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The effect of TAD based cleaning solution on post Cu CMP process

Sang Won Lee [a], Ki Ho Bae [a], Oh Joong Kwon [b,*], Jae Jeong Kim [a,*]

[a] School of Chemical and Biological Engineering, Institute of Chemical Process, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Republic of Korea
[b] Department of Energy and Chemical Engineering, Incheon National University, 119 Academy-ro Yeonsu-gu, In-cheon 406-772, Republic of Korea

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ABSTRACT

A cleaning solution has been introduced to remove the residue from Cu substrate after the Cu chemical mechanical polishing (CMP) process. In this study, the effects of complexing agents on the performance of cleaning solutions were studied depending on different functional groups and concentration based on a lift-off mechanism. The cleaning performance of the cleaning solution was assessed based on zeta potential, residual particle density, and etch rates. To prove that the cleaning is based on the lift-off mechanism, the Cu oxide layer composition and thickness were investigated by X-ray photoelectron spectroscopy. The thickness of Cu oxide increased up to 3.48 nm after the Cu CMP process; however, it dramatically decreased to 0.80 nm after the cleaning process. As the number of functional group for complexing agent and its concentration increased, the cleaning performance improved. In alkali condition, the amine functional group was found to be superior to other functional groups.

1. Introduction

High-speed complementary metal oxide semiconductor (CMOS) development has been enabled by introducing Cu as an interconnection material by a damascene process [1–3]. Its successful adoption may rely on various processes such an electrodeposition and a chemical mechanical polishing (CMP) [4–7]. In particular, CMP contributes to the successful realization of a Cu interconnection by solving problems associated with the non-volatile characteristics of $CuCl_2$. Since its introduction, various issues including a cleaning issue have been studied in an attempt to improve the efficiency of the CMP process. In particular, a strong adsorption of abrasives on the Cu substrate has been a highlighted issue in the cleaning process for several years [8–10].

In general, cleaning process mechanisms can be categorized into three types depending on their characteristics: physical, chemical, and lift-off. The physical and chemical mechanisms, which can be accomplished by using brush scrubbing and chemical dissolution of abrasives, respectively, have been used for a long time [8]. However, nanoscale-sized abrasives are not easily removed by physical process or simple chemical dissolution because of the strength of the electrostatic force between the abrasive particles and the substrate. The lift-off cleaning mechanism is a method of selectively dissolving a layer from the substrate [11]. When residues lie on a Cu substrate as shown in Fig. 1(a), an optimized chemical solution removes the residues by dissolving Cu oxide layers underneath, as presented in Fig. 1(b). Moreover, by ensuring that the zeta potentials of the abrasive particles and the Cu oxide substrate have the same polarity, as shown in Fig. 1(c), re-adsorption of abrasive particles on the Cu substrate is hindered by the repulsive force exerted between the two materials [12–16]. Because the lift-off mechanism can overcome the adsorption problem between the abrasive particles and the substrate, it can relatively show better cleaning performance than the physical and chemical mechanisms [11].

To apply the lift-off mechanism to the Cu etching, investigating the structure of Cu oxide is necessary. There have been several reports about the native Cu oxide structure. Boggio et al. claimed that a Cu native oxide layer is composed of Cu_2O and CuO [20]. According to the report by Suzuki et al., a native Cu oxide, formed on ultrahigh-purity copper, comprises an inner Cu_2O layer and an outer CuO layer [21]. Lim et al. reported their X-ray photoelectron spectroscopy (XPS) spectra analyses under the assumption of uniform oxide formation indicating that the thickness of Cu oxide formed by air oxidation is 1.6 nm, whereas that obtained by H_2O_2 oxidation is 8.5 nm [22]. Therefore, we assumed that a native Cu oxide might consist of Cu_2O and CuO and could be homogeneous and uniform layered structure with the thickness in the range 1.6 nm–8.5 nm depending on the oxidation methods. Thus, to apply the lift-off mechanism to the Cu material etching effectively, the investigation of the composition and thickness of the Cu material is necessary.

