

Environmentally benign Chemical Mechanical Planarization slurries aided by amino acids

Hoang Tran Thi Thuy, Juster Gichovi, Ian Morrow, Elizabeth J. Podlaha, and Jihoon Seo
Department of Chemical and Biomolecular Engineering, Clarkson University, Potsdam, New York, United States of America
jseo@clarkson.edu

Abstract

Aliphatic amino acids were examined as potential replacements for toxic and problematic azoles in chemical mechanical planarization (CMP) slurries. A representative polishing slurry with 35 nm colloidal silica abrasives, 1 wt % hydrogen peroxide (H_2O_2) as an oxidizer, and 0.5wt% arginine (Arg) as a complexing agent, was used to compare two amino acids (L-glutamic acid (Glu), and L-leucine (Leu)) as potential corrosion inhibitors at pH 8. The electrochemical behavior of polishing slurries aided by the amino acids was characterized using voltammetry on a rotating disk electrode to determine corrosion parameters. Leu-based silica slurry controlled the corrosion potential difference and galvanic current for the Cu-Co couple effectively compared to the Glu. The removal rates (RRs) of both Cu and Co decreased in presence of Glu and Leu with Cu being comparatively lower in case of Leu. Plus, slurries consisting of Glu and Leu showed comparable removal selectivity for Cu and Co. The degradation of the slurry compositions was also monitored using electrochemical oxidation to assess the ease of degradation of the spent slurry, which indicated that Leu is more easily decomposed than benzotriazole during the electrochemical oxidation.

Keywords: Copper CMP, Slurry, Sustainability, Green corrosion inhibitors.

Introduction

Copper (Cu) has been widely used as interconnect metal in the back end of line (BEOL) due to its superior conductivity and electromigration resistance properties. For advanced technology semiconductor nodes at 7 nm and smaller, Co liner has been integrated in Cu interconnects to prevent electromigration and pinch-off failure.^{1,2} In interconnect technology, Cu and Co metals are placed in direct contact creating the potential for enhanced corrosion of the Co by the more noble Cu.

Azole derivatives such as benzotriazole (BTA) and 1,2,4-triazole have been extensively investigated as corrosion inhibitors for both Cu and Co films during polishing, and it has been found to be beneficial in reducing the galvanic corrosion current density between Cu and Co.² However, azole compounds are not only poorly biodegradable under wastewater treatment conditions but they also lead to surface contamination after polishing. The effluent wastewater from a semiconductor fabrication plant may contain high concentrations of azoles, etc., and is problematic for wastewater treatment processes.³⁻⁶ Hence, there has been increasing demand to develop Cu CMP slurries containing corrosion inhibitors that can effectively passivate metal surfaces and exhibit sufficiently high biodegradation rates during the wastewater treatment process.

The main objective of this study is to identify environmentally friendly and stable substitutes for azole compounds as corrosion inhibitors in Cu CMP slurries by understanding the interaction of the inhibitors with Cu and Co surfaces. Determining the degradability of the corrosion inhibitor in the waste CMP slurry in an electrochemical oxidation environment is also studied here. Amino acids are chosen as corrosion inhibitors because (1) they are non-toxic to living organisms and the environment, (2) they have functional groups containing heteroatoms, and (3) the ability to cover large and uniform surfaces of Cu and Co films. Amino acids sometimes act as mixed-type inhibitors depending on what the cathodic reaction is.⁷ Corrosion inhibitors that act through adsorption can do so through electron-donating functional groups characterized by their pK_a values, where molecules with amine groups (NH_2) perform better than the carboxylic acid groups ($COOH$) as the function of pH (e.g. glutamic acid (negative charge ion) and leucine (zwitterion) at pH 8) [Figure 1].⁸

