Materials Science Forum *Online: 2010-11-11*
ISSN: 1662-9752, Vols. 663-665, pp 1111-1114
doi:10.4028/www.scientific.net/MSF.663-665.1111

The important role of oxidant in copper interconnection chemical mechanical polishing for GLSI

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Keywords: Chemical mechanical planarization; Copper interconnection; Hydrogen peroxide; Alkaline slurry; Chemical kinetics; Planarity surface

Abstract. Chemical mechanical planarization (CMP) of copper interconnection in hydrogen peroxide (H_2O_2) as oxidizer based alkaline slurry was investigated. The new model is put forward, which is based on the characteristic of H_2O_2, chemical kinetics and mechanical removal. This properties of H_2O_2 can be effectively compensated the defect of surface topology during the process of polishing. Researcher previous study has shown that the surface is largely copper metal with Cu_2O at low H_2O_2 concentrations and largely CuO at high H_2O_2 concentrations. Cu_2O is more easily removed by both chemical and mechanical processes than CuO. During the CMP process, as the oxidizer concentration increases, the removal rate goes up initially followed by a gradual decay. This characteristic of oxidizer is used to achieve copper surface global planarity. The surface planarity was achieved by removing high area on the surface more quickly relative to the low area, because the concentration of Cu_2O in the low area as the passivation film is more than the high area. Meanwhile the passivation film of the low area is thicker than the high area. In order to achieve polishing process optimization, the influence of pH adjustment and pressure, are also taken into consideration. Combining both RR and PE, the optimal H_2O_2 concentration and pressures are in range 1.0 ~1.5 vol% and 0.04 ~0.07 mp_a, respectively. The roughness of surface which is measured by AFM is 0.49 after CMP.

Introduction

Copper as a multi- level interconnecting material in GLSI manufacturing technology has attractive properties due to its low resistivity and high electromigration resistance [1]. The copper must be removed until a perfectly flat surface. Chemical Mechanical Planarization (CMP) is well recognized as a powerful method for planarizing surface topography. In metal CMP process, the metal undergoes complicated chemical reactions and physical action. Thus the control of CMP is often difficult, especially for a high corrosion-sensitivity metal like Cu. In order to well control the process, many researchers attempted to investigate copper CMP with hydrogen peroxide (H_2O_2)-based slurry, because the removal rate (RR) is a non-monotonic function of the H_2O_2 concentration [2]. It is shown that the removal rate of Cu is at a maximum value at low concentration of H_2O_2, and then it decreases with further increase in concentration of H_2O_2 [3]. At low oxidizer concentrations, the surface is largely copper metal with Cu_2O. At high oxidizer concentrations, the surface is largely CuO [4-5].

In this paper, these properties of H_2O_2 can be effectively compensated the defect of surface topology during the process of polishing. Understanding the fundamental effects of the H_2O_2 on the material removal of copper in CMP can offer guidance to the control and optimization of the polishing process.

Experiment

Copper CMP was carried out on a X62815-I polisher.The experimental slurry (pH=11.00) with $Si0_2$ abrasive (15 to 20 nm) and FA/O chelating agent are obtained from Hebei University of Technology. The pressure was varied between 0.01 to 0.1 mpa, the concentration of H_2O_2 was changed from 0 to 2.5 vol%. The slurry flow rate was set to 230 ml/min. The concentration of FA/O chelating agent was set to 1.5 vol%. RR was determined from the thickness loss (measured with an Electronic thickness gauge). The PE of CMP, calculated according to the Eq.(1), provides a measure of the quality of the surface topography . where Δ(Down) and Δ(Up) are the thickness differences of the bottom and top of the feature.

$$PE = \left[1 - \frac{\Delta(Down)}{\Delta(Up)}\right] \times 100\% \tag{1}$$

Results and Discussions

Figure 1 shows Cu-CMP reaction for peroxide-based slurries. The copper surface can be modeled with the fresh surface [Cu] and the oxidizing surface including the cuprous ions compounds [Cu^+], the cupric ions species [Cu^{2+}]. The complexing agents [L] react with copper ions forming complexes [Cu^{+L} , Cu^{2+L}]. k_1 , k_2 and k_3 mean the rate constants. k_1 and k_2 are given by Arrhenius's equation:

$$k_{1,2} = Ae^{-\frac{Ea}{RT}} \tag{2}$$

Here *A, R* are constants. E_a and *T* mean activation energy and temperature. It is well known that the rate value of k_3 varies locally as a function of the polishing pressure and the velocity. This makes it possible to use the Preston equation that describes k_3

$$k_3 = k_c PV \tag{3}$$

Here k_c is the Preston's coefficient. *P* and *V* respectively indicate the down-pressure and the relative velocity. *RR* including the etchant rate and the abrasive removal rate can be written as:

$$RR = k_2\left[Cu^+, Cu^{2+}\right]\left[L\right] + k_3\left[Cu^+, Cu^{2+}\right] \tag{4}$$

