Effect of corrosion inhibitors on chemical mechanical planarization of molybdenum

Chan-Hee Lee[1], Heon-Yul Ryu[1], Lieve Teugels[2], Katia Devriendt[2], Herbert Struyf[2], Tae-Gon Kim[3], and Jin-Goo Park[1]

[1] Department of Materials Science and Chemical Engineering, Hanyang University ERICA, Ansan, 15588, Republic of Korea

[2]Imec, Kapeldreef 75, 3001 Leuven, Belgium

[3] Department of Smart Convergence Engineering, Hanyang University, Ansan 15588, Republic of Korea

INTRODUCTION

The effect of H_2O_2 and corrosion inhibitor on the Static etch rate (SER) and removal rate (RR) of molybdenum (Mo) was investigated. SER and chemical mechanical planarization (CMP) experiments were performed using H_2O_2-based slurries and amino acid groups at pH 7. The Mo surfaces were evaluated in order to maintain high RR and lower SER conditions. Several inhibitors were selected during the study and results showed that during CMP, the RR of Mo surfaces increased by increasing the concentrations of silica particles and H_2O_2. However, the increase in H_2O_2 concentration showed significant effect on the surface roughness than increasing the silica concentration in the slurry. Consequently, lower concentration of H_2O_2 was selected for the optimal surface roughness during the CMP process.

BACKGROUND

As the sizes of integrated circuit (IC) devices continued to shrink below 10 nm, the resistivity of Cu increased to a high level at a narrower interconnect due to an increase in electron scattering of Cu materials and generation of barrier scaling. [1] The new interconnect material to replace Cu should be a material with low resistance and high melting temperature. [2] Table 1 shows the melting temperature and bulk resistivity of certain metals where tungsten (W) has the highest melting temperature which is similar to bulk resistance of molybdenum (Mo), however the mean free path value of Mo and W is 11.2 nm and 5.5 nm, which is used as an indicator of the expected line resistance in small dimensions.[3] Barrierless metallization has another potential advantage of Mo due to its high adhesion energy with low k.

To use Mo in the interconnects requires demarcated polishing conditions during CMP process. which includes the selection of a suitable slurry, to achieve high removal rate and low CMP defects. Generally, metal CMP slurries commonly uses H_2O_2 as an oxidizer to polish metal oxide films that can be easily removed from the surface. [4-9] Currently Cu, Ru and Mo are considered as the better candidates for the application as an interconnect material, whereas as the research on the Mo is an innovative approach therefore the literature on Mo CMP is very limited. Ryu et al., have worked on Mo films during the CMP process where they have mentioned the important role of H_2O_2 as an oxidizing agent for polishing of Mo films. [10] The usage of oxidizers in the metal CMP slurries has a significant role to achieve the desired polishing requirements. Also, among the specific literature on Mo materials, GuangYang et al., found that the amino acids had an inhibition effect on the etching and removal of Mo from the surfaces. In this study, the effect of H_2O_2 and amino acid groups on the polishing of Mo thin films was investigated. [11] Chemical etching and CMP experiments were performed using H_2O_2-based solutions and slurries.

EXPERIMENTAL

A 100 nm Mo film was deposited on the SiO_2 layer by PVD (Physical Vapor Deposition) method. Samples were stored at room temperature and air dried after deposition. The wafer was cut into coupon sizes for SER and CMP experiments. The SER of Mo was evaluated by immersing Mo coupons in a solution containing H_2O_2 for 90 seconds, rinsing with deionized (DI) water, and drying with N_2 gas. All CMP experiments were performed on a Mecapole E460 polisher (Alpsitec CMP, France) with a hard pad Visionpad 5000 (DuPont, USA). For polishing the platen and head speed was 90 and 80 rpm and slurry flow rate was maintained at 150ml/min, respectively, whereas, polishing pressure was 3-5 psi. CMP pad conditioning was performed for 1 min between each sample using diamond discs to avoid any reaction due to the presence of by-products left after CMP as well as for the better pad surface conditions. However, before changing the slurry conditions pad conditioning was performed for 5 mins. 0.1~2.5% H_2O_2 (30 wt.%; KMG Chemicals, USA) and 4~8 wt.% colloidal silica particles (average size 35 nm, PL-3, FUSO, Japan) were used as an oxidizing agent and abrasive particle, respectively. The pH of the solution was adjusted with HNO_3 (69.5 wt.%; KMG Chemicals, USA). SER and RR were calculated by measuring the sheet resistance (Rs) of the Mo film with a four-point probe (OmniMap RS75, KLA-Tencor, US) before and after the experiment. The surface roughness of Mo was analyzed with an atomic force microscope (Dimension Icon, Bruker, US) in an area of 5 × 5 μm^2.

