Title

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Abstract

Our recent work on particle scale interactions in chemical mechanical planarization (CMP) is summarized from several perspectives – particle-material interactions and the influences of material properties and surface films; particle-to-particle interactions and the influence of slurry chemistry; and particle-pad interactions. A mechanistically-based tribo-chemical model for copper CMP that treats material removal as wear-enhanced corrosion has been developed. Agglomeration of particles is affected by the slurry chemistry.

Introduction

A fundamental understanding of the chemical and mechanical effects in CMP, and the synergy between them, is necessary to insure efficient and controllable processing. Our research at the University of California (UC) over the past few years has been to develop a comprehensive view of the mechanisms of material removal in CMP over a range of scales from the wafer scale, through the device level [1], to the atomic level [2]. Our recent work views particle scale interactions in CMP from several perspectives – particle-material interactions and the influences of material properties and surface films; particle-to-particle interactions and the influence of slurry chemistry; and particle-pad interactions.

We have been developing a mechanistically-based tribo-chemical model for copper CMP that treats material removal as wear-enhanced corrosion [3]. This model considers abrasive and pad properties, process parameters (speed, pressure etc.), and slurry chemistry to predict material removal rates. During CMP, abrasive particles interact intermittently with a particular point on copper undergoing material removal. The model considers the copper surface to be protected by an inhibitor or a protective film, depending upon the chemical nature of the slurry. The protective film is periodically removed at locations that interact with pad asperities and abrasive particles in the slurry. The corrosion current abruptly increases, then decays as the protective film builds up again until the next abrasive event. The chemical action of the slurry passivates the surface of copper. Thus, a comprehensive mechanistic study of copper CMP has three important components: 1) passivation kinetics of copper (oxidation rate of copper as a function of thickness of passive film); 2) mechanical properties of passive films (the ease with which abrasives can remove passive film, exposing bare copper, thereby enhancing the subsequent reaction rates); and 3) abrasive-copper interaction force and frequency.

An important element in CMP is slurry behavior and interaction with materials during the process. Slurry agglomeration behavior has been characterized using various common copper CMP chemistries both with and without the presence of copper. The nanohardness of copper exposed to various slurry chemistries has also been measured [4]. The agglomerated size and distributions and nanohardness have been incorporated into the earlier CMP model of Luo and Dornfeld [5] to predict the MRR and compare to experimental copper CMP material removal rates. More recently, we have been studying the agglomeration of alumina particles as a function of slurry chemistry [6], which may also be added to this recent tribo-chemical model.

Mechanistic Model for Copper CMP

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

Modeling this mechanism for local copper material removal rate during CMP requires the passivation kinetics of copper in the particular slurry; the frequency and force of interaction of abrasive particles and/or asperities at a particular point on the surface; and the mechanical response of the passive film to forces applied on a sliding abrasive/asperity. If the process operates in a quasi-steady-state (after each interaction the oxidation rate returns to the same value) as shown in Fig. 1, the removal rate during the process can then be obtained as follows.

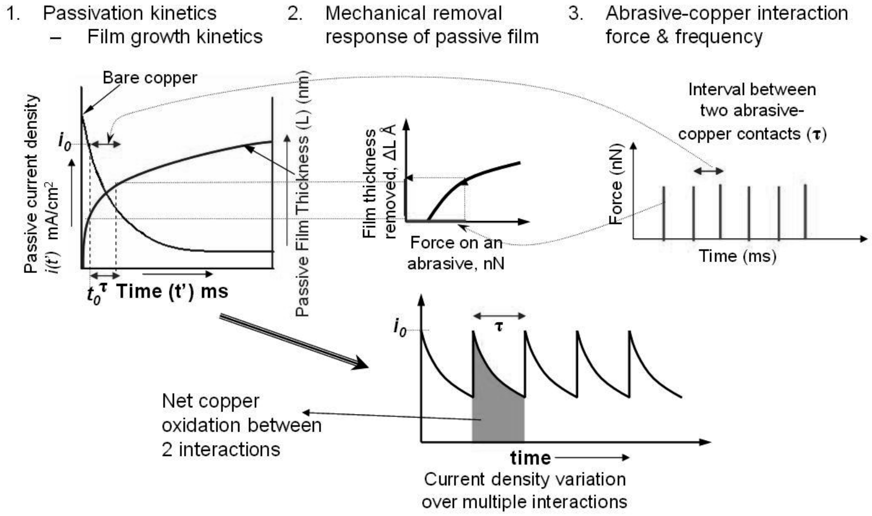

Fig. 1: Determination of copper removal rate during CMP from passivation kinetics of copper, mechanical response of passive films, and abrasive-copper interaction force and frequency

