

Chemical-mechanical polishing of copper wafers utilizing an eco-friendly slurry

Le Dang Ha^{a,*}, Nguyen Nhat Minh^a

^a Hanoi University of Industry, 298 Cau Dien, Bac Tu Liem, District, Hanoi, Vietnam

Abstract—Copper (Cu) is extensively utilized in super-large-scale integration circuits, yet its machining presents challenges due to its soft and oxidized characteristics. Chemical mechanical polishing (CMP) is a common method employed to refine Cu wafers; however, it often leaves scratches, corrosion pits, and elevated surface roughness. This study introduces an eco-friendly CMP slurry tailored for Cu wafers, composed of hydrogen peroxide, silica, glycine, and deionized water. Initially, Cu wafers are lapped with silicon carbide abrasives to eliminate deep scratches incurred during traditional slicing. Subsequently, polishing is conducted using the developed slurry. Finally, wafers are cleansed and dried with deionized water and compressed air, respectively. The resulting surface roughness, characterized by the arithmetic average Ra and peak-to-valley (PV) values, is 0.857 and 7.169 nm, respectively, over a scanning area of 70×53 μm². These outcomes are achieved utilizing a slurry formulation comprising 4%, 4%, 1%, and 91% weight percentages of hydrogen peroxide, silica, glycine, and deionized water, respectively. This environmentally friendly CMP approach offers promising prospects for enhancing the surface quality of Cu wafers, addressing prevalent issues encountered during polishing processes.

Keywords: Copper; Chemical mechanical polishing; Surface roughness; Slurry.

Date of Submission: 14-06-2024

Date of acceptance: 27-06-2024

I. INTRODUCTION

Copper is renowned for its versatility and widespread application across various fields, particularly in super-large-scale integration circuits. Given its superior electro-migration resistance and lower electrical resistivity compared to aluminum, copper metallization has emerged as a pivotal material for circuit interconnection, necessitating the attainment of global planarization of copper wafers.

Chemical mechanical polishing (CMP) stands out as an effective technology for achieving this global planarization, leveraging a synergistic blend of chemical reaction and mechanical action. Traditionally, CMP processes utilize polishing slurries comprising a multitude of additives, including oxidants, abrasives, complexing agents, film-forming agents, and pH controllers. However, the inclusion of numerous additives often leads to complex chemical reactions and unpredictable outcomes. Thus, there is a pressing need to streamline slurry formulations by minimizing the number of additives.

In this study, we present the development of a simplified CMP slurry composed of oxidant, abrasive, and complexing agent. While nitric acid (HNO₃) and ferric ion (Fe³⁺) have been commonly employed as oxidants in previous research, concerns regarding metal ion pollution and excessive corrosion prompted the selection of hydrogen peroxide (H₂O₂) as the oxidant in our experiment.

Regarding abrasives, alumina (Al₂O₃), cerium dioxide (CeO₂), and silica sol are frequently utilized in CMP processes. Notably, silica sol exhibits excellent suspension properties and nanoparticle size capabilities, making it an ideal choice for achieving fine surface finishes. Given copper's inherent softness, silica sol was chosen as the abrasive in our slurry formulation to minimize the occurrence of deep scratches.

Furthermore, we employed glycine as the complexing agent due to its robust complexing ability and environmentally friendly characteristics. By carefully selecting these components, our study aims to develop an optimized CMP slurry formulation that ensures efficient planarization of copper wafers while mitigating adverse effects associated with traditional additives.

II. EXPERIMENTAL PROCEDURES

The experiments were conducted on square copper sheets measuring 15×15 mm², with a purity of 99.99% Cu. Three copper sheets were affixed to the periphery of an aluminum alloy circular plate using strong double-sided adhesive. The experimental procedure comprised three main steps: lapping, chemical mechanical polishing (CMP), and measurement. Precision polishers, namely YJ-Y380 (Shengyang Yanjia, China) and ZYP230 (Shengyang Maikē, China), were employed for lapping and polishing, respectively.

Initially, fixed abrasive silicon carbide (SiC) sandpaper with mesh sizes of 1500 and 2000 was utilized for lapping the wafers. Deionized water served as the lapping solution, with lapping parameters set at 5 minutes of lapping time, 1 kPa of lapping pressure, and a rotation speed of 30 rpm on the ZYP230 polisher.