Table 1 Melting temperature and bulk resistivity of metals, for interconnecting material

Element	Melting Temperature (°C)	Bulk Resistivity (μΩ-cm)
Aluminum	660	2.65
Copper	1085	1.68
Cobalt	1495	6.20
Ruthenium	2335	7.80
Molybdenum	2620	5.34
Tungsten	3400	5.28

DISCUSSION

The SER and RR of Mo were evaluated to understand the effect of corrosion inhibitors on the corrosion and abrasive behavior of Mo. Fig. 1 shows the SER and RR of Mo according to various corrosion inhibitors in 2.5 wt% H_2O_2 solutions at pH. The results showed that presence of amino acids decreased the SER and RR of Mo surfaces. Table. 2 shows the comparison of Mo film ratio (RR/SER) for different corrosion inhibitors. At Fig1 and Table2, L-Histidine had a lower SER compared to a higher RR It shows that L-Histidine has the best inhibition role in the group of amino acids. Fig. 2 shows the etching and RR of Mo according to the concentration of L-Histidine in 2.5 wt% H2O2 solutions at pH 7. As the concentration of L-Histidine increased, the RR and SER of Mo decreased.

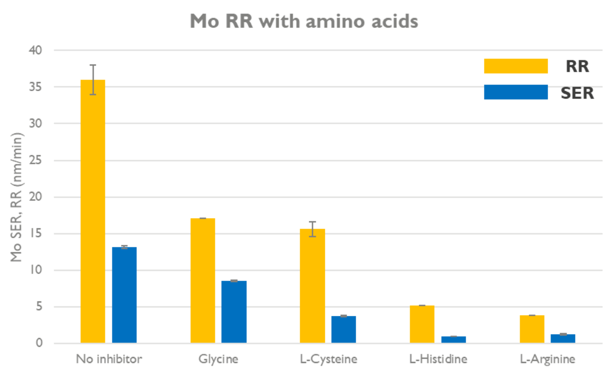

Figure 1 Mo Removal Rate & Static Etch Rate with amino acids

Table 2 Mo film ratio (RR/SER) according to the type of corrosion inhibitor

Inhibitor	Glycine	L-Cysteine	L-Histidine	L-Arginine
Ratio (RR/SER)	2.01	4.22	4.73	3.17

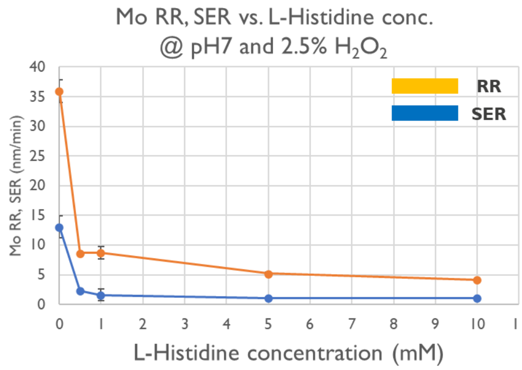

Figure 2 Mo Removal Rate & Static Etch Rate each L-Histidine concentration

The removal rate also decreased due to the addition of L-Histidine. Additional experiments were performed to increase the reduced removal rate to a certain level. Fig. 3 shows the result of increasing the RR by increasing the concentration of H_2O_2 as an oxidizing agent, and silica as an abrasive particle. As the concentration of H_2O_2 and silica increased, RR increased. To confirm the surface of the Mo film according to the increased RR, surface analysis was conducted through AFM. The R_a value of the Mo surface measured during AFM analysis has been showed in Fig. 4, which shows that the roughness value of the Mo surface increases when the concentration of silica and H_2O_2 increases. However, the increase of the R_a value when the H_2O_2 concentration value increased had more effective than the increase of the R_a value when the silica concentration value increased. It can be confirmed that the increase in the H_2O_2 concentration has a more effect on the increase in the surface roughness of Mo after CMP than the increase in the silica concentration during CMP.

Therefore, in this study, 6% Silica, 1wt% H_2O_2, and 5mM L-Histidine showed the most favorable conditions for Mo CMP slurry.

