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IN-SITU ACOUSTIC EMISSION MONITORING OF SURFACE CHEMICAL REACTIONS FOR COPPER CMP

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ABSTRACT

Acoustic emission (AE) is used as a technique to monitor and characterize surface interactions between wafer and pad in a chemical-mechanical planarization (CMP) process for copper. A significant variation in in-situ AE signal was observed during controlled variation of the slurry composition, demonstrating the sensitivity of AE to the unique surface reactions taking place. Two different levels of AE were observed; a high root-mean-square (RMS) signal when polishing H_2O_2 treated copper, and a low RMS signal when polishing bare copper. The rate of change in the AE signal was also tied to variations in species concentration and pH in slurry.

Keywords: acoustic emission, CMP, monitoring, copper.

INTRODUCTION

With the advent of low-k dielectric materials in semiconductor processing, the copper damascene process is of increasing use as an interconnect technology. To avoid stress-induced defects during the low-k/copper damascene process, the role of electrochemical reactions at the wafer/pad interface is becoming more important than mechanical abrasion during copper CMP. Hence, understanding the nature of surface chemical reactions during copper CMP is of increasing importance for developing abrasive-free or electrochemistry-based polishing systems. It is generally believed that the basic chemical reactions during copper CMP are 1) oxidization (i.e. passivation) of copper, and 2) removal of this oxide layer by a combination of dissolution and mechanical abrasion. The type and thickness of the copper oxide are dependent on the oxidant concentration in the slurry, and greatly affects the material removal rate (MRR) (Hernandez et al., 2001). The frictional behavior at the wafer/pad interface (including wear mechanisms) in copper CMP depends on the nature of the oxide films, and the energy associated with interface frictional affects oxide layer formation as well (Liang et al., 2001). Understanding the mechanisms of the formation and removal of the oxidized copper layer during CMP is a key component for a comprehensive model of the copper CMP process, and an in-situ monitoring technique for characterization of these reactions during the actual CMP operation is a key issue for model development.

As a form of ultrasonic vibration, acoustic emission (AE) has been established as an effective monitoring tool for issues in CMP such as endpoint detection and material-removal rate, thanks to its increased sensitivity and improved signal-to-noise ratio (relative to other sensor technology) to material removal mechanisms at the micro and nanoscale, including the abrasive mechanisms taking place at the wafer/pad interface (Dornfeld et al., 2003; Lee, D.E. et al., 2004). Previous work with AE for endpoint detection in CMP also demonstrated a high degree of sensitivity of the signal to the surface

and material properties (hardness in particular) of the polished material Lee, D.E. et al., 2004). This paper further establishes the sensitivity of AE to transitions in surface chemical reaction states of the copper during CMP, with a focus on AE characteristics during variation of the slurry composition and pH during the CMP process.

EXPERIMENTAL DETAILS

A series of unpatterned blanket copper wafers were used for the AE monitoring experiments. 700 Å of Ti was deposited onto 4" Si wafers via e-beam evaporation, followed by 1000 Å of Cu as a seed layer. 3 μm of copper was then deposited by electroplating. For the formation of surface oxide, the copper-plated wafers were first dipped into 0.1 wt.% oxalic acid ($HOOCCOOH.2H_2O$) solution for 1 minute to remove any native oxide on the surface, then treated in 30% hydrogen peroxide for 5 minutes. For the CMP operation, a Toyoda ultra precision float polishing machine (model SP46) was used with a specially designed wafer head for sensor integration. All experiments were conducted with an IC1400 pad with ex-situ pad conditioning. Down pressure was maintained at 2 psi, and a constant pad rotation speed of 20 RPM was used for all experiments. Slurry of varying chemical composition and pH was supplied at a constant rate of 25 ml/min. All chemicals were pre-mixed and supplied as needed into a slurry delivery system for baseline signal generation, dissolution of pre-existing oxide layer, and re-oxidation.

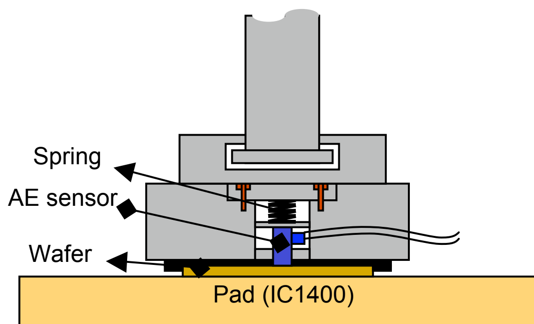


FIGURE 1. WAFER HEAD WITH INTEGRATED AE SENSOR.

A DECI SE25 AE sensor was used due to its relatively flat frequency response (relative to other commercial sensors) over the 50-500 kHz range. The AE sensor was integrated into the wafer holder, directly coupled to the backside of the wafer with a spring-loading mechanism (see Figure 1) to minimize signal attenuation. The raw AE signal was preamplified by 50 dB, filtered through a high pass filter at a cutoff frequency of 50 kHz to reduce ambient system noise, and subsequently amplified by another 100 dB. The filtered signal was then processed by a root-mean-square (RMS) filter with time constant of 1 millisecond. A National Instruments DAQScope PCMCIA data acquisition card was used to acquire the signal at a sampling rate of 100 Hz within a Labview software environment, and data postprocessing was conducted with MATLAB.