Subsequently, the YJ-Y380 polisher was used for CMP, employing a polishing slurry comprising hydrogen peroxide as an oxidant, silica sol as an abrasive, and glycine as a complexing agent. Citric acid or sodium hydroxide was employed to adjust the pH of the slurry. To assess the individual effects of each slurry component and optimize their concentrations, single-factor optimization experiments were conducted. Following the CMP process, wafers were rinsed with deionized water and dried with compressed air. The polishing parameters were set at 3.5 kPa of polishing pressure, 8 minutes of polishing time, and a rotation speed of 60 rpm, utilizing a non-woven fabric polishing pad.

Material removal rates (MRR) were calculated using an analytical balance (CP225D, The Sartorius Group, Germany) to weigh wafers before and after CMP. Post-CMP, surface topographies were examined using an optical metallographic microscope (OLYMPUS MX 40, Japan), while surface roughness parameters, including Ra and peak-to-valley (PV), were measured using a non-contact optical surface profiler (NewView 5022, ZYGO, USA).

This detailed experimental setup allowed for precise evaluation of the CMP process and its effects on copper wafers, facilitating comprehensive analysis of surface characteristics and material removal rates.

III. RESULTS AND DISCUSSION ANALYSIS

3.1. Effect of Hydrogen Peroxide (H₂O₂) Concentration

Hydrogen peroxide (H₂O₂) boasts excellent oxidizing capabilities and poses no threat of pollution to wafers. Unlike nitric acid (HNO₃) or potassium ferricyanide (K₃[Fe(CN)₆]), H₂O₂ is non-corrosive and non-toxic to operators, rendering it a safe and environmentally friendly oxidant. In this segment of the experiment, the concentrations of silica sol and glycine were set at 6% and 3% by weight, respectively.

As the concentration of H₂O₂ increases, the material removal rate (MRR) initially rises and then exhibits a slight decrease, as depicted in Fig. 1(b). This trend is likely attributable to the enhanced oxidation rate facilitated by H₂O₂. However, excessive H₂O₂ concentrations lead to the formation of a dense oxide film on the wafer surface, resulting in a marginal decrease in MRR.

Optimal surface morphology is attained at a H₂O₂ concentration of 4% by weight, as illustrated in Fig. 1(a). This concentration strikes a balance between effective oxidation and preventing the formation of excessive oxide film, thereby yielding superior surface quality.

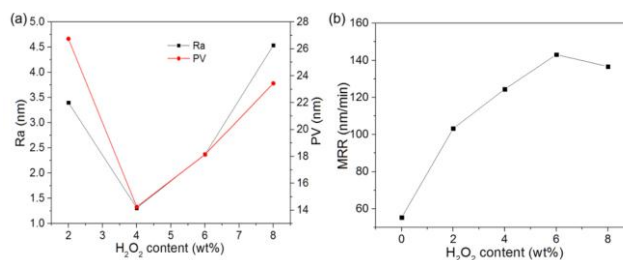


Fig. 1 Effect of H₂O₂ concentration on (a) Ra and PV and (b) MRR

3.2. Effect of Silica Sol Concentration

In the experiment, the SiO₂ particle size is 20 nm. The concentrations of H₂O₂ and glycine were maintained at 4 wt% and 3 wt%, respectively. As the concentration of silica sol increased from 2 wt% to 4 wt%, both the Ra and PV values decreased. However, when the silica sol concentration exceeded 4 wt%, the surface morphologies of the wafers deteriorated, as observed in Fig. 2(a). This degradation can be attributed to the inadequate removal of the oxide film by insufficient abrasives, resulting in uneven removal rates across the entire surface. Conversely, an excessive concentration of abrasives leads to an imbalance between mechanical and chemical actions, resulting in a deterioration of surface quality.

Regarding the material removal rate (MRR), it exhibited an increasing trend with increasing silica sol concentration, as depicted in Fig. 2(b). This phenomenon can be attributed to the enhanced abrasive action facilitated by higher concentrations of silica sol.

