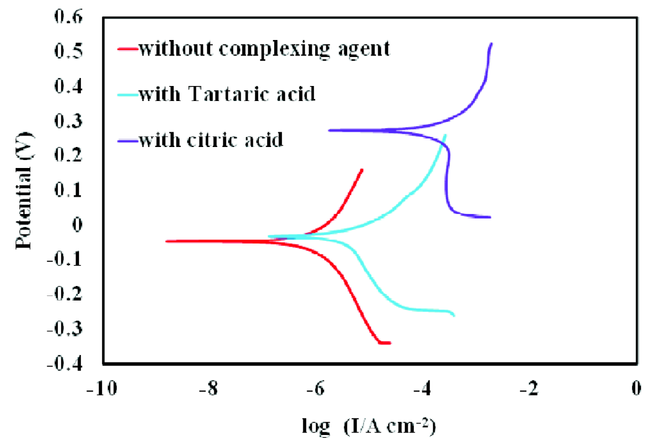

Fig. 6. Potentiodynamic polarization curves for Ta with and without complexing agents.

Fig. 7 depicts Z_{im} vs Z_{re} plot for Ta with and without complexing agents. An electrical equivalent circuit (EEC) is proposed as shown in Fig. 8. R_{sol}, R_{film} and R_{ct} indicate the resistance because of electrolyte solution, formed oxide layer and charge transfer respectively. CPE_{film} and CPE_{dl} denote the corresponding constant phase element[9]. R_{film} decreases from 39800 Ω cm^2 to 12073 Ω cm^2 for tartaric acid and citric acid respectively. The same trend is observed for R_{ct} which decreases from 5.33 Ω cm^2 to 0.01 Ω cm^2. The no-

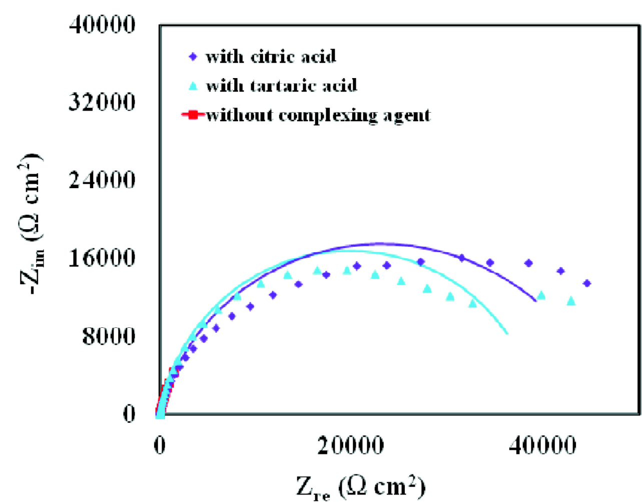

Fig. 7. Nyquist plot for Ta with and without complexing agents.

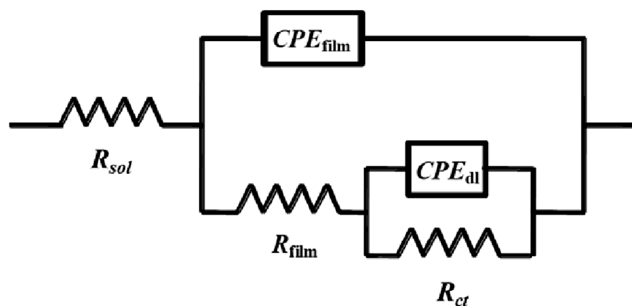

Fig. 8. Proposed electrical equivalent circuit.

ticed decrease in resistance value for both the complexing agent is perchance associated with the increase in metal dissolution and Ta RR. The noticed trend, matches very well with CMP experiment results. Hence, this explains the increase in Ta RR with citric acid as compared to tartaric acid.

Conclusion

Ta CMP was done to study the effect of two complexing agents, tartaric acid and citric acid. Experiments were performed with slurry comprising 2 wt% alumina, 1 wt% Na_2CO_3 and 1 wt% tartaric acid/citric acid. The CMP result reveals that citric acid proves to be more effective complexing agent as compare to tartaric acid. The electrochemical studies also shows same trend as Ta CMP. The obtained corrosion current density from potentiodynamic polarization is more in case of citric acid. And the resistance is less for electrolyte comprising citric acid. Which together shows that citric acid is a more promising complexing agent as compare to tartaric acid.

Acknowledgements

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