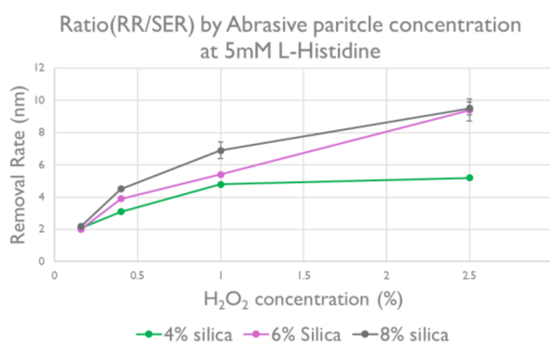

Figure 3 Mo Ratio (RR/SER) results, the effect of H_2O_2 concentration

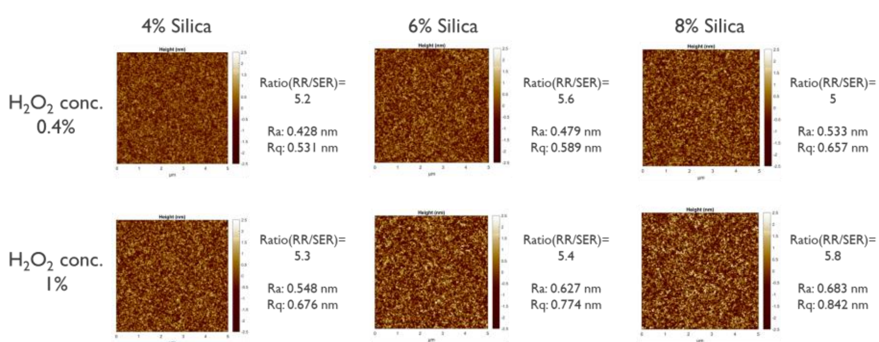

Figure 4 AFM image, Mo surface by silica and H_2O_2 concentration

CONCLUSIONS

In this study, Mo etching and removal rates during CMP process were investigated by adding amino acids-based corrosion inhibitors to slurries containing H_2O_2 as an oxidizer. and proposed a suitable slurry which has been optimized for Mo CMP. L-Histidine was selected from the group of amino acids as a corrosion inhibitor suitable for Mo slurries at pH 7. L-Histidine showed high removal rate as compare to etch rate. In addition, to secure a certain level of removal rate, the concentration of abrasive particles and oxides in the slurry was increased. turned out to be to have a low surface roughness of the Mo surface after CMP. The results suggest that a slurry with a low H_2O_2 concentration is suitable for Mo CMP be specific to the results in the study.

Acknowledgments

This research was supported by the MOTIE (Ministry of Trade, Industry, and Energy) in Korea, under the Fostering Global Talents for Innovative Growth Program (P0008745) supervised by the Korea Institute for Advancement of Technology (KIAT).

Corresponding Author:
Jin-Goo Park.
Tel: +82 31-400-5226
Fax: +82 31-400-4729
E-mail: jgpark@hanyang.ac.kr
Hanyang University ERICA
Ansan, 15588, Republic Korea

References

1. P. Kapur, J. P. McVittie, and K. C. Saraswat, “Technology and reliability constrained future copper interconnects. I. Resistance modeling.” IEEE Trans. Electron Devices, 49, 590 (2002).
2. C. Adelmann, L. G. Wen, A. P. Peter, Y. K. Siew, K. Croes, J. Swerts, M. Popovici, K. Sankaran, G. Pourtois, and S. Van Elshocht, “Alternative metals for advanced interconnects.” IEEE International Interconnect Technology Conference, IEEE, San Jose, CA, 20–23 May 2014 (IEEE, Picastaway, NJ) p. 173 (2014).
3. D. Gall, J. App. Phy., 119, 085101-1-5 (2016).
4. F. B. Kaufman, D. B. Thompson, R. E. Broadie, M. A. Jaso, W. L. Guthrie, D. J. Pearson, and M. B. Small, “Chemical-mechanical polishing for fabricating patterned W metal Features as chip interconnects.” J. Electrochem. Soc., 138, 3460 (1991).
5. Y.-J. Seo and W.-S. Lee, “Effects of different oxidizers on the W-CMP performance.” Materials Science and Engineering: B, 118, 281 (2005).
6. P. Bernard, S. Valette, S. Daveau, J.-C. Abry, P. Tabary, and P. Kapsa, “Nature and removal of the modified layer in Cu CMP with ferric nitrate as oxidizer.” Tribol. Int., 41, 416 (2008).
7. M. Hariharaputhiran, J. Zhang, S. Ramarajan, J. Keleher, Y. Li, and S. Babu, “Hydroxyl radical formation in H2O2-Amino Acid mixtures and chemical mechanical polishing of copper.” J. Electrochem. Soc., 147, 3820 (2000).
8. M. K. Poddar et al., “Nanocatalyst-induced hydroxyl radical ((OH)-O-center dot) slurry for tungsten CMP for next-generation semiconductor processing.” J. Mater. Sci., 55, 3450 (2020).
9. L. Jiang, Y. Y. He, Y. Li, Y. Z. Li, and J. B. Luo, “Synergetic effect of H2O2 and glycine on cobalt CMP in weakly alkaline slurry.” Microelectron. Eng., 122, 82 (2014).
10. Heon-Yul Ryu et al 2021 ECS J. Solid State Sci. Technol. 10 094001
11. G Yang, P He and XP Qu, “Inhibition effect of glycine on molybdenum corrosion during CMP in alkaline H2O2 based abrasive free slurry”. Applied Surface Science. 427, 148-155(2018)