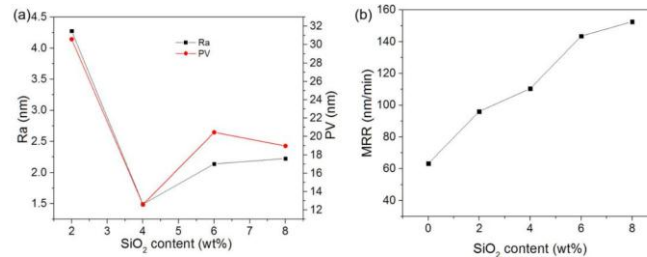


Fig. 2 Effect of SiO₂ concentration on (a) Ra and PV and (b) MRR

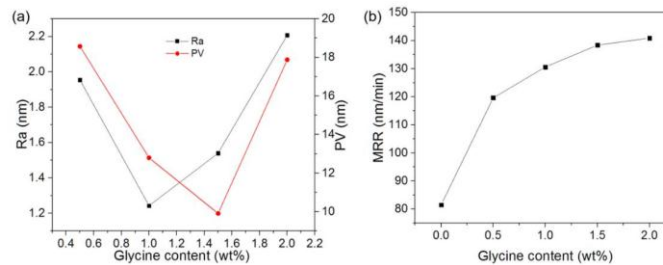


Fig. 3 Effect of glycine concentration on (a) Ra and PV and (b) MRR

3.3. Effect of Glycine Concentration

In this segment of the experiment, the concentrations of H₂O₂ and silica sol were set at 4% each by weight. Glycine, a molecule comprising an amino group and a carboxyl group, possesses nitrogen and oxygen atoms capable of providing lone pair electrons for complexation. Moreover, Cu²⁺ ions offer numerous empty orbitals, allowing glycine to exhibit a strong complexing effect on copper ions (Cu²⁺).

Consequently, as depicted in Fig. 3(b), the material removal rate (MRR) increases with higher concentrations of glycine. This phenomenon arises due to the accelerated rate of complexation reactions, which facilitate the removal of the oxide film. However, the CMP process necessitates a delicate balance between reaction rates to ensure timely oxide film removal without causing surface damage. Therefore, while slower reaction rates impede timely oxide film removal, excessively rapid reactions may result in abrasive-induced surface damage.

The influence of glycine content on reaction rates is significant, impacting surface morphology. Initially, the surface morphology improves with increasing glycine concentration, as observed in Fig. 3(a). However, beyond an optimal concentration, the surface morphology deteriorates, underscoring the importance of glycine concentration in achieving optimal CMP outcomes.

3.4. Effect of pH Value

In the final phase of the experiment, the slurry composition comprised 4% H₂O₂, 4% silica sol, and 1% glycine by weight, with pH values adjusted to 3, 5, 7, and 9 to investigate the impact of pH on polishing. pH plays a crucial role in the polishing slurry, influencing corrosion and complexation processes. The oxidation capacity of H₂O₂ is intricately linked to the pH value of the slurry, while the complexing capacity of glycine fluctuates with changes in pH.

As illustrated in Fig. 4(b), the material removal rate (MRR) increases as the pH value decreases. However, a noteworthy trend emerges when the pH value rises from 3 to 9: surface quality improves up to a pH of 7, beyond which it deteriorates. Fig. 5(a) showcases the consequences of acidic conditions (pH = 3), characterized by extensive traces of excessive corrosion due to heightened corrosive action of the slurry. Conversely, at pH = 9 (Fig. 5(d)), corrosion traces persist on the wafers, indicating insufficient material removal rates under alkaline conditions.

These observations underscore the intricate interplay between pH value, material removal rate, and surface quality in CMP processes. Optimal pH conditions, typically around neutral pH values, are critical for achieving superior polishing outcomes while minimizing surface damage.

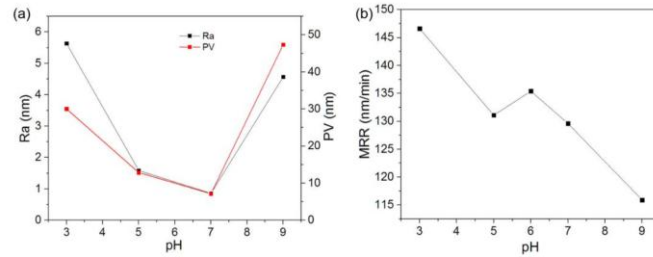
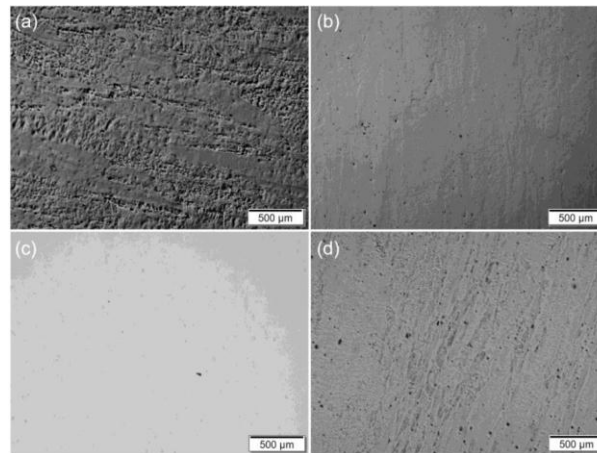


