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Material removal mechanism of copper chemical mechanical polishing in a periodate-based slurry

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ABSTRACT

The material removal mechanism of copper in a periodate-based slurry during barrier layer chemical mechanical polishing (CMP) has not been intensively investigated. This paper presents a study of the copper surface film chemistry and mechanics in a periodate-based slurry. On this basis, the controlling factor of the copper CMP material removal mechanism is proposed. The results show that the chemical and electrochemical reaction products on the copper surface are complex and vary considerably as a function of the solution pH. Under acidic conditions (pH 4) the copper surface underwent strong chemical dissolution while the corrosion was mild and uniform under alkaline conditions (pH 11). The corrosion effect was the lowest in near neutral solutions because the surface was covered with non-uniform $Cu(IO_3)_2{\cdot}H_2O$/Cu-periodate/copper oxides films, which had better passivation effect. The surface film thickness and mechanical removal properties were studied by AES and AFM nano-scratch tests. Based on the combined surface film analysis and CMP experiment results, it can be concluded that the controlling factor during copper CMP in a periodate-based slurry is the chemical-enhanced mechanical removal of the surface films. The periodate-based slurry should be modified by the addition of corrosion inhibitors and complexing agents to achieve a good copper surface quality with moderate chemical dissolution.

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1. Introduction

As the feature size of ultra-large scale integrated circuit continues to shrink below 22 nm, the conventional Ta/TaN bilayer barrier structure will be inadequate because of the large film thickness and gap filling problems [1,2]. To solve these problems, Ruthenium (Ru) has been considered as the most suitable candidate for replacing the Ta/TaN barrier layer in copper interconnect structures [3,4]. During the production process of microelectronic chips, the chemical mechanical polishing (CMP) process is the key for enabling both global and local planarization [5,6]. The CMP of Cu/Ru structure has been studied, especially the ruthenium polishing in a periodate-based slurry [7–9]. However, the copper polishing process in a barrier layer slurry has not been intensively investigated. The material removal mechanism, surface chemistry characteristics, galvanic corrosion problem, and chemical-mechanical interactions during the CMP process are not well known yet [10,11]. Y. Li et al. studied the material removal rate (*MRR*) of copper and tantalum as a function of pH value in an iodate-based slurry. The results showed that the polishing rate of copper at pH 2 was considerably higher because the passivation film on the copper surface was more likely to exist at higher pH values [12]. L. Jiang et al. found that the copper *MRR* in a KIO_4-based slurry increased with the concentration of KIO_4 increasing, which was due to the formation of Cu-periodate and Cu-iodate compounds [13]. Nevertheless, lots of work needs to be done to reveal the material removal mechanism of copper in a periodate-based slurry.

Copper CMP can be identified as a transient chemical process with intermittent mechanical phenomena [14]. The total material loss during CMP process could be divided into three parts: the chemical dissolution, the mechanical removal and the chemical–mechanical interactions [15,16]. However, the situation may differ greatly due to different slurry compositions and polished materials [17]. T. Du et al. believed that at low H_2O_2 concentrations, the copper material removal was caused by electrochemical dissolution, while it was due to the mechanical abrasion of the oxidized surface when the H_2O_2 concentration was comparatively high [18]. J. Li et al. investigated the material removal mechanism of copper in a H_2O_2-based slurry. They found that the chemical-mechanical synergistic effect played an important role in near-neutral slurries, while the corrosion effect dominated when the slurry was strongly acidic or alkaline [19]. Little work has been done to study the material removal mechanism of copper with periodate as oxidant. Therefore, it is essential to find out the controlling factor of

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material loss during the copper CMP process in a periodate-based slurry.

In our previous study, the passivation behavior of copper in KIO_4-based slurry at different pH values was investigated by tribo-corrosion experiments. The results revealed that the copper repassivation process is obviously faster in alkaline slurries than that in acidic slurries. Moreover, the CMP-chemical tests indicated that the corrosion current density during polishing (I_{cc}) reached the minimum at pH 7, and ascended when the pH value increased or decreased [20]. It can be inferred from the experimental data that the corrosion under acidic conditions was more severe than that under alkaline conditions. Raman spectroscopy experiments of the copper surface products showed that the copper surface was mainly passivated with copper oxides, copper hydroxide and copper iodide, but these varied as a function of the pH value of slurry. However, further complementary experiments should be performed to confirm this opinion.

The existing investigations of copper in periodate-based slurry mainly focus on copper CMP performance rather than intensive surface property analysis and material removal mechanism. The surface chemistry of the copper oxidation films needs to be intensively investigated to determine the key factor dominating material removal during CMP in a periodate-based slurry. In this study, the copper surface reaction products were analyzed. The mechanical effect during the CMP process was evaluated as well. Finally, in order to indicate the controlling factor of material removal during the CMP process, CMP tests were carried out over a wide pH range of 4.0–11.0.

