



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI  
SHORT ABSTRACT OF THESIS

Name of the Student : Jenasree Hazarika  
Roll Number : 166107118  
Programme of Study : Ph.D.  
Thesis Title : **Formulation of Slurry for the Process of Interconnect Metal (Cu)-Barrier Metal (Ru/Co) Chemical Mechanical Planarization**  
Name of Thesis Supervisor(s) : Dr. R. Prasanna Venkatesh  
Thesis Submitted to the Department/ Center : Chemical Engineering Department  
Date of completion of Thesis Viva-Voce Exam : 10<sup>th</sup>  
March  
2023  
Key words for description of Thesis Work :

---

**SHORT ABSTRACT**

Failure of Integrated Circuits (IC) due to maintenance of diffusion barrier property is a major concern in the semiconductor industry. Hence, cobalt (Co) and ruthenium (Ru) are introduced as new promising barrier metals. After deposition of the metals, better surface uniformity is required for further level metallization for which Chemical Mechanical Planarization (CMP) is opted. The main rationale behind using CMP process is the removal of interconnect and barrier metal without excessive thinning. This demands a slurry which gives a removal selectivity of 1:1. In the present work, slurries giving desired removal selectivity for Ru/Cu and Co/Cu CMP are proposed.

In the initial part of the study, an optimized formulation of slurry for CMP of Copper (Cu) as interconnect material and Ruthenium (Ru) as barrier line with removal selectivity is investigated. Thermogravimetric analysis (TGA), effect of abrasives concentrations, pH and solution temperature on etch rate are also examined. The results revealed that a Ru-Cu selectivity of  $\sim 1.003: 1$  is obtained using 2 wt. % fumed silica, 0.2 M potassium iodate (KIO<sub>3</sub>) and 5 mM 1,2,3 Benzotriazole (BTA) based slurry.

CMP of interconnect metal copper and barrier metal cobalt using NaOCl based slurry is investigated as the second objective in this study. The slurry consists of 2 wt. % silica, 0.5 wt. % NaOCl and 5 mM BTA as inhibitor. It is seen that the formulated slurry gives a combination of low etch rates and comparatively fair removal rates along with selectivity of  $\sim 1:1.006$  at pH 9, which are desired to be used in semiconductor industry.

The third objective focuses on the reduction of galvanic corrosion associated with Co and Cu along with investigation of Co/Cu removal rate (RR) selectivity by using oxalic acid (weak acid) as the complexing agent and imidazole as an inhibitor in hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and fumed silica-based slurry. The

corrosion potential difference ( $\text{CuEcorr} - \text{CoEcorr}$ ) is reduced to 12 mV by using 0.1 wt.%  $\text{H}_2\text{O}_2$  + 0.02 M oxalic acid + 5 ppm imidazole solution at pH 9. Meanwhile, a removal rate of  $\sim 147$  nm/min for Co and  $\sim 140$  nm/min for Cu was achieved using the same composition in a fumed silica slurry which resulted in Co/Cu selectivity ratio of 1.05:1, which is acceptable for cobalt barrier and copper interconnect CMP.

In the fourth part of the study, the anodic dissolution of Co in  $\text{H}_2\text{O}_2$  solution is investigated both in the presence and absence of complexing agent, oxalic acid by using various techniques including electrochemical impedance spectroscopy (EIS). Anodic polarization measurements of both the solutions show that active dissolution occurs in the potential range of 0 to 600 mV w.r.t open circuit potential (OCP) and the addition of oxalic acid enhances the dissolution rate significantly. EIS measurements at OCP confirm the same trend while the kinetics of dissolution is investigated by performing EIS measurements at various overpotentials under anodic conditions. EIS spectra exhibit two loops; capacitance (higher frequency) followed by inductance (lower frequency) at all the overpotentials and it is modelled by a multi- step mechanism with 3 intermediate adsorbed species. The dissolution via both chemical and electrochemical steps is considered in the proposed model. From the parameters obtained, dominance of Co (III) compound formation is observed for both the systems. The oxides formed on the Co surface on addition of oxalic acid to  $\text{H}_2\text{O}_2$  are higher than using only  $\text{H}_2\text{O}_2$  thus properly justifying the role of a complexing agent in a CMP slurry. Products formed on exposure of Co to  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}_2$ +oxalic acid solution at pH 9 are analyzed using Contact angle analysis and FESEM and XPS analysis. The results confirm the formation and dominance of Co-oxalate complexes for  $\text{H}_2\text{O}_2$ +oxalic acid system.

We believe that these results obtained can significantly improve the polishing efficiency and providing desired selectivity without excessive thinning of the interconnect barrier interface and thereby reducing failure in IC production.