RESULTS AND DISCUSSION

Basic characteristics

The AE RMS signal during copper CMP operation with varying slurry composition is shown in Figure 2. Three different levels of AE were observed. First, a relatively high AE RMS signal (~1.3 V) during the polishing of the hydrogen peroxide-treated surface with DI water was established. After switching to a 0.1 wt.% oxalic acid solution, the signal dropped to ~0.44 V. After one minute of polishing with the oxalic acid solution, a 30% hydrogen peroxide solution was supplied, and the AE RMS signal increase again to ~0.84 V. The surface conditions during these variations are shown schematically in Figure 3.

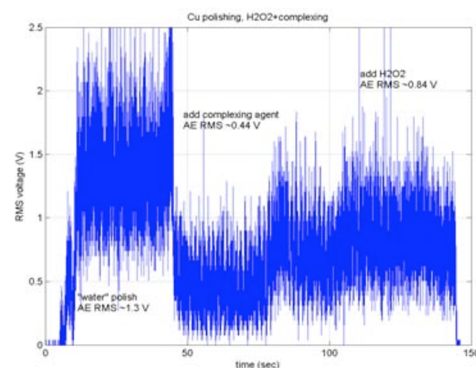
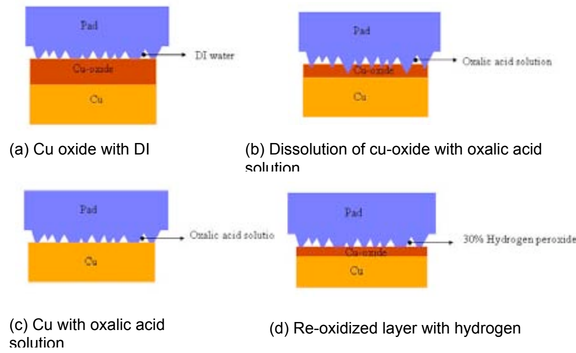


FIGURE 2. IN-SITU AE SIGNAL DURING COPPER CMP OPERATION.



(a) Cu oxide with DI
(b) Dissolution of cu-oxide with oxalic acid solution
(c) Cu with oxalic acid solution
(d) Re-oxidized layer with hydrogen

FIGURE 3. STATES OF AE WITH VARYING SLURRY CHEMICAL COMPOSITION.

First, the pre-existing oxidized copper layer (through hydrogen peroxide treatment) and pad asperities interact together with DI water under mechanical motion (see Figure 3a). Then, when the oxalic acid solution is introduced, the oxidized copper layer begins to be abraded away through a combination of mechanical motion and chemical reaction with the oxalic acid solution (see Figure 3b), and corresponds to the sharp drop in AE RMS signal in Figure 2. The AE RMS signal remains around 0.44 V during the surface interaction between the newly-generated copper surface, pad asperities, and oxalic acid solution (see Figure 3c). Finally, a 30% hydrogen peroxide is supplied to re-oxidize the surface (see Figure 3d). The AE RMS signal increased to approximately ~0.84 V (ie. lower than the first AE RMS signal associated with the oxidized surface state in Figure 3a).

It is initially believed that the variation in AE RMS signal between the states in Figures 3a and 3d is due to the varying surface properties of the copper wafer (mainly, frictional characteristics) as a function of the slurry chemistry. A significant dependency in the hydrophobic or hydrophilic characteristics of a surface on its coefficient in friction has been previously established, with hydrophobic surfaces exhibiting an extraordinarily low coefficient of friction with respect to water (Hiratsuka et al., 2001; Suzuki and Uyeda, 2003). As AE RMS signal has been demonstrated as being representative of the energy consumed during the material removal process (Dornfeld et al., 2003; Lee, D.E. et al., 2004), assuming all other process parameters are identical, an increased AE RMS signal is expected to occur when there is an increased coefficient of friction between wafer and pad. Likewise, decreasing frictional characteristics at the wafer/pad interface will be reflected by a decrease in the AE RMS signal, indicating the decrease in energy consumption as the two surfaces slide over another more easily. As the slurry composition changes from DI water to oxalic acid, the resulting transition from an oxidized hydrophilic surface (case of increased friction) to a native copper hydrophobic surface (and decreased friction) manifests itself as a decrease in resultant AE signal. Hence, the observed shift in the AE signal is believed to directly correlate to the shift in the frictional characteristics between the pad and wafer. In addition, the AE RMS signal difference observed during polishing of different types of oxide formed under different conditions (i.e. hydrogen peroxide treatment for oxidized copper layer formation with and without mechanical motion) is initially believed to be due to a difference in the surface energy (and possibly frictional characteristics as well) between the two oxidized layers.