2. Experimental

2.1. CMP-electrochemical experiments

CMP-electrochemical experiments were carried out to study the electrochemical behavior of copper during CMP. The apparatus was modified on a chemical mechanical polishing machine connected with an electrochemical workstation (CHI600C, Chenhua). The copper sample (99.99%) was 12.5 mm in diameter and about 1 mm in thickness. The pad was IC1010/Suba IV and the slurry contained 0.015 M KIO_4 without any abrasives. The pH was adjusted to 4, 6, 7, 9, 10 and 11 respectively. The counter electrode was platinum and the reference was an Ag/AgCl (3.5 M) electrode. During the polishing process, the applied force on the copper sample was 2.9 psi. The copper sample was stationary and the pad rotated at a speed of 100 rpm. The potentiodynamic polarisation experiments were conducted at a scan rate of 1 mV/s. The corrosion current density under both the polishing and static conditions has been calculated using the linear fitting method of E and Log (I) in Tafel strong polarization region thereafter.

2.2. Surface chemistry characterization

The chemical and electrochemical reaction products on the copper surface were analyzed using an X-ray microprobe (PHI Quantera Scanning XPS Microprobe, ULVAC-PHI Inc.). The copper samples were cut from electroplated copper on a wafer. Prior to the experiments, the copper samples were immersed in 0.05 M citric acid (pH $\approx$ 2) for 5 min to remove the native oxide layer, and then cleaned in absolute ethyl alcohol and dried using a N_2 gas stream. The immersion solution contains 0.015 M KIO_4 as oxidant. The pH value was adjusted to 4, 6, 9 and 11 with KOH and H_2SO_4 as pH adjustors. The copper samples were immersed in the solutions for 5 min and cleaned in DI water. The Cu 2p and I 3d XPS peaks were analyzed and the data were fitted by the XPSPEAK software. The surface morphology of copper after the immersion experiments was observed using AFM (Asylum Research MFP-3D) and scanning electron microscopy (SEM, FEI Quanta 200 FEG).

The thickness of the copper surface passivation film was obtained by AES (Physical Electronics, Inc., PHI-700) with a co-axial cylindrical mirror analyzer (CMA). The sputtering rate was 5 nm/min or 18 nm/min according to the different surface film thickness. The preparation of the copper samples was identical to that discussed previously. The immersion solution contained 0.015 M KIO_4, and the immersion time was also 5 min.

2.3. Nano-scratch tests.

Copper (99.99% purity) was cut into 20 mm × 20 mm × 2 mm squares. Before the experiments, the copper samples were polished on a Struers bench top polisher (TegraPol-35) until the surface roughness was below 3 nm, and then immersed into solutions containing 0.015 M KIO_4 with different pH values for 5 min. The nano-scratch experiments were performed using AFM (Veeco Co., RTESP) with a silicon rectangular cantilever probe. The constant applied force during scratching was 0.126 μN.

2.4. CMP experiments.

Electroplated copper on a 2 inch wafer was used. A polisher (CETR CP4) was used with a platen/carrier speed of 100/100 and a slurry flow rate of 100 mL/min at a down pressure of 4 psi. The slurry contained 5% Nexsil 85k-40 colloidal silica abrasive (Nyacol Nano Technologies Inc.), and 0.015 M KIO_4 at different pH values. The pad was IC1010/Suba-IV (K-type groove, Dow Electronic Materials). The *MRR*s were measured using the weight-loss method after polishing for 1 min. Prior to the experiments, conditioning was carried out for 10 min. Between each polishing, a pad ex-situ conditioning was executed for 45 s. The surface morphology after CMP was observed using an optical interferometer surface-mapping microscope (MicroXAM, Veeco).

3. Results and discussion

3.1. Surface chemistry characterization

During the corrosion of copper, the electrode potential is the key factor to control the ionization of copper while the pH value greatly affects the stability of the surface film. The relative stability regions of aqueous substances in a Cu-I-H_2O system are shown in the Pourbaix diagram (Eh-pH), presented in Fig. 1. The activities of I^- and Cu^{2+} are assumed equal to their $[I^-]$ and $[Cu^{2+}]$ concentrations, respectively. The equilibrium constant K used in Fig. 1 are listed in Table 2, which correspond well to the literature [21]. It is clear that the copper surface reaction products in the periodate-based slurry are significantly more complex than that in H_2O_2-based slurry [22–24]. The surface reaction products consist not only of copper oxides ($CuO/Cu_2O/Cu(OH)_2$), but also copper iodide (CuI), iodine (I_2) and copper iodate ($Cu(IO_3)_2{\cdot}H_2O$) [13,25]. However, as shown in Fig. 1, the copper surface film composition varies with different pH values. The $Cu(IO_3)_2{\cdot}H_2O$ and I_2 are more likely to be present in more acidic solutions whereas the copper surface tends to be covered with CuO and Cu_2O when the solution is extremely alkaline.

The opinion mentioned above is supported by XPS experiments. Fig. 2 shows the XPS Cu 2p results on the copper surface immersed into KIO_4 solutions with different pH values for 5 min. When the solution pH was 6 and 9, the Cu 2p3/2 peaks obviously shifted to higher binding energies. At the same time, satellite peaks were observed between 940 and 945 eV, indicating the formation of CuO and $Cu(OH)_2$ [26,27]. The deconvolution of the Cu 2p3/2 spectra on the untreated copper surface showed two peaks, at 933.8 eV (peak

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