Cleaning solutions adopting the lift-off mechanism generally comprises a complexing agent, corrosion inhibitor, and pH adjustor [23–25]. The conventional cleaning solutions using the lift-off cleaning mechanism contain tetramethylammonium hydroxide (TMAH), ethanolamine, and ascorbic acid [17–19]. Hydrogen fluoride (HF) and nitric acid (HNO_3) have been widely used as Cu oxide etchants [26,27]. However, complexing agents containing amine or carboxyl functional groups have been suggested as alternatives to HF and HNO_3 because

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* Corresponding authors.
E-mail addresses: ojkwon@inu.ac.kr (O.J. Kwon), jjkimm@snu.ac.kr (J.J. Kim).

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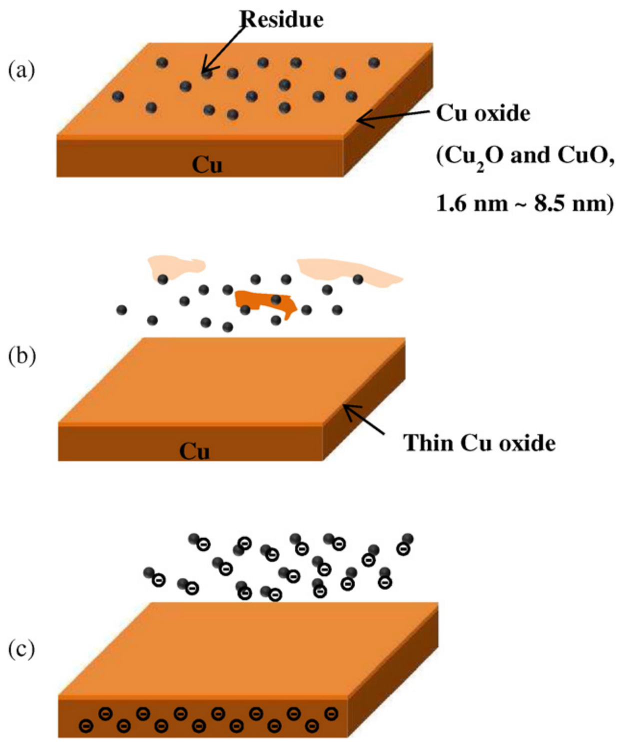

Fig. 1. Schematic diagram of (a) Cu substrate after contamination, (b) residual removal occurring during cleaning process, and (c) the repulsion between residue and Cu substrate based on zeta potential after cleaning process.

of their handling risk and excessive Cu dissolution [28–36]. Amine and carboxyl functional groups have been used as the key components of complexing agents owing to their ability to form strong complexes with a variety of metals. Based on the report of Hauer et al., ethylenediamine and diethylenetriamine with two and three amine functional groups, respectively, successfully form complexes with Cu ions under alkaline condition [31]. According to Piispanen et al. and Krishnan et al., carboxyl functional groups can produce hydroxo complexes with Cu at pH over 11. This indicates that citric acid and ethylenediaminetetraacetic acid (EDTA) with three and four carboxyl functional groups, respectively, can form a soluble hydroxyl complex with Cu at pH over 11 [32–35]. Both the amine and carboxyl functional groups have been widely reported to produce complexes with Cu ions at pH over 11.

There are many reports on the Cu CMP process; however, the properties of the functional groups as complexing agents for the Cu cleaning process have been scarcely studied. Thus, in this study, various cleaning solutions containing different complexing agents with distinct functional group were studied to investigate their lift-off mechanism and performance in the cleaning process. In our complexing agent investigation, amine and carboxyl functional group were selected. To investigate the effect of the numbers of functional groups, oxalic acid, citric acid, EDTA, ethylenediamine (EDA), diehylenetriamine (DETA), and 1.2-bis-(3-aminopropylamino)ethane (TAD) were elected. Oxalic acid, citric acid, and EDTA have two, three, and four carboxyl functional groups, respectively, whereas EDA, DETA, and TAD contain two, three, and four amine functional groups, respectively. The molecular structures of oxalic acid, citric acid, EDTA, EDA, DETA, and TAD are shown in Fig. 2(a)–(f).