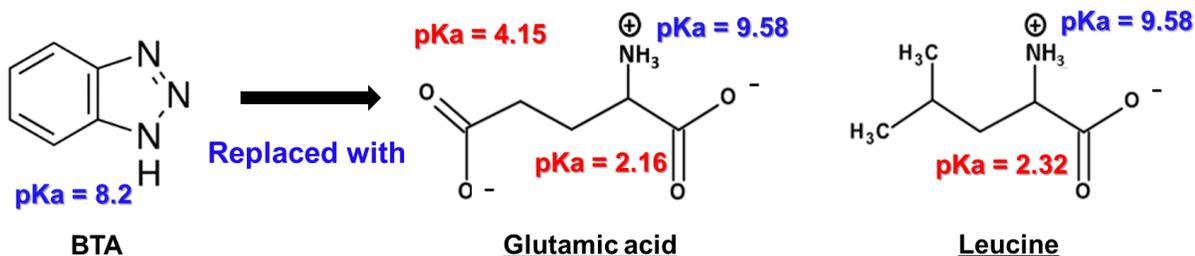


Figure 1. Amino acids glutamic acid (negative charge ion) and leucine (zwitterion) were considered potential replacements for BTA as corrosion inhibitors in Cu CMP slurries at pH 8.

Experimental Methods

Materials: Electrochemically plated (ECP) 200 nm Cu and physical vapor deposited (PVD) 200 nm Co films on 200 mm diameter Si wafers were purchased from DK Nanotechnology. These wafers were diced into 4x4 cm² coupons. Aqueous colloidal silica dispersions (DVSTS027, mean particle size ~35 nm) were obtained from Nalco Water-Ecolab. Amino acids were reagent grades purchased from Sigma-Aldrich. Hydrogen peroxide (30 wt% H₂O₂) was obtained from VWR International. Colloidal silica slurries containing 1 wt% silica, 1 wt% H₂O₂, 0.5 wt% arginine (Arg), 10mM variable concentration of amino acids (L-glutamic acid-Glu, L-leucine-Leu) or BTA were prepared and adjusted to pH 8 using HNO₃ and KOH.

Electrochemical characterization: Corrosion was assessed using linear sweep voltammetry. A three-electrode cell was used containing a Cu or Co rotating disk ($A_{Cu} = 0.094 \text{ cm}^2$, $A_{Co} = 0.2 \text{ cm}^2$ surface area) working electrode, at 900 rpm, a Pt coil counter electrode, and a saturated calomel electrode (SCE). The potentiodynamic polarization of Cu and Co was carried out using an electrochemical workstation (VersaSTAT4, Princeton Applied Research) with a scan rate of 5 mV/s, a potential range from 0.5 V to 0.8 V versus SCE and the polarization curves were corrected for the ohmic drop with impedance spectroscopy.

Polishing: The coupons were polished for 1 min on a bench-top polisher (CP-4, Bruker) at 93/87 rpm platen/carrier speed, 2 psi down-pressure, and a slurry flow rate of 120 ml/min. The polishing pad (Ikonik TM 2060H, Dupont) was used and conditioned ex-situ using a Saesol AM02B80C1 diamond conditioner. Film removal rates were determined from the change in the sheet resistance measured using a four-point probe (ResMap 273, CDE) before and after polishing. The data were obtained from two different wafers, and the average numbers were reported here.

Electrochemical oxidation: Chronoamperometry was used to determine the degradability of the slurry components in the electrochemical oxidation process at a constant potential of 2 V vs SCE for 2 hr by using 900 rpm rotating Pt disk with $A_{Pt} = 0.2 \text{ cm}^2$ surface area as working electrode; electrolytes contained 0.1 M KCl and amino acid. The high-range COD test (816 kits, Hach) measured the amount of dichromate (oxidant) consumed in the breakdown of organic compounds in slurries after being treated by electrochemical oxidation.

Results and Discussion

The flowchart to design the environmentally benign amino acids-based silica slurries for Cu-Co CMP processes was shown in Figure 2. Our research was conducted in five phases: (1) selection of green corrosion inhibitors (in our case, amino acids); (2) the polarization behavior of Co and Cu in a representative CMP electrolyte containing 10 mM of glutamic acid or leucine, (3) film removal rates of Cu and Co films, (4) analysis of degradability of the waste slurry in the electrochemical oxidation system, (5) proposed degradation pathway of amino acids.

