Effect of Linear Aliphatic Polyamines on Copper Removal Rate in Chemical Mechanical Planarization (CMP)

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The role of homologous linear aliphatic polyamines as additives in Cu CMP slurries was investigated. We show that, in addition to forming stable complexes with copper ions in solution, the polyamines also interact with the copper metal preventing its corrosion. The latter effect increases with the polyamine chain length making the superior members of the homologues series effective passivating agents. A mechanism that explains the trend in the anticorrosion activity of polyamines is proposed.

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In-depth investigation of Cu-CMP has gained recently significant impetus in response to increasingly sophisticated applications. From the chemistry viewpoint, the removal of copper is the result of two consecutive processes: the oxidation of the metal and the complexation of copper ions to facilitate their transport in the liquid phase. Hydrogen peroxyde (H₂O₂) is the oxidant most widely used to ‘extract’ electrons from copper. The resulting ions easily hydrolyze at neutral and alkaline pH forming insoluble oxide films that hinder the oxidation. The role of complexing agents is to dissolve the oxides and ensure the access of H₂O₂ molecules to the metal. In their presence, the oxidation can continue indefinitely but its rate is often uncontrollable. The corrosion inhibitors (passivating agents) added to the slurry allow the ‘fine-tuning’ of Cu dissolution. The copper passivation can be caused by an adherent insoluble film on the copper surface or the chemisorption of species capable of preventing the reaction with the oxidizer. The corrosion inhibition provided by benzo triazole (BTA) is an example of the first mechanism. It is widely accepted that its effectiveness is due to a strongly attached insoluble multi-molecular layer on the copper surface, the precise structure of which is still being debated. In the case of the chemisorption mechanism, the extent of the stability gained by copper depends on the strength of the metal-ligand interactions as well as on how the ligand molecule is attached to the surface (conformational factor). Starting from the hypothesis that in the case of linear aliphatic polyamines the latter aspect varies widely, we initiated a systematic investigation of their passivating action in the corrosion of copper. In doing so, we fill a gap in Cu-CMP research as the study of linear aliphatic polyamines was limited until now to the first member of the series (ethylenediamine, EDA) and only in its role as complexing agent.

Experimental

The aqueous polishing slurries were freshly prepared by dissolving ethylenediamine (EDA), diethylentriamene (DETA), triethylenetramine (TETA), tetraethylenepentamine (TEPA) and pentaethylenehexamine (PEHA) in deionized water followed by the addition (if needed) of H₂O₂. In all cases the pH was adjusted at 9.0 ± 0.1.

Dynamic polishing experiments were carried out for 1 min on an Allied benchtop unit using an IC 1000 polyurathane pad under a down force of 58 Lbf. The platen and carrier rotation speed were 200 and 150 rpm respectively. The slurry flow rate was 120 ml/min. The polished substrates were 4” Cu disks (99.99%) and Cu blanket wafers. The static etch rate (SER) experiments were performed in thermally regulated vessels with 1” Cu disks (99.99%). Cold-SER was tested at 20°C for 5 min and Hot-SER at 50°C for 10 min. Electrochemical polarization curves were generated with a CHI 400B three-electrode work station (Cu working electrode, Pt counter-electrode, and saturated calomel reference electrode) using abrasive-free aqueous formulations.

In the experiments with copper powders, 5,000 g (+/- 1 mg) of ~1.5 μm crystalline uniform copper particles (BET surface 0.67 m²/g) were first mixed in dilute HNO₃ (pH 2.0) for 15 minutes and then rinsed with ethanol. The settled particles were re-suspended in ethanol and a 2 wt% aqueous polyamine solution (with and without H₂O₂) was added. After 15 minutes of stirring, the polyamine treated particles were separated by centrifugation, rinsed twice with ethanol, and dried in vacuum at 60°C. The dry samples were accurately weighed again (+/-1 mg precision) and submitted for nitrogen analysis via LECO combustion method.

Results

Figure 1 shows the effect of aliphatic linear polyamines on the polishing rate of copper discs at two H₂O₂ concentrations in the absence of abrasive particle. In both cases the Cu MRR decreases gradually with the increasing polyamine chain length. The high removal rate recorded in the case of short polyamines (EDA and DETA) drops sharply with the insertion of the 4th amine group (TETA). The addition of the fifth and sixth ethyleneamine fragments in TEPA and respectively PEHA caused a gradual but less pronounced decrease. The same slurry composition was used to compare the effect of polyamines in Cu blanket wafer polishing, Cold-SER, and Hot-SER. The decreasing trend in the Cu MRR with chain length was observed in all three cases although the magnitude of the drop varied (Figure 2). The decrease was less pronounced in the presence of abrasives due to an effective disruption of the strongly passivating films formed by longer polyamines. The SER measurements, which better reflect the true ligand-copper interactions, show that the bidentate EDA interacts rather weakly with the copper. The chemisorption becomes markedly stronger with the insertion of the third amine group in the chain resulting in a significant drop in MRR. With the addition of subsequent amine groups the passivating effect strengthens only slightly.

