REMOVAL OF DISSOLVED COPPER FROM CMP WASTE WATER BY DIRECT ELECTROREDUCTION

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Copper CMP waste streams contain water from the spent slurry as well as from post-CMP clean waste. The dissolved copper level in these wastes is typically below Resin ion exchange followed by electro 20 ppm. deposition is a method that is currently favored by many fabrication plants. Direct electro deposition of copper from the wastewater would eliminate the use of ion exchange but the difficulty lies in removing such low levels of copper using conventional electrodes on which other cathodic reactions may compete with copper deposition. One approach to remove low levels of copper with higher current efficiency is to use electrodes that do not allow water decomposition over a wide potential range. Examples of such electrodes are reticulated vitreous carbon (RVC), highly porous foam of glassy carbon, and boron doped diamond film electrode (BDD). Recently, there have been many reports on the use of BDD electrodes in the general area of wastewater treatment [1, 2].

The feasibility of using glassy carbon and boron doped diamond electrodes for the electro deposition of copper from dilute solutions has been investigated using the technique of cyclic voltammetry (CV). An acidic sulfate system, a citric acid system and a hydroxylamine based system at different pH values have been used for the investigations. Figure 1 displays cyclic voltammograms obtained on glassy carbon and BDD electrodes in a hydroxylamine system at pH 5.8. In the absence of cupric ions, no significant electrochemical reactions take place on the BDD electrode in the potential range of +0.8 V to -1.1 V. Under similar conditions, the glassy carbon electrode provides a potential range of only 0.2 V to -0.6 V. In the presence of 20 ppm, the potential range where there is minimal current is reduced on both electrodes. As may be evident by the relative current densities in the potential range -0.4 V to -0.6 V, copper reduction is accompanied by other reduction reactions on glassy carbon as well as on BDD. However, the extent of competitive reactions is higher on glassy carbon than on BDD. It thus appears that BDD can be used to remove dissolved copper at a higher current efficiency.

The removal of copper from a simulated copper CMP waste stream has been investigated using a continuous flow through cell with BDD electrodes separated by a (NAFION) membrane. The solution is first pumped through the anode chamber where organic additives and corrosion inhibitors present in CMP wastewater are oxidized. The treated solution is pumped through the cathode chamber where copper is removed. The efficiency of this flow through cell has been investigated as a function of applied potential and current density.

Acknowledgment:

Financial support by the NSF-SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing at The University of Arizona is gratefully acknowledged.

References:

- A. Perret, W. Haenni, N. Skinner, X. M. Tang, D. Gandhini, C. Comninellis, B. Correa, G. Foti, *Diamond and related materials*, 8, 820 (1999).
- 2. G. Foti, D. Ghandhini, C. Comninellis, A. Perret, W. Haenni, *Electrochemical and solid State letters*, 2 (5), 228 (1999).



Figure 1: CV scans of hydroxylamine solution in the presence and absence of copper on BDD and glassy carbon electrodes.