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Publication Date
2009-04-16

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Integrated Tribo-Chemical Modeling of Copper CMP

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ABSTRACT

Copper CMP is a corrosion-wear process, in which mechanical and chemical-electrochemical phenomena interact synergistically. Existing models generally treat copper CMP as a corrosion enhanced wear process. However, the underlying mechanisms suggest that copper CMP would be better modeled as a wear enhanced corrosion process, where intermittent asperity/abrasive action enhances the local oxidation rate, and is followed by time-dependent passivation of copper. In this work an integrated tribo-chemical model of material removal at the asperity/abrasive scale was developed. Abrasive and pad properties, process parameters, and slurry chemistry are all considered. Three important components of this model are the passivation kinetics of copper in CMP slurry chemicals; the mechanical response of protective films on copper; and the interaction frequency of copper with abrasives/pad asperities. The material removal rate during copper CMP was simulated using the tribo-chemical model, using input parameters obtained experimentally in accompanying research or from the literature.

INTRODUCTION

Any mechanistic model of copper CMP must capture the synergistic interaction of mechanical and chemical/electrochemical phenomena. The overall corrosive wear rate, V_{CW}, exceeds the sum of the material loss rates observed in pure corrosion, V_C, or pure wear in the absence of corrosion, V_W[1]. This excess removal rate is due to the combined effect of corrosion-induced wear, ΔV_W, and wear-induced corrosion, ΔV_C. The former results from phenomena such as abrasion by hard, oxidized wear products; the removal of work hardened layers by oxidative dissolution, or stress-corrosion cracking. The latter, wear-induced corrosion, can be due to enhanced corrosion after mechanical removal of protective films, the enhanced activity due to strained surfaces or other defects, local increases in temperature or improved mass transport.

Direct wear of metallic copper would not be expected during CMP, as has been observed experimentally[2,3], hence V_W is zero. Slurries are formulated to minimize direct dissolution of copper, V_C, in the absence of mechanical action, to prevent attack of recessed regions of the wafer surface. Planarization can only be achieved if $V_{CW} >> V_C$.

Much of the existing copper CMP research considers the difference between the total removal rate during CMP and the rate of dissolution in the absence of polishing to be mechanical (corrosion enhanced wear, ΔV_W), attributed to modification of hardness and/or Young's modulus by the chemical environment. This generates material removal models that are primarily mechanical, with empirical inputs from the chemical processes. This approach provides no route for fully describing the mechanisms thought to be involved in CMP.

From a mechanistic perspective, passive or protective films containing oxidized copper are mechanically removed (or partially removed) during CMP by pad-abrasive action. This leaves a more reactive surface on which the protective layer starts to reform, until it is removed by the next abrasive particle or pad asperity. This regular removal of the protective film leads to overall oxidation rates significantly higher than those that would occur without mechanical disruption. Hence this phenomenon is best described as wear-enhanced corrosion, ΔV_C, rather than the corrosion enhanced wear, ΔV_W currently considered in most CMP models. Since only oxidized copper is removed during CMP (dissolved or abrasion of films), the most appropriate way to model this is electrochemically, using oxidizing currents along with inputs that describe the mechanical phenomena. Here we present a new modeling approach for material removal at the abrasive scale, based on copper oxidation rates influenced by intermittent mechanical action.

MECHANISTIC MODEL FOR COPPER CMP

As discussed above, passive or protective films form on copper under typical CMP conditions. As these thicken, the oxidation rate of copper decreases at rates that vary for different slurries The films are removed periodically during polishing by interaction with abrasive particles and pad asperities, causing a dramatic increase in oxidation rate, followed by progressive thickening of the new passive film and a concurrent decrease in oxidation kinetics.

To capture this mechanism in a mathematical model for the local copper material removal rate during CMP, one must consider: the passivation kinetics of copper in the particular CMP slurry; the frequency and force of interaction of abrasive particles and/or asperities at that particular point on the surface; and the mechanical response of the passive film to forces applied on a sliding abrasive/asperity. If the passivation kinetics, frequency of interaction, and amount of passive film removed per interaction are known and remain unchanged during the process, and the process operates in a quasi-steady-state (after each interaction the oxidation rate returns to the same value), the removal rate during the process can be obtained as follows (Figure 1).