Figure 2a shows the polarization curves of Cu and Co films in 10 mM of Glu and Leu, all containing 1wt% H₂O₂ as an oxidizer and 0.5 wt% Arg as a complexing agent at pH 8. A sample containing 10 mM BTA was considered as a control sample. The corrosion potentials (E_{corr}), current densities (I_{corr}), and the potential difference ($|\Delta E_{corr}|$) of Cu and Co films and their galvanic current densities (I_{gc}) were obtained from Tafel analysis of the data. The ΔE_{corr} between Cu and Co was 20 mV in the absence of an inhibitor (black line in Figure 2a) while the galvanic current of the Cu-Co couple was a high 134 $\mu\text{A}/\text{cm}^2$. Not surprisingly,

the addition of BTA was very effective in passivating Cu corrosion and reducing galvanic current densities to $7.2 \mu\text{A}/\text{cm}^2$ (blue line in Figure 2a). However, the potential difference of the Cu-Co couple increased to a large 25 mV, which caused galvanic corrosion of the Cu-Co films during polishing. Glu was not effective in both $|\Delta E_{\text{corr}}|$ and I_{gc} of Cu-Co films, the I_{gc} and $|\Delta E_{\text{corr}}|$ value was found to be $80.5 \mu\text{A}/\text{cm}^2$ and 13 mV (red line in Figure 2a). Leu was able to lower $|\Delta E_{\text{corr}}|$ of the Cu-Co couple to 5 mV (green line in Figure 2a), but I_{gc} value was still high ($\sim 15.2 \mu\text{A}/\text{cm}^2$), which needed to be further reduced.

Removal rates of Cu and Co films with a slurry containing 1wt% silica abrasive, 1wt% H_2O_2 , and 0.5 wt% Arg as a complexing agent were ~ 390 and ~ 510 A/min (Figure 2b), respectively. BTA led to very low RRs of Cu and Co films at pH 8, probably due to the formation of a dense passivation layer on both the films. The addition of Leu and Glu reduced both the corrosion parameters and RRs of both Cu and Co films, with Cu being comparatively low in presence of Leu. The slurries consisting of Leu, Glu showed comparable removal rates of Cu-Co.

The degradation of the slurry compositions was monitored using an electrochemically advanced oxidation process (EAOP) to assess the ease of degradation of the spent slurry. (Figure 2c) represents the time-dependent current density profile of BTA (black curve) and Leu (green curve). There was minimal change observed in the time-dependent current density profile which suggests that BTA is more stable and is more difficult to degrade in the EAOP process. However, in the case of Leu, under an applied current density of 2 hr, the current density decreased, which indicated changes in the electrolyte. In order to determine if Leu was decomposed during the electrochemical oxidation, the chemical oxygen demand (COD) was examined and a clear color change confirmed oxidation of Leu but not BTA (Figure 2d).