2. Experimental

Cu coupon wafers (1.5 cm × 1.5 cm) were used for the estimation of the effectiveness of the cleaning solutions. The Cu coupon wafers, prepared by the physical vapor deposition (PVD), were: PVD Cu (900 nm)/PVD Ta (30 nm)/PVD TaN (30 nm)/thermal Si oxide (1000 nm)/and Si substrate. The Cu CMP slurry included 5 wt% colloidal silica (~50 nm, Fuso Chemical), 0.2 M glycine (Sigma-Aldrich), 0.5 mM 5-aminotetraozole (ATRA, Sigma-Aldrich), and 1 wt% H_2O_2 (Daejung Chemical and Metal Co., Ltd.). The pH of solution was fixed at 7 by adding potassium hydroxide (KOH, Daejung Chemical and Metal Co., Ltd.) and sulfuric acid (H_2SO_4, Daejung Chemical and Metal Co., Ltd.). To reduce substrate damage under acidic condition and the increase in the Cu oxide formation at alkali condition, neutral condition, pH 7, was chosen.

To investigate the characteristics of the cleaning solution, Cu wafer contamination and cleaning process were conducted in four steps: contamination, buffing, cleaning, and rinsing. In the contamination step, the Cu coupon wafer was dipped in the Cu CMP solution for 20 s without agitation. In the buffing and rinsing steps, the Cu coupon wafers were submerged in deionized water and stirred at 200 rpm for 60 s and 30 s, respectively. The cleaning step was conducted with the cleaning solution and processed under the agitation condition at 250 rpm. The cleaning solution comprised a complexing agent, corrosion inhibitor, and pH adjustor. The six candidates for the complexing agents were oxalic acid (Sigma-Aldrich), citric acid (Sigma-Aldrich), EDTA (Sigma-Aldrich), ethylenediamine (EDA, Sigma-Aldrich), diethylenetriamine (DETA, Sigma-Aldrich), and 1.2-bis-(3-aminopropylamino) ethane (TAD, Sigma-Aldrich). ATRA was used as the corrosion inhibitor. The pH of the cleaning solution was controlled by adding tetramethyl ammonium hydroxide (TMAH, Sigma-Aldrich) and H_2SO_4.

To determine the etch rate obtained with the various complexing agents, the amount of Cu ions dissolved from the Cu and Cu oxide was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, JP/ICPS-7500, Shimdzu). For the etch rate measurement, two types of spherical Cu oxide particles (CuO and Cu_2O) were dipped in the cleaning solution for 5 h with agitation at 250 rpm. Subsequently, the solution underwent filtration by using a 100 K pore size filter paper (Milipore), and the etch rate was calculated from the amount of Cu ion in the filtrate analyzed by ICP-AES.

To analyze the repulsive force between the particles and substrate, zeta potential analyzer measurement was used (Zeta Plus, Brookhaven Corp.). The solution used for the zeta potential measurement of silica particles was diluted with deionized water at a ratio of 1:50. The zeta potentials of CuO (~45 μm, Wako), Cu_2O (~45 μm, Wako), and silica particles were determined at various pH levels by controlling the solution's pH by adding TMAH and H_2SO_4.

To calculate the average residual particle density and its standard deviation on the Cu coupon wafer, five regions were randomly selected for the investigation by field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL). The residual particles were manually counted and divided it by selected surface area. We repeated this process into 5 samples per each conditions and calculated average and standard deviation values. The chemical state of the Cu surface was analyzed using X-ray photoelectron spectroscopy (XPS, AXIS-His, KRATOS). The radiation source of XPS was Mg Kα, and the take-off angle was 90°.

3. Results and discussion

To prove the lift-off mechanism occurring on Cu surface by a complexing agent, the study of the structure and composition of Cu surface is necessary. Thus, the structure and composition of Cu surface were investigated by XPS analysis after the Cu CMP process and compared to those of the as-prepared Cu surface. Fig. 3 shows the de-convolved XPS spectra of the Cu $2p_{3/2}$ peaks for the as-prepared Cu surface and the Cu surface after CMP process. Cu_2O, CuO and metallic Cu $2p_{3/2}$ were detected at the binding energies of 932.7 eV, 934 eV, and 932.4 eV, respectively, in the XPS data