The transient current density is *i(t')* at time *t'* after bare copper is exposed to a given oxidizing passivating environment, and i_0 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 is 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 in Eq. (1) gives the total oxidizing charge passed during interval τ, assuming that a continuous flow of slurry and good agitation ensure that oxidation conditions do not vary from one abrasive-copper interaction to the next.

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 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 for Eq. (1). 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 [7] 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:

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

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 10 μ s. 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 the Protective Film

The amount of material removed by each interaction between the passivated copper surface and a pad asperity is needed to evaluate the tribo-chemical model of copper CMP. 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 one atomic layer (the atomic radius of copper is 1.4Å), and physically means that the likelihood of removing 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 [8]). 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 a time 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, then 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.

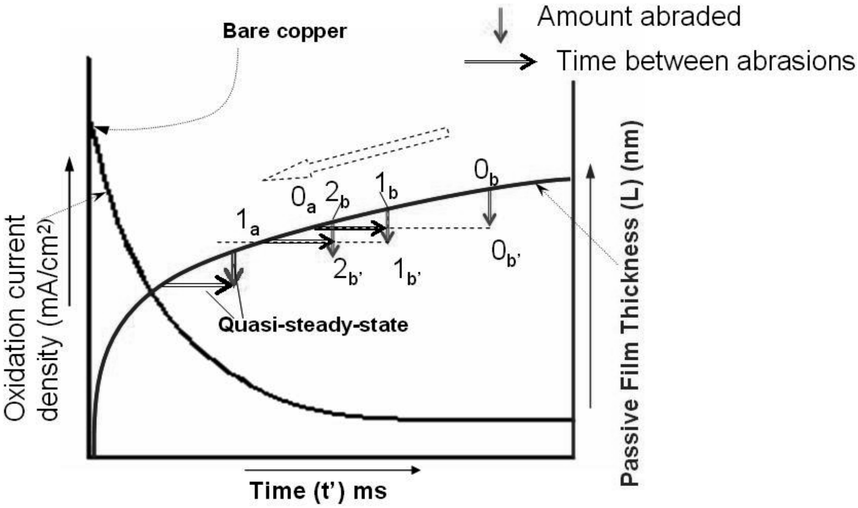

Fig. 2: Attaining a quasi-steady-state during copper CMP.

The functional form of the current decay shown schematically in Fig. 2 was obtained from potential-step experiments using a copper microelectrode [9] and for slurries containing BTA is:

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

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 removed (through Faraday's law). Only a portion of this is responsible for the thickening protective film; the rest represents copper that dissolves directly 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. 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, Fig. 3 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.

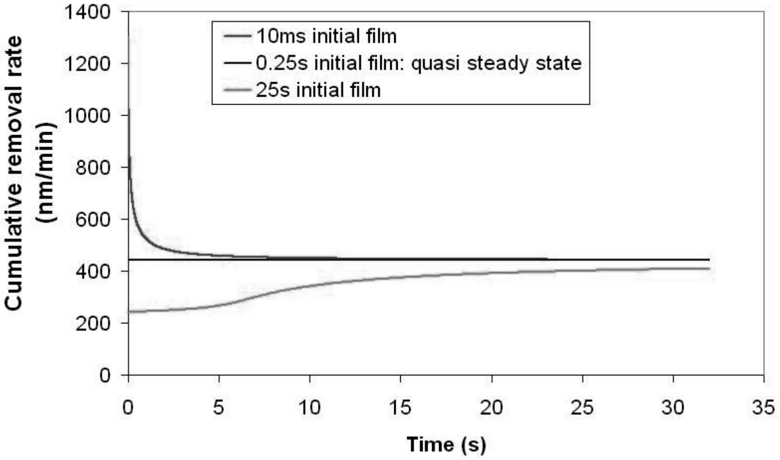

Fig. 3: Simulation of copper removal rate over time for different initial film formation times, assuming 50% direct dissolution of oxidized copper, 1ms interaction frequency (τ); 10μC/cm^2 charge in thickness removed per interaction; passivation kinetics – $i(t)=0.01t^{-0.5}$A/cm^2 and t_{bare}=0.1ms

