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TRIBO-CHEMICAL MODELING OF COPPER CMP

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Technical Area: CMP (Copper)

Abstract

We are developing an integrated tribo-chemical model of copper CMP that considers abrasive and pad properties, process parameters (speed, pressure etc.), and slurry chemistry to predict material removal rates. In this paper, the framework of the model is explained, and two important constituents of the model are presented: transient passivation behavior and characteristics of mechanical interactions.

Introduction

Copper CMP, a key enabler for copper interconnect technology, remains underutilized; better planarity at lower pressure with higher removal rates, and lower defects (dishing, erosion, fangs & corrosion) could be achieved by investigating and understanding the fundamental mechanism(s) of the process, and by bringing together different existing segments of CMP knowledge.

Extensive modeling and analysis of metal CMP process has been done from a purely mechanical or a purely chemical perspective, without explicitly addressing their synergism. The mechanical models, considering abrasive wafer interaction, assume that chemical reactions are fairly fast compared to mechanical interactions, and hence that the chemical reaction rates are not influenced by the mechanical interactions [1]. On the other hand, chemical models such as that of Paul [2] assume that mechanical action is a continuous phenomenon and can thus be included in rate kinetics and used to form a steady state removal rate model. However, recent investigations of copper CMP using a quartz crystal microbalance [3] and studies on corrosive wear [4] suggest otherwise. Copper CMP is a transient chemical process with intermittent mechanical phenomena.

In this research we are developing an integrated tribo-chemical model of copper CMP that considers abrasive and pad properties, process parameters (speed, pressure etc.), and slurry chemistry to predict material removal rates. We present here the framework of this model, and two important constituents of the model: transient passivation behavior and some characteristics of mechanical interactions.

Copper CMP Mechanistic Model

Copper CMP is a corrosive wear process, which may be described by the following equation [4]:

$$V_{CW} = V_C + V_W + \Delta V_W + \Delta V_C \qquad \text{....(1)}$$

The total corrosive wear, V_{CW}, is higher than the simple superposition of material loss due to pure corrosion, V_C, without the influence of wear and the material loss due to wear, V_W, measured in the absence of corrosion. This additional removal is attributed to the combined effect of corrosion-induced wear, ΔV_W, and wear-induced corrosion, ΔV_C [4]. In the case of copper CMP, V_W is significantly lower than V_{cw} [5, 6], as is V_c [7]. Hence ΔV_W and ΔV_C are the most significant components of the overall removal rate.

Under typical CMP conditions, where the slurry chemistry allows passive or protective films to form on copper the oxidation rate of copper decreases as the passivating surface film progressively thickens. Accordingly, the rate of oxidation at a given site upon a copper surface undergoing polishing will change, as indicated schematically in Figure 1. There will be periodic removal of passive film (for example by interaction with abrasive particles), with a sudden, dramatic increase in oxidation rate, followed by formation and progressive thickening of new passive film with a concurrent decrease in oxidation kinetics. The total amount of copper oxidized will be given by the area under the oxidation rate curve.

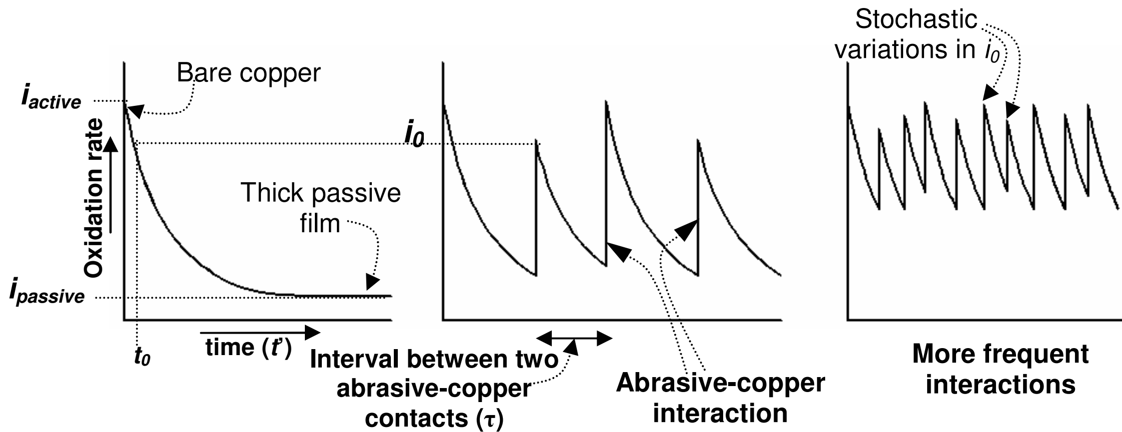

FIGURE 1. a) Copper: Transient passive current i(t') b) Copper oxidation influenced by abrasive interactions c) Copper oxidation with more frequent abrasive interactions

This principle provides the basis for integrating chemical behavior with mechanical phenomena into a model for CMP. The interaction frequency, a key determinant in this model, can be estimated from the local asperity-wafer contact area, its shape and distribution [8]; and the distribution of abrasive particles over an asperity. The interval between interactions is estimated to be of the order of a few milliseconds to a few tenths of a second.