Based on the mass balance theory, the change rates of [Cu^+ ,Cu^{2+}] can be obtained:

$$\frac{\partial\left[Cu^+, Cu^{2+}\right]}{\partial t} = k_1\left[Cu\right]\left[OX\right] - k_2\left[Cu^+, Cu^{2+}\right]\left[L\right] - k_3\left[Cu^+, Cu^{2+}\right] \tag{5}$$

Substitute of Eq. (5) into Eq. (4) gives

$$\frac{\partial\left[Cu^+, Cu^{2+}\right]}{\partial t} = k_1\left[Cu\right]\left[OX\right] - RR \tag{6}$$

CMP involves chemical and mechanical effects, both of which are required to obtain the desired results from a copper polish process. If the CMP process is too mechanical in nature, then the resulting surface will be left scratched [6] and the byproducts of the polish may not dissolve into the slurry and therefore may redeposit onto the copper surface [7]. However, if the polish is too chemical in nature, surface planarity will be very difficult to achieve and maintain and surface roughness may increase. Consequently, a balance of chemical and mechanical activity must be maintained in order to obtain high-quality, planar surfaces. Then the equilibrium is reached when the rate of passivation is equal to the rate of mechanical abrasion and chemical dissolution. The equilibrium can be described:

$$RR \Big/ \frac{\partial\left[Cu^+, Cu^{2+}\right]}{\partial t} = k_4 \tag{7}$$

Substitute of Eq. (7) into Eq. (6) gives

$$RR = k_{RR}[Cu][OX] \tag{8}$$

Here k_{RR} is constant

Eq.(8) presents the important role of oxidant in CMP.

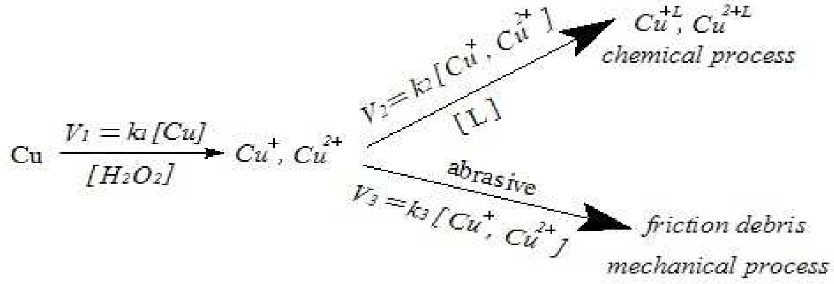
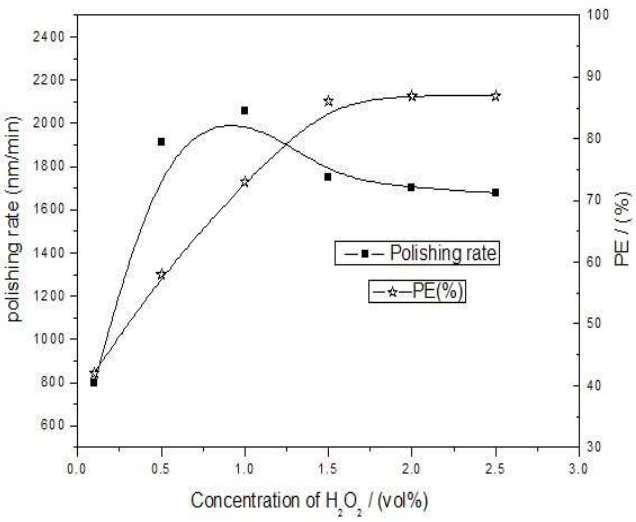


Fig. 1. Cu-CMP reaction diagram for peroxide-based slurries

Fig. 2 illustrates that the RR initially enhances with the increase in concentration of H_2O_2 and reaches maximum value, then decreases with further increase in H_2O_2concentration. The PE increases at lower H_2O_2 concentration and approaches a constant at higher H_2O_2 concentration. At low H_2O_2 concentrations, the surface is largely copper metal and Cu_2O. At high H_2O_2 concentrations, the surface is largely CuO. At intermediate H_2O_2 concentrations, Cu_2O predominate. The concentration of Cu_2O as the passivation film in the low area is more than the high area. Meanwhile the passivation film of the low area is thicker than the high area. Removal of Cu_2O by both chemical and mechanical means is more effective than removal of either copper metal or Cu_2O [8]. The trend of removal rate is consistent with the Fig.2.



