Chemical Mechanism of Suppression of Copper Electrodeposition by Polyethylene Glycol

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Polyethylene glycol (PEG) is an important additive to electroplating baths used in the damascene process for the fabrication of copper interconnects on semiconductor wafers. When used in combination with chloride ions, PEG promotes filling of submicron cavities by suppressing deposition on surfaces outside the cavities (1-3). Suppression is considered to be due to an adsorbed polymer layer, and requires a polymer molecular weight of at least ~ 1000 g/mol. In earlier papers, Yokoi and Reid found a direct relationship between the deposition rate in the presence of PEG and the open circuit potential measured after plating (E_R) (4,5). This suggests that E_R reflects the chemical state of reactive copper ions within a surface polymer film. Here, these measurements were corroborated and then interpreted in terms of a proposed mechanism of copper deposition in the presence of PEG.

Experimental measurements of the rest potential were carried out using a Cu rotating disk electrode (RDE) in a bath of 0.4 M $CuSO_4$, 0.5 M H_2SO_4, 0.02 g/liter PEG (20,000 g/mol) and 2 mM HCl. E_R measurements in oxygen-saturated solutions were quantitatively consistent with those of Yokoi. Cathodic values of E_R were stable for tens of seconds after deposition, before increasing over 10-12 min to values close to the open circuit potential in PEG-free solution. E_R was independent of disk rotation speed, but was significantly attenuated in deaerated solutions. In the latter case, E_R was determined by the concentration of solution-phase Cu^+ ions, which in aerated solution were consumed by reaction with dissolved oxygen.

In the proposed reaction pathway, aqueous cupric ions are first cathodically reduced to form a Cu^+ complex with adsorbed Cl^- ions and ether oxygen atoms of PEG, which is located at the interface between a surface polymer film and the metal. The cuprous complex is then further reduced to copper metal. The complex was identified in an earlier Raman spectroscopy investigation (6). Cu^{+2} reduction is the rate determining step.

The mechanism was applied to quantitatively explain the rest potential measurements of Yokoi et al. (4). They had found simple relationships of E_R with deposition potential (E) in a given plating bath, and with deposition current density (i) as the PEG molecular weight and concentration were varied at constant potential. Straight-line slopes characterized the dependences of E_R on both E and log i. According to the proposed mechanism, E_R is determined by the equilibrium potential of the kinetically facile Cu/Cu^+ reaction, a function of the concentrations of Cu^+-PEG complexes and free ether oxygen ligands. The former concentration is determined by balancing rates of Cu^+ complex formation and consumption during deposition. The oxygen ligand concentration is dictated by the equilibrium for absorption of Cu^{+2} ions into the polymer at open circuit. The consumption of ligands by Cu^{+2} absorption accounts for the relative stability of the Cu^+ complex concentration on open circuit, and hence that of E_R. The Cu^{+2}- O coordination number in PEG was taken to be four, as suggested earlier by Stoichev (7). The mechanism successfully accounted for the observed straight-line slopes of E_R vs. E and E_R vs. log i.

The consistency of the mechanism with the detailed E_R measurements of Yokoi is evidence in its favor. Therefore, the present results support the concept that deposition is mediated by a PEG film acting as a polymer electrolyte, with Cu^+ ions coordinated with the polymer acting as intermediates. The deposition rate is proportional to the number of sites available for Cu^+ complex formation. The number of these sites decreases as the molecular weight and solution-phase concentration of the polymer are increased, possibly because these factors promote PEG film conformations which hinder exchange of metal ions with the solution.

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