Let $i(t')$ be the transient passive current density at time t' after bare copper is exposed to the given oxidizing passivating environment, with $i(t'=0)=i_{active}$ and $i(t'=\infty)=i_{passive}$ (Figure 1a). i_{active} and $i_{passive}$ may never be attained at any point on copper during CMP, because passive film may never completely be removed by abrasive interaction and passive film will never grow indefinitely during actual CMP. The $i(t')$ relationship is obtained by tribo-electrochemical experiments. Further discussion on the nature of this relationship and ways to obtain i is provided below.

Let τ be the interval of time between two consecutive abrasive-copper interactions (Figure 1b).

Let t be the time since an abrasive-copper interaction, before the next interaction.

Let i_0 be the current density immediately after an abrasive-copper interaction; this would be i_{active} if there has been complete removal of the passive film, but would be less than i_{active}

if there is incomplete removal of the film. Assuming consistent composition of the passive film, i_0 could be correlated to the thickness of the remaining film.

Let t_0 be defined such that $i(t'=t_0)=i_0$.

τ, t_0 and i_0 are stochastic variables because the interaction frequency, the duration and force of contact would vary from one abrasive-copper interaction to other (Figure 1c). It is possible that the oxidation conditions could vary from one abrasive-copper interaction to next, but this has not been considered here.

Then the average removal rate of copper (in nm/min) between the two abrasive-copper interactions is

$$\dot{V}_{CW} = \frac{M_{Cu}}{\rho n F \tau} \int_0^{\tau} i(t_0 + t)dt \qquad \text{... (2)}$$

where M_{Cu} is the atomic mass of copper, ρ is the density of copper, n is the oxidation state of the oxidized copper, F is Faraday's constant.

Transient Passivation Behavior

There has been very little research on the repassivation kinetics of copper, mainly because it is difficult to obtain bare metal surface while keeping other conditions constant, and to measure and analyze very rapidly changing current densities [9]. In addition, copper is rarely used in environments that can cause corrosive wear. However, relevant information is available from repassivation studies of other metals and alloys, in addition to some studies on copper corrosion inhibitors.

Transient current densities associated with repassivation can be measured by activating the surface of a passivated metal in different ways. The most commonly used methods are mechanical activation (by scratching the surface of the metal using a sharp tip, or by rubbing the surface using a hard rough surface, etc.) [9]; and electrochemical activation, where the surface of the metal is held at a relatively low potential, where the metal corrodes actively, and suddenly stepped up to a voltage in the passive region [10] (obtained from corresponding Tafel behavior).

Many researchers have observed that the transient current on an activated metal surface drops in a manner shown in Figure 2 [11, 12]. The log-log relationship is attributed to a constant or increasing potential field across the film [11].

As would be expected, the time required for the current to decrease by 2 orders of magnitude varies widely for different materials and conditions. Bastek et al [9] measured the repassivation time for a scratched 304 stainless steel in a neutral solution to be about 10ms, whereas Madsen and Adler [12] measured it to be 1s for Fe-5Al alloy in 1N H_2SO_4.

Transient passivation studies on copper have primarily been conducted using inhibitors. Beier and Schultze [10] studied the formation of layers of 3-amino-5-heptyl-1,2,4-triazole (AHT) on copper in 1 N H_2SO_4 by potentiostatic pulse measurements of the current density. The observed behavior is illustrated in Figure 3. They observed that it takes about 100ms to form a monolayer of inhibitor and for the current density to drop by one order of magnitude. Brusic et al. [13] observed that it takes about 10s for a 2nm thick layer of inhibitor to form on copper.