Particle Agglomeration

The effects of common slurry additives on the colloidal behavior of alumina suspensions used for copper CMP have been studied by measurement of zeta potential and agglomerate size distribution [10, 11]. It was found that the presence of copper can increase or decrease the agglomeration of the alumina depending on the chemical additives and pH of the solution [10]. The abrasive particle agglomerates were able withstand the shear force during CMP without breaking up [11]. Common slurry additives and the pH of the solution significantly affected the nanohardness and etch rate of the copper surface [4]. With the addition of chemical additives and changes in the pH of the solution, the nanohardness of the copper film was observed to range from 0.05 – 20 GPa, due to the formation of different films, such as CuO, Cu_2O, or $Cu(OH)_2$, and/or changes in the compactness of the surface film from complexing reactions or dissolution.

During CMP, alumina abrasive particles may agglomerate into undesired larger particles that can cause scratches and other defects. By understanding the rate of agglomeration as a function of chemistry, new slurries can be developed that will ultimately reduce scratches and defects. Also, modeling of CMP is very sensitive to the abrasive size, which may change if the particles agglomerate over time. It has been shown that colloidal aggregates are fractal and therefore, follow a power law relationship, in which the mass of the aggregate (or number of particles) is proportional to the primary particle size raised to the fractal dimension, d.

The fractal dimension, ranging from 1 to 3, is dependent on the physical and chemical nature of the solution and can infer the type of aggregates formed. For example, d values close to 3 are typical for 3-dimensional structures, while values closer to 2 are characteristic of 2-dimensional structures, such as flake-like aggregates [12]. The fractal dimension is also indicative of the agglomeration mechanism. A fast diffusion-limited aggregation (DLA) is indicated by a smaller fractal dimension, which yields open, loosely packed agglomerate structures. Since particle repulsion is small, particles stick together almost as soon as they contact. Larger values indicate slow reaction-limited aggregation (RLA) where particle-particle repulsion has a greater effect. Agglomerates produced by the RLA mechanism are more densely packed. This is because the particles can penetrate farther into agglomerate structures without being captured initially. By using the Smoluchowski equation, which describes aggregation kinetics in terms of cluster-cluster formation [13], with simple scaling arguments for the cluster distributions, a power law governing the agglomeration kinetics can be obtained follows:

$$R(t) = Ct^{1/d} \tag{3}$$

where R is the effective agglomerate diameter, t is time, and C is a constant. This equation implies that the kinetics is Brownian in nature and was used for an analysis of our data [6]. The rate of agglomeration was measured for alumina particles with and without the copper in KNO_3 at various pH values. For solutions without copper, agglomeration was greatest at pH of 7.5, near the isoelectric point of 6.5, at a rate of 82 nm/min, following a reaction-limited mechanism. Solutions with a pH away from the isoelectric point underwent reversible agglomeration, reaching a small agglomerate size at steady-state. The addition of copper did not affect agglomeration at pH 4. However, an increase in the agglomeration rates at pH 7.5 and 10 was observed with copper in the solutions, following a diffusion-limited mechanism.

Future experiments investigating the effects of additives on agglomeration rate are underway. The additives to be investigated include glycine, a complexing agent, hydrogen peroxide, an oxidizer used to etch the copper surface, benzotriazole, a corrosion inhibitor; and sodium-dodecyl-sulfate, an anionic surfactant. These additives have been studied previously in CMP experiments, as well as their effects on particle size distribution and copper surface hardness [4, 11]. Ultimately, the effects of particle size and agglomeration will be incorporated in the modeling of CMP.

Summary

A new tribo-chemical copper CMP model is based on the physical mechanism responsible for the synergism of mechanical and chemical effects during CMP. 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. The slurry chemistry affects the effective aggomerate size and rate of agglomeration.

Acknowledgment

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