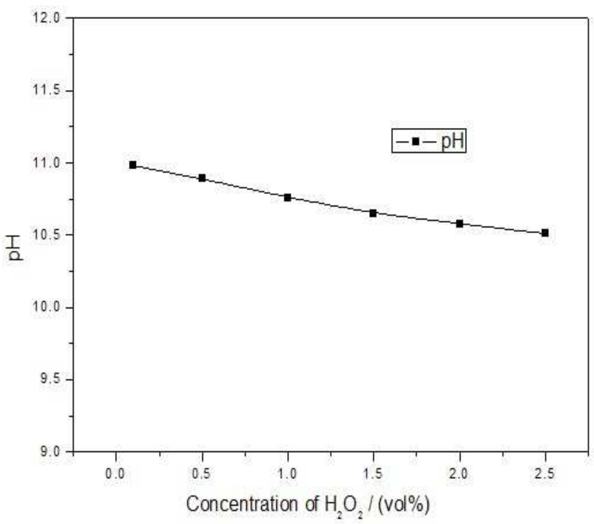


Fig. 2. Effect of H_2O_2 concentration on RR and PE Fig. 3. Relation of H_2O_2 concentration and pH

Fig.3. clearly indicates that, as the oxidizer concentration is varied between 0 to 2.5 vol%, the pH gradual decay but the minimum pH value is still greater than 10, When the pH falls in range 7~13, the capability of Cu_2O formation is low. However, the capability of CuO is more positive[9] . There is litter effect on the alkaline of slurry. Copper is expected to form CuO film while maintaining removal rate in an alkaline solution, which the optimal PE can be achieved. Thus the PE while maintaining certain removal rate is achieved by adjustment of H_2O_2 concentration. Combining both RR and PE, the optimal H_2O_2 concentration is in range 1.0 ~1.5 vol%.

As shown in Fig.4, the removal rate of copper increases with the increase in pressure. The PE increases, as the pressure increases, The PE goes up followed by a gradual decay. At low pressure, This region is a chemical reaction controlled process. As the pressure increases, the process is gradually controlled by mechanical reaction. RR increases but PE decreases in this region where surface is largely composed of copper and Cu_2O. Combining both RR and PE, the optimal pressures is in range 0.04 ~0.07 mp_a.

Topography of copper surface is measured by AFM. Fig 5 shows the AFM images of copper surface after polishing, which reveals the roughness of surface is 0.49.

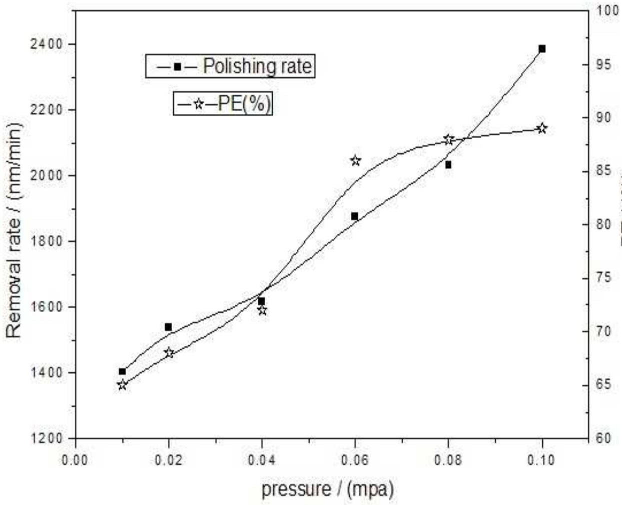


Fig.4. Effect of pressures on RR and PE

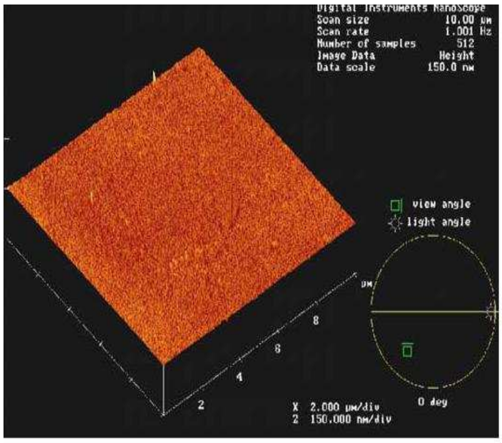


Fig 5 copper surface measured by AFM

Summary

In this paper, H_2O_2 properties can be effectively compensated the defect of surface topology during the process of polishing. A new model that presents the important role of oxidant in copper CMP based on the characteristic of H_2O_2, chemical kinetics and mechanical removal is presented. In order to achieve polishing process optimization, the influence of pH adjustment and pressure, are also taken into consideration. Combining both RR and PE, the optimal H_2O_2 concentration and pressures are in range 1.0 ~1.5 vol% and 0.04 ~0.07 mp_a, respectively. The roughness of surface which is 0.49.

Achnowledgement

This work was financially supported by the following funds: (1) Specialized Research Fund for the Doctoral Program of Higher Education of China (No.20050080007); (2) Natural Science Foundatio n of China (No.10676008); (3) Tianjin Natural Science Foundation of China (No.10JCZDJC15500); (4) Major national science and technology program(No.2009ZX02308).

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