Let $i(t')$ be the transient passive current density at time t' after bare copper is exposed to a given oxidizing passivating environment, and i_0 be the current density immediately after an abrasive-copper interaction (which would only be $i(t')$ if the interaction removed the entire film). If τ is the interval of time between two consecutive abrasive-copper interactions, and t the time since the last abrasive-copper interaction, with t_0 defined such that $i(t'=t_0)=i_0$, then the average removal rate of copper (in nm/s) between the two abrasive-copper interactions is:

$$\dot{V}_{CW} = \frac{M_{Cu}}{\rho n F \tau} \int_0^{\tau} i(t_0 + t)\,dt \tag{1}$$

where M_{Cu} is the atomic mass of copper, ρ is the density of copper, n is the oxidation state of the oxidized copper, and F is Faraday's constant. The integral gives the total oxidizing charge passed during interval τ. Although the oxidation conditions may vary from one abrasive-copper interaction to the next, this is unlikely to be a significant factor for modeling CMP with a continuous flow of slurry and good agitation.

For most commercial pads, τ, t_0 and i_0 would be stochastic variables; the interaction frequency, the duration and force of contact would vary from one abrasive-copper interaction to

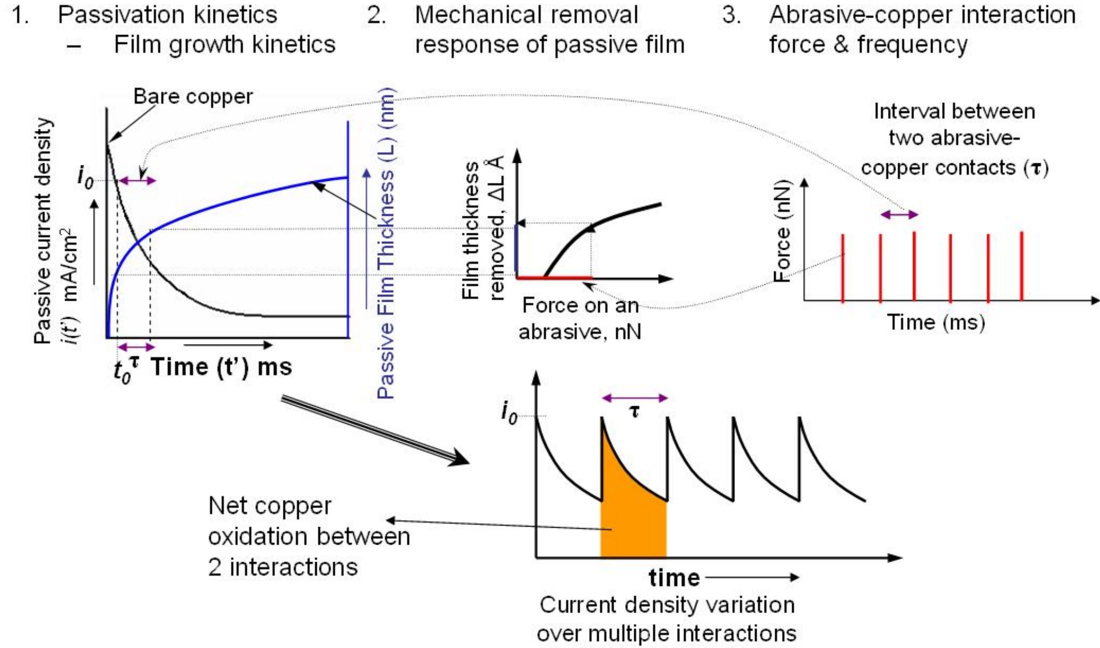

Figure 1: Determination of copper removal rate during CMP from passivation kinetics of copper, mechanical response of passive films, and abrasive-copper interaction force and frequency

another. Using averaged values of stochastic parameters to evaluate a non-linear function of these parameters, as is the case for copper CMP, could introduce significant errors. A Monte-Carlo based scheme would be appropriate for accounting for these stochastic variations during copper CMP. For pads with well-defined structures, such as fixed abrasive pads, τ, t_0 and i_0 would be expected to be constants that could be determined experimentally.

INPUT PARAMETERS FOR CMP MODEL

To evaluate the CMP model, it is necessary to measure or estimate the parameters within equation 1, and assess the validity of the quasi-steady state assumption underlying equation 1.

Frequency of Mechanical Interactions

The frequency and amount of passive/inhibitor film removed from copper during CMP depends on the frequency, force and duration of abrasive-copper and pad asperity-copper interactions. The pad properties, applied pressure and conditioning determine the size and shape of local contact areas and their spatial distribution. Elmufdi and Muldowney[4] have measured the real contact area of asperities on a typical commercial pad using confocal reflectance interference contrast microscopy (C-RICM), and found the real contact ratio, $Ar_{\%}$, to be between 1 and 10% for the usual operating CMP pressures. Under conditions where $Ar_{\%}$ was 0.01, the average asperity contact area, $\overline{Asp_{area}}$ was about 100 μm^2. Taking the relative pad-wafer velocity as 1 m/s, this gives the average interval between consecutive asperity-copper contacts, τ, and the duration of contacts as:

$$\tau = \frac{\sqrt{\overline{Asp_{area}}}}{V \cdot Ar_{\%}} = 1 \text{ ms} \qquad \text{and duration of contact} = \frac{\sqrt{\overline{Asp_{area}}}}{V} = 10 \mu\text{s}$$