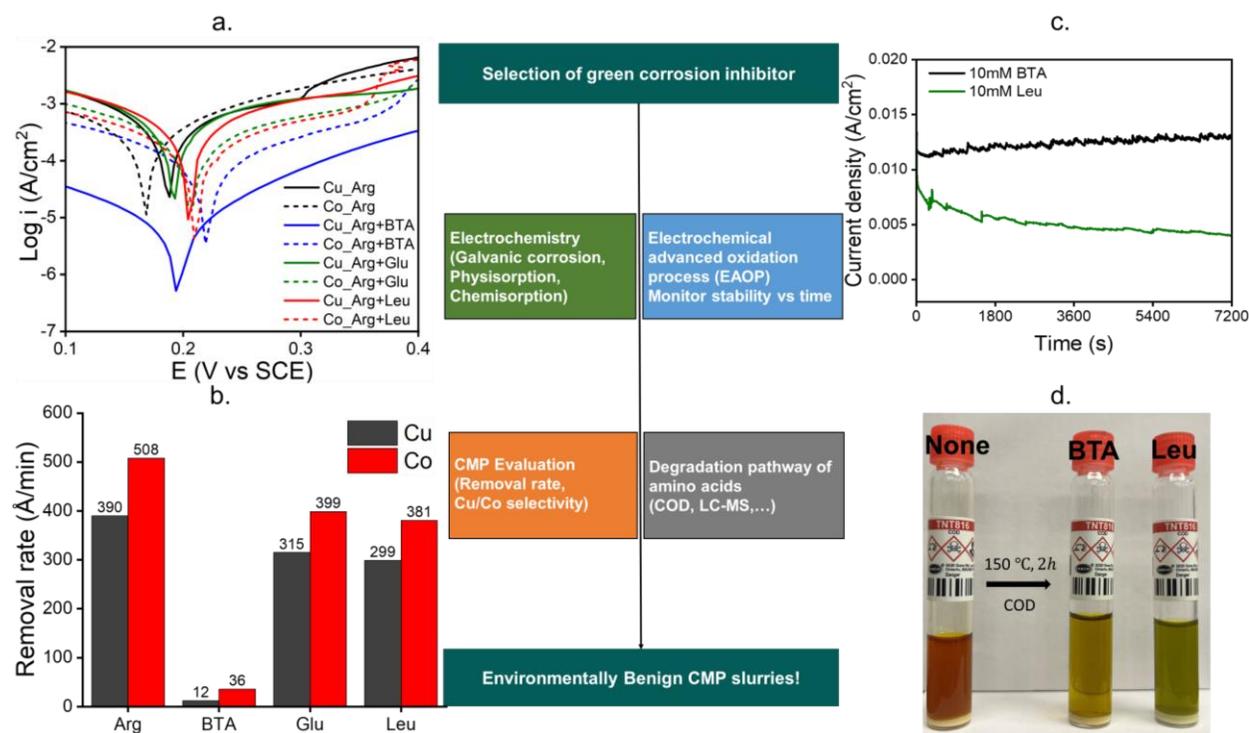


Figure 2. (a) Potentiodynamic curves of Cu (solid lines) and Co (dash line), (b) Cu and Co RRs with 1wt% colloidal silica + 1wt% H_2O_2 + 0.5wt% arginine + 10mM different corrosion inhibitors (glutamic acid, leucine, BTA) at pH 8. (c) the influence of the applied current density on the time evolution for 10mM BTA (black curve) and 10mM Leu (green curve) containing 0.1M KCl at pH 8 before and after EAOP, (d) color change from brown-yellowish (none sample) to yellowish (BTA) and greenish (Leu) treated by COD 816 kits.

Table. Corrosion potentials, potential differences, and galvanic corrosions of Cu-Co films dipped measured in 10mM aqueous solution of three different corrosion inhibitors in presence of 0.5wt% Arg + 1wt% H₂O₂ at pH 8.

Inhibitors	No inhibitor		BTA		Glu		Leu	
	Cu	Co	Cu	Co	Cu	Co	Cu	Co
E _{corr} (mV)	187	167	194	219	193	206	204	209
ΔE (mV)	20		25		13		5	
I _{gc} (μA cm ⁻²)	134		7.2		80.5		15.2	

Conclusions

An evaluation of Glu and Leu to replace BTA in slurries for Cu/Co CMP processes showed that at pH 8 Cu-Co had comparable removal rates with a low ΔE_{corr} for the Cu-Co couple and low galvanic currents. This study also revealed that the slurry consisting of Leu was more easily degradable than the slurry containing BTA by the electrochemical advanced oxidation treatment. In the future, our study will focus on understanding inhibition mechanisms, further optimization of slurry that can further control the galvanic corrosion between Cu and Co in the alkaline medium, and figuring out the degradation pathway of amino acids.

Acknowledgments

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References

1. Krishnan, M.; Lofaro, M., *Advances in Chemical Mechanical Planarization (CMP)*, Elsevier: 2016; pp 27-46.
2. Seo, J.; Vegi, S. S. R. K. H.; Babu, S.V. *ECS Journal of Solid State Science and Technology* 2019, 8 (8), P379–P387.
3. B.C. Peethala, H. P. Amanapu, U. Lagudu, and S.V. Babu, *J. Electrochem. Soc.*, 159(6), H582-H588, 2012.
4. Seo, J., A review on chemical and mechanical phenomena at the wafer interface during chemical mechanical planarization. *Journal of Materials Research* 2021, 1-23.
5. D.E. Speed, Chapter 11, *Advances in chemical mechanical planarization (CMP) 2nd edition*, Babu, S. V., Ed. 2021.
6. G. Li et al. / *Chemosphere* 241 (2020) 1249932.
7. Hamadi, L.; Mansouri, S.; Oulmi, K.; Kareche, A., *Egyptian journal of petroleum* **2018**, 27 (4), 1157-1165.
8. S. Maloy, in *Brenner's Encyclopedia of Genetics (Second Edition)*, 2013.