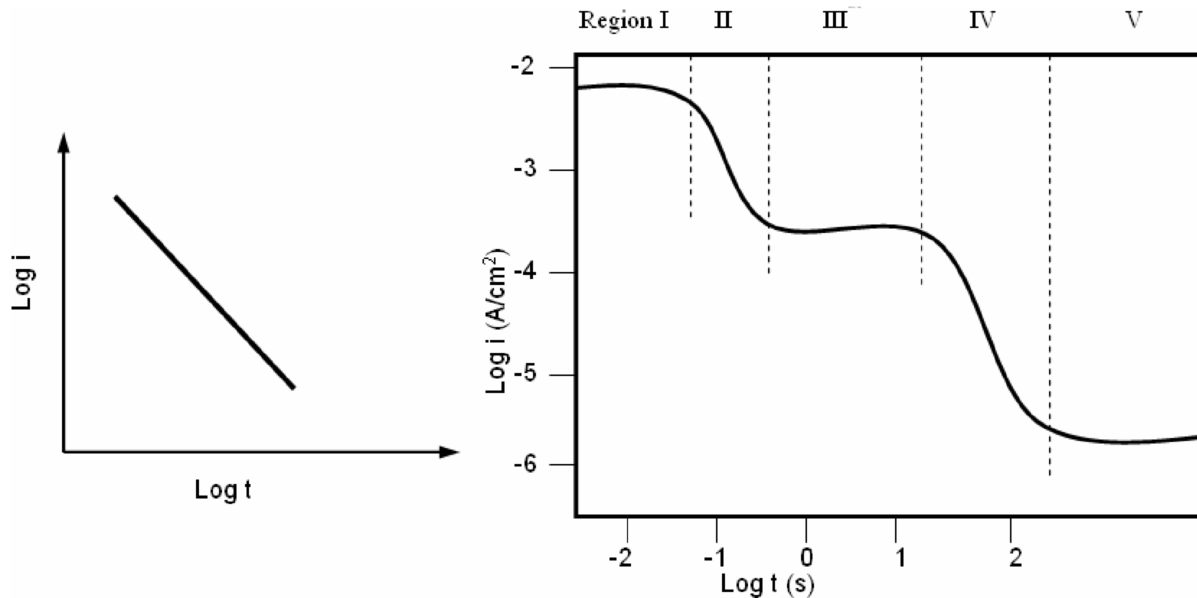

FIGURE 2. log-log plot of passivation current with time. FIGURE 3. Kinetics of inhibition of copper by AHT (after [10])

Given the significant variations seen experimentally in the decay of current density upon passivation, future work is planned to characterize the decay kinetics in solution chemistries representative of those encountered in CMP. Because the current decays due to thickening of the passive film, the current at any time could be correlated to the thickness of the passive film present. Thus the initial current density after a given abrasive-copper interaction could be predicted from the new film thickness (or start at i_{active} if the passive film were removed completely).

Mechanical Interactions

The frequency and amount of passive/inhibitor film removed from copper depends on the frequency, force and duration of abrasive-copper interactions and pad asperity-copper contacts. The pad properties (topography, hardness, visco-elasticity etc.) and applied pressure determine the size and shape of local contact areas and their spatial distribution (real contact area ratio). This, along with the relative pad-wafer velocity, determines the interaction frequency and duration of contact. An asperity-abrasive-copper system is shown in Figure 4, the plan view displays how the duration of contact could change due to differing wear distances.

Elmufdi and Muldowney [8] have measured real contact area using confocal microscopy, and found the real contact ratio to be between 1-10% for the usual operating CMP pressures, whereas previously researchers [1, 14] have frequently used a value of around 0.1% for their CMP models. Based on their results, it can be estimated that the interval between consecutive asperity-wafer contacts is about 1ms. The duration of contact is estimated to be about 10µs. There are no empirical results yet to calculate abrasive-copper interaction frequency.

As discussed above, a crucial input to the model would be the amount of material removed during each interaction between the passivated copper surface and an abrasive particle. Different patterns of behavior are expected, according to the properties of the passive film or abrasive. The wear of a passive film when an abrasive particle presses down upon it at a particular contact pressure could be linear (Figure 5a) with sliding distance until all of the

passive film is removed (as in the typical cases of abrasive or adhesive wear, wear depth is proportional to pressure and sliding distance and inversely proportional to the hardness of the material [15]), if the film is of uniform composition throughout its thickness. The actual film composition could be bi- or multi-layer, as has been proposed for the case of inhibitor AHT film [10], hence, the wear rate of different layers could be different (Figure 5b). If the abrasive gets 'loaded' with worn material the wear rate could be expected to decrease with wear distance (Figure 5c).