The distribution of abrasives under each asperity-copper contact is needed to calculate the abrasive-copper interaction frequency. This depends upon the slurry composition and colloidal properties of the abrasive. At present, there are no experimental data on the distribution of abrasive particles under pad asperities. However, we can set bounds on the abrasive interaction frequencies. If there are multiple abrasive particles under the same asperity, then the interval between these contacts must be less than the duration of the asperity-copper contact, i.e. the abrasive-copper interaction interval is less than 10μs. If there is an abrasive contact once every (or every few) asperity contact(s), then the abrasive interaction interval will be similar to the asperity contact interval, about 1ms. Regardless, since the time interval between consecutive asperity contacts is about 2 to 3 orders of magnitude larger than the interval between consecutive abrasives contacts under the same asperity, the electrochemical changes on copper between sequential abrasive contacts under the same asperity will be minor compared to the electrochemical changes between two asperity contacts. This justifies using a single parameter to describe passive film removed by a pad asperity and all abrasive particles under that asperity.

Mechanical response of protective film

To evaluate the tribo-chemical model of copper CMP one needs to know how much material is removed by each interaction between the passivated copper surface and a pad asperity. Typical copper removal rates during CMP are in the range of 50 to 600 nm/min. For intervals between two asperity copper contacts of 1 to 10ms, this corresponds to removal of a copper layer of 0.1 to 1Å thick per interaction (due to both dissolution between the two interactions and removal of oxidized copper film by the interaction). This is less than 1 atomic layer (the atomic radius of copper is 1.4Å). Since one cannot physically remove a fraction of an atom, this means that the likelihood of removal of a single surface copper species is less than unity per interaction. This is consistent with experimental observation that the roughness achieved during copper CMP is less than a nanometer. The mechanical phenomena during CMP must be akin to the plucking of certain atoms/molecules from the surface during each asperity/abrasive interaction (the "chemical tooth" model proposed by Cook[5]). Enhanced dissolution between interactions also contributes to the overall material removal. This illustrates the inappropriateness of attributing the synergy between chemistry and mechanical effects in CMP to modification of the mechanical properties of surface layers by the chemical environment.

Passivation Rates and Quasi-Steady State Condition

Figure 2 shows schematically the attainment of steady state during copper CMP. The oxidation current decreases with time as protective films of oxide or inhibitor develop, while the thickness (or completeness) of these films increases. CMP is assumed to start at time t_{0b} ('b' denotes before abrasion), where the passive film thickness is 0_b. Part of the film is removed (denoted by the vertical arrow), leaving a film thickness of 0_a.The film grows to 1_b during the interval τ, when more of the film is removed. The process continues, eventually reaching a quasi-steady state, where the amount of film formed between abrasions is equal to that removed by the abrasion.

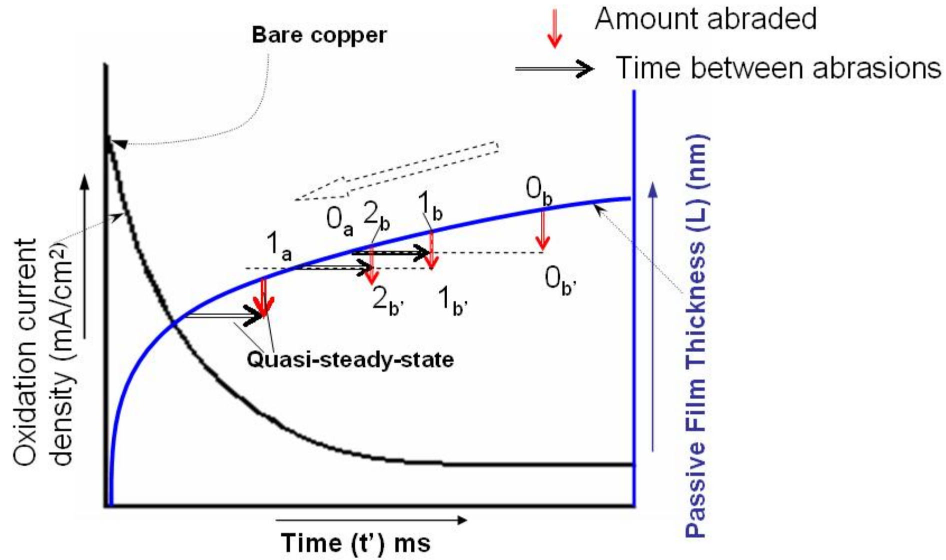

Figure 2: Attaining a quasi-steady-state during copper CMP.