Fig. 4 Effect of pH value on (a) Ra and PV and (b) MRR



IV. CONCLUSIONS

The study successfully developed an environmentally friendly slurry, with the optimal formulation determined based on experimental results. The optimal slurry composition comprises 4% hydrogen peroxide solution, 4% silica sol, 1% glycine, and 91% deionized water by weight. Additionally, the optimal pH value for the slurry is determined to be 7.

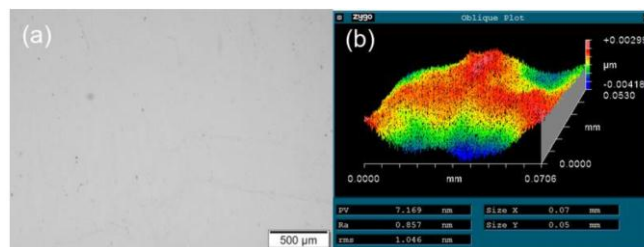


Fig. 6 (a) Surface morphology and (b) surface roughness when the slurry contains 4, 4, 1, 91 weights percentages for hydrogen peroxide solution, silica sul, glycine and deionized water

Utilizing the optimal slurry formulation, the wafers underwent polishing processes. As a result, surface roughness parameters were significantly improved, with a measured Ra value of 0.857 nm and a PV value of 7.196 nm over a measurement area of $70 \times 53 \mu\text{m}^2$, as depicted in Fig. 6. These findings underscore the effectiveness of the developed slurry in achieving superior surface finishes during the polishing process.

REFERENCES

- [1] Mengting, J., Yuling, L. (2014). Reducing the mechanical action of polishing pressure and abrasive during copper chemical mechanical planarization. *Journal of Semiconductors*, 35, 126001.
- [2] Pandija, S., Roy, D., Babu, S. V. (2009). Achievement of high planarization efficiency in CMP of copper at a reduced down pressure. *Microelectron Eng*, 86, 367.
- [3] Jang, S., Jeong, H., et al. (2016). Effect of Glycine on Copper CMP. *International Journal of Precision and Manufacturing-green Technology*, 3, 155-159.
- [4] Petitdidier, S., Bartosh, K., et al. (2007). Effect of an organic inhibitor in high pH chemical rinse on the platen for Cu-CMP. *Solid State Phenomena*, 134, 299-302.
- [5] Hanwei, H., Yuehua, H., Kelong, H. (2002). Electrochemical Behavior of Copper in HNO_3 Aqueous Solution Containing BTA during CMP. *The Chinese Journal of Process Engineering*, 2, 67-70.
- [6] Akonko, S.B., Li, D.Y., et al. (2005). Effects of $\text{K}_3[\text{Fe}(\text{CN})_6]$ slurry's pH value and applied potential on tungsten removal rate for chemical-mechanical planarization application. *Wear*, 259, 1299-1307.

- [7] Lee, D-W., Kim, T-G., et al. (2005). Stability of H₂O₂ as an Oxidizer for Cu CMP. *Transactions on electrical and electronic materials*, 6, 29-32.
- [8] Weiyan, Z., Yuling, L., et al. (2013). Role of Nano SiO₂ Abrasive in Alkaline Slurry During Cu CMP. *Micronanoelectronic Technology*, 50, 52-56.
- [9] Lee, D-W., Kim, N-H., Chang, E-G. (2005). Effect of nonionic surfactants on the stability of alumina slurry for Cu CMP. *Materials Science and Engineering B*, 118, 293-300.
- [10] Tanaka, T., Minami, H., et al. (2014). Nano Size Cerium Hydroxide Slurry for Scratch-Free CMP Process. *International Conference on Planarization/CMP Technology*, 21, 22-24.
- [11] Darj, M. M., Malinowski, E. R. (1996). Complexation between Copper(II) and Glycine in Aqueous Acid Solutions by Window Factor Analysis of Visible Spectra. *Analytical Chemistry*, 68, 1593-1598.
- [12] Huan, Z., Jianwei, Z., et al. (2017). Effect of Hydrogen Peroxide on Chemical Mechanical Polishing of Ru Under Different pH Values. *Micronanoelectronic Technology*, 54, 65-70.