Effect of oxalic acid concentration

AE RMS variation during oxidized copper dissolution under CMP conditions with three different oxalic acid solutions of varying concentration and pH (0.1 wt.%: pH 2.31, 0.05 wt%: pH 2.49, 0.02 wt.%: pH 2.65) is plotted together in Figure 4 (time averaged values of AE RMS with a time constant of 3 s are used for clarification). Figure 4 clearly shows the effect of oxalic acid concentration (and pH) on the speed of dissolution of copper oxide, with 15 seconds for the transition to take place from high to low values with the 0.1 wt.% oxalic acid solution. With the 0.05 wt.% solution, the AE RMS signal dropped to a lower value over a much longer period of time; approximately 75 seconds. However, with the 0.02 wt.% solution, the signal didn't level off within the experiment time (120 seconds); it only demonstrated a slight drop in RMS signal level to about 0.25 V. These transitions from high to low values of AE RMS correspond to the state shown in Figure 3b where the oxidized copper layer is polished off. During the transition from (a) to (c) in Figure 3, the total oxidized copper surface area continues to decrease, with a corresponding increase in newly-generated copper surface area. The oxidized copper area generates higher AE RMS signal and copper area generates lower AE

RMS signal due to the friction hypothesis explained in the previous section. Hence, during the surface state transition from oxidized copper to plain copper, the total signal drops. The rate of change in surface area of oxidized copper and plain copper can be expressed as

$$\frac{dA_{ox}}{dt} = -A_{ox}k[Acid]^n \qquad (1)$$

$$\frac{dA_{cu}}{dt} = (A - A_{cu})k[Acid]^n \qquad (2)$$

where the total oxidized copper surface area is A_{ox}, and the total copper surface area is A_{cu}. The area of oxidized and plain copper can then be expressed as

$$A_{ox} = Ae^{-k[Acid]^n t} \qquad (3)$$

$$A_{cu} = A(1 - e^{-k[Acid]^n t}) \qquad (4)$$

where A is total area, *[Acid]* is the concentration of oxalic acid, k is a parameter for area sensitivity, and n is a fitting parameter for the acid concentration effect on oxide area variation during the CMP operation. If we assume that the total AE signal is linearly propositional to the source area, and the total AE signal can be modeled as a linear sum of AE from each area

$$AE_{RMS} = \alpha A_{ox} + \beta A_{cu} \qquad (5)$$

where α is a fitting parameter for the higher AE RMS signal associated with oxidized copper and β is a fitting parameter for the lower AE RMS signal associated with plain copper. Combining equations 3, 4, and 5, the AE RMS signal can be modeled as

$$AE_{RMS} = A\left[(\alpha - \beta)e^{-k[Acid]^n t} + \beta\right] \qquad (6)$$

This model is plotted along with the raw AE RMS data in Figure 5 for comparison. With the limited experimental dataset, this model reasonably explains the AE RMS transition, and parameters in this model can be used as a means for characterization of oxidized copper dissolution and removal during the CMP operation.

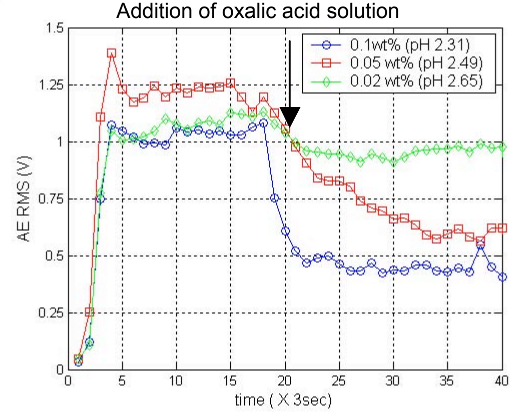


FIGURE 4. AE RMS VARIATIONS DURING OXIDIZED COPPER DISSOLUTION WITH VARYING OXALIC ACID COMPOSITION.

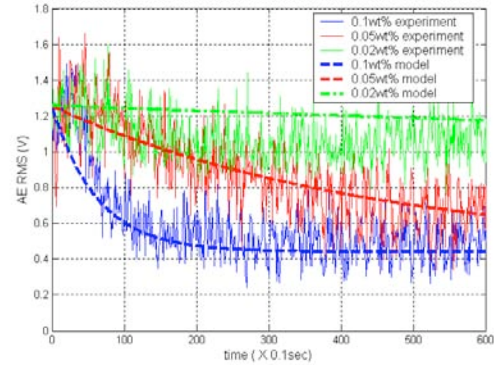


FIGURE 5. COMPARISON BETWEEN MODELED AND EXPERIMENTAL DATA IN THE AE RMS SIGNAL TRANSITION REGIME (50-110 SEC).

CONCLUSIONS

In-situ acoustic emission monitoring experiments demonstrated high AE RMS signal during polishing of oxidized copper, and low AE RMS signal during polishing of plain copper. Also, oxide formed under different conditions demonstrated different levels of AE signal under polishing conditions. With these basic AE characteristics, three different concentrations of oxalic acid solution were tested for comparison in the signal transition regime. Higher acid concentration resulted in a more rapid signal transition. With the assumption that the AE RMS signal is linearly proportional to the fractional area of a specific surface state during CMP, a model for AE RMS in the signal transition regime was suggested.

ACKNOWLEDGEMENT

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