The functional form of the current decay shown schematically in Figure 2 was obtained from potential-step experiments using a copper microelectrode[6] and is taken as:

$$i(t) = i_{bare} \cdot \left(\frac{t}{t_{bare}} \right)^{-n} ; \forall t \geq t_{bare} \qquad (2)$$

where i_{bare} is the current density on bare copper, up to the point when the formation of oxidized films or adsorption of inhibitor causes current decay. The integral of the current with respect to time gives the total material removal (through Faraday's law). However, only a portion of this is responsible for the thickening protective film; the rest represents copper that dissolves in the slurry.

PREDICTIONS

The charge of oxidized copper in a passive film (a convenient measure of the thickness) was estimated using representative literature values for model parameters, assuming different passive film thicknesses at the time of the first abrasion. These film thicknesses are shown in Figure 3 in terms of the time that the copper was exposed to the slurry before polishing started. With short initial exposure times, the film must thicken before attaining quasi-steady state, whereas with long initial exposure times it must thin down. It may take on the order of 10s before quasi-steady state is attained, but this is still relatively short compared to the duration of CMP (of the order of 100s). Hence a model based upon quasi-steady state seems reasonable.

The material removal rate is the primary parameter of interest from CMP models. We are currently working on detailed evaluation of the amount of dissolution occurring as a function of the thickening film, using potential-step chronoamperometry data. As a first approximation, however, Figure 4 shows the predictions from the integrated tribo-chemical model, assuming that 50% of the current passing at any time results in copper ions dissolving directly into the slurry. One sees that if the original protective film was very thin, there is rapid material removal in the first few seconds of polishing, until quasi-steady state is reached. In contrast, if the film is thick, the removal rate is lower for several seconds until quasi-steady state is reached.

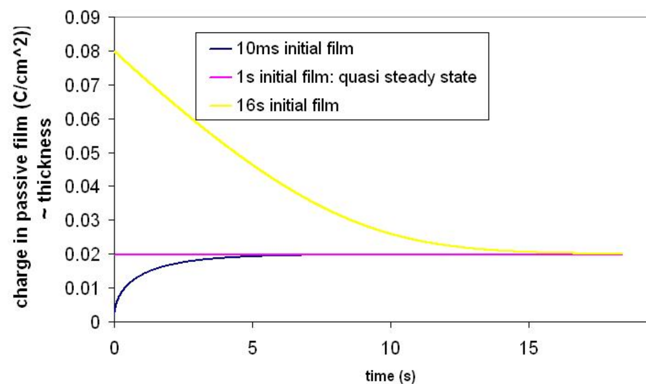

Figure 3: Simulation of charge of oxidized copper in passive film for different initial film formation times: 1ms interaction frequency (τ); 10μC/cm^2 charge in thickness removed per interaction; passivation kinetics $i(t)=0.01t^{-0.5}$ A/cm^2 and t_{bare}=0.1ms

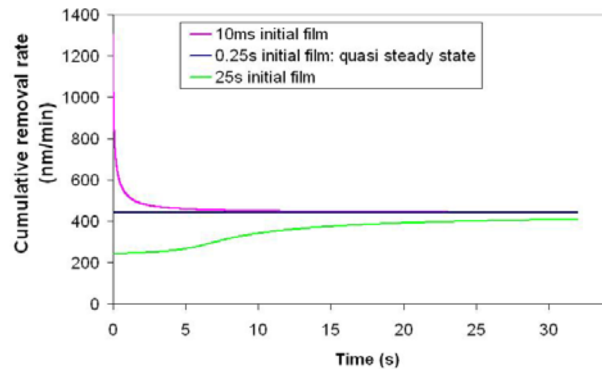

Figure 4: Simulation of copper removal rate over time for different initial film formation times, assuming 50% direct dissolution of oxidized copper, other parameters as for Figure 3

CONCLUSIONS

A new tribo-chemical copper CMP model is based on the physical mechanism responsible for the synergism of mechanical and chemical effects during CMP, unaddressed in previous models. Copper removal is tracked by the oxidation rate of copper, which fluctuates significantly due to regular removal of protective species by pad asperities and abrasives in the CMP slurry.

ACKNOWLEDGMENTS

This work was funded by AMD, Applied Materials, ASML, Cadence, Canon, Ebara, Hitachi, IBM, Intel, KLA-Tencor, Magma, Marvell, Mentor Graphics, Novellus, Panoramic, SanDisk, Spansion, Synopsys, Tokyo Electron Limited, and Xilinx, with donations from Photronics, Toppan, and matching support by the U.C. Discovery Program.

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