The electrochemical polarization curves, corrosion potentials (Ecorr), and MRR values obtained in the presence of polyamines are shown in Figure 3. The data for glycine and BTA based slurries generated at pH 5.0 are included for comparison. With the increasing chain length, the Ecorr values (Figure 3, upper) shift toward more positive potentials following the same trend as the material removal rates (Figure 3 lower) and static etch rates (Figure 2). Using a much larger exposed surface (30,000 cm²) for 5 g powder vs. ~5 cm² for the 1” Cu disks), the copper particles shown in Figure 4 (upper) provide more accurate material removal measurements and the ability to quantify the amount of chemisorbed ligand.

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Figure 1. The change in material removal rate as a function of H2O2 concentration for copper discs when using slurries containing 0.25 wt% (upper) and 0.50 wt% polyamine (lower) at pH = 9.0 and in absence of abrasive particles.

Figure 2. Cu-MRR data for blanket wafer polishing, hot static etch, and cold static etch rates for slurries adjusted at pH 9.0 and containing 0.25% chelating agent, 1 wt% H2O2, and 1 wt% silica (in the case of blanket wafer polishing only).

Figure 3. (Upper) The electrochemical polarization curves for glycine (1), EDA (2), DETA (3), TETA (4), TEPA (5), PEHA (6), and BTA (7) generated with a Cu-CMP slurry containing 0.25 wt% polyamine and 1 wt% H2O2. (Lower) The plot of MRR for the same slurries.

The plot in Figure 4 (lower) represents the weight of copper removed after subjecting the particles to the action of hydrogen peroxide in presence of polyamines. The descendent trend in the removal rate observed in the polishing and etching experiments holds here as well, indicating that the passivation of Cu surface increases with the number of amino groups in the molecule.

Discussion

Compounds containing amino groups interact with both copper ions and metallic copper fulfilling equally well the complexation and passivation functions in Cu-CMP. In the case of complexation, the lone electron pairs from the nitrogen atom are donated to the empty orbitals of Cu²⁺ ions. Molecules with multiple amino groups, may bind to more than one location in the inner sphere of coordination forming complexes of increased stability due to the ‘chelate effect’. In both scenarios the stability of the complex is determined by the coordination geometry in solution where there are no spatial or mobility restrictions for the molecule. In contrast, the passivation effect relies on the chemisorption of the amines and the ligand-metal bonds are spatially ‘confined’ to the surface of the solid. The interactions involve the same nitrogen lone electron pairs and are ‘governed’ by the principles of molecular orbital theory. In this view, atomic orbitals merge in the solid to form molecular orbitals that extend over all atoms. Being only partially filled with the valence electrons from the contributing atoms, these ‘energy bands’ can receive electrons from chemisorbed species. Since all superficial Cu⁰ atoms can in principle interact with the ligands, the metal surface possesses a higher ‘coordination
capacity’ than single ions in solution. This implies that the strength of surface attachment (and passivating effect) in the case of homologous linear aliphatic polyamines should progressively increase with the number of amino groups in their molecule. The results of this research support this hypothesis.

The data in Figure 1 clearly show that for a broad range of polyamine and oxidant concentration the Cu MRR decreases with the chain length. The drastic difference between the two short polyamines and the rest of the series’ members suggests that with the insertion of the 4th amino group the balance between the complexation and the passivating action of the molecules is tilted in favor of the latter. The descending trend in the copper removal rate holds for cold and hot static etch experiments as well (Figure 3).

Electrochemical methods are the most relevant tools for assessing the strength of ligand-copper interactions. The polarization curves in Figure 4 and the values of the associated corrosion potentials reinforce the trend observed in the polishing and etching experiments. The fact that a more positive external potential is required to extract electrons from copper atoms as the chain length increases indicates that the polyamine-Cu\(^{0}\) interaction becomes stronger with each additional anchoring amino groups inserted in the molecule. The alternative explanation that the trend is the result of a more complete surface coverage in the case of longer polyamines was dispelled by the results of the experiments with copper particles. The sensitive LECO combustion analysis revealed that the amount of elemental nitrogen retained on the surface attachment (and passivating effect) in the case of longer polyamines was dispelled by the results of the polishing and etching experiments. The sensitive LECO combustion analysis revealed that the amount of elemental nitrogen retained on the surface is not affected by the polyamine chain length and the trend in the passivation activity is the result of the cumulative action of the amino groups in the molecule.

The practical implications of this study are noteworthy. The fact that the corrosion of copper can be controlled by simply changing the molecular weight of the aliphatic polyamine provides an effective way to tailor the polishing rate of copper with only minor changes of slurry’s chemical composition. The shortest polyamine (EDA) has complexing properties comparable or exceeding those of glycine while the longest one (PEHA) is a very effective passivating agent. The corrosion inhibiting activities of the rest of polyamines are spread in this range permitting the tuning of copper dissolution with beneficial effects on the outcome of Cu-CMP. In more general terms, this study provides a blueprint for potential investigations of other homologous series of compounds containing different functional groups.

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