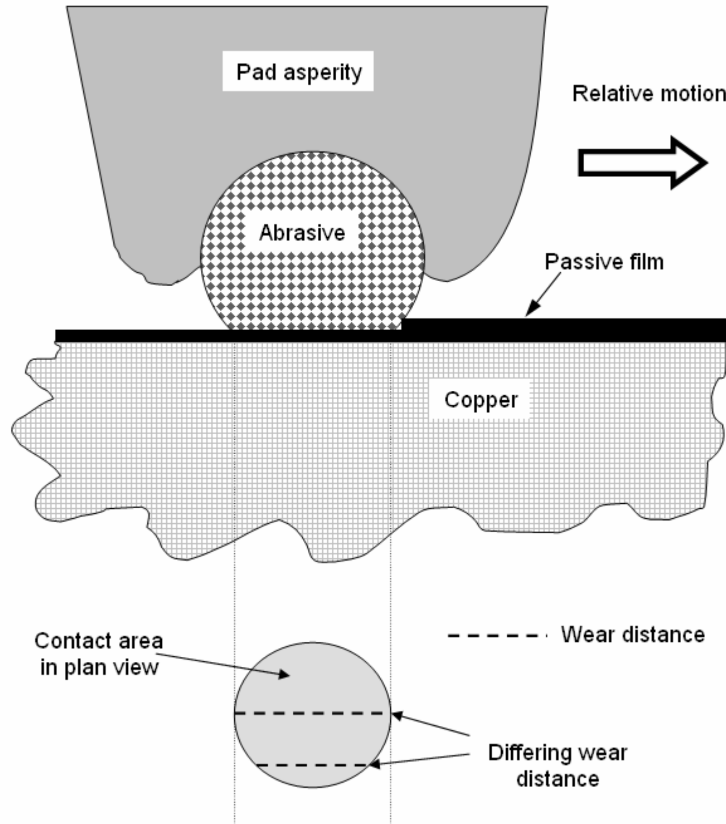

FIGURE 4. (Top) Cross section of asperity-abrasive-copper contact; (bottom) abrasive-copper contact area and differing wear distances

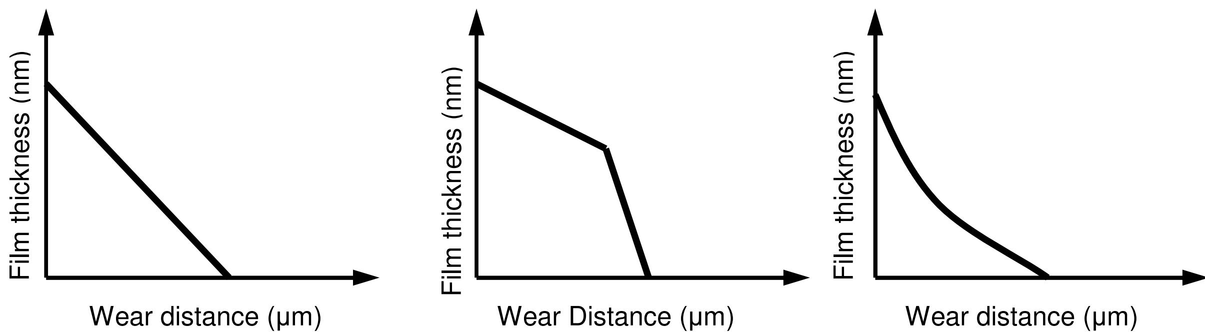

FIGURE 5 a) linear wear rate b) bilayer passive film c) deteriorating abrasive condition

The mechanical properties (hardness) and thickness of the passive film (while the interaction frequency is constant) depend on the chemical conditions under which they were formed. As depicted schematically in figure 6, this would result in different wear rates.

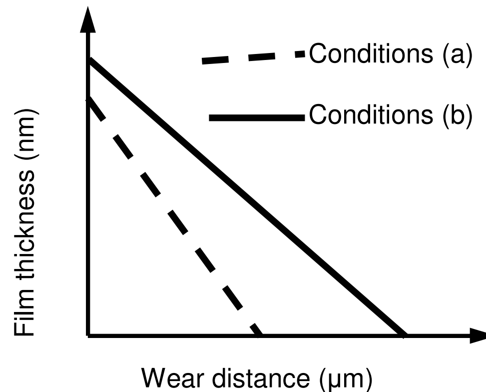

FIGURE 6. Mechanical properties and thickness of film as a result of different chemical conditions

Conclusion and Future Work

This paper presents tribochemical copper CMP modeling work in progress. The model is based on the synergism of mechanical and chemical effects during CMP, previously unaddressed in other models. Further investigation and verification is planned using detailed experiments on the transient passivation behavior of copper in CMP slurries by means of the potentiostatic pulse method and the electrochemical scratch method. The mechanical properties of passive films are also under study using AFM experiments.

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