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Characterization of non-amine-based post-copper chemical mechanical planarization cleaning solution ☆

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ABSTRACT

Copper surfaces can become contaminated by slurry particles and organic residues during chemical mechanical planarization (CMP). Silica particles are widely used as abrasives, while benzotriazole (BTA) is widely used as corrosion inhibitor, in copper CMP slurries. The contaminated copper surface needs to be cleaned by using an effective cleaning solution. These material contaminate the copper surface during CMP and need to be removed by using an effective cleaning solution. The objectives of this work were to develop a non-amine-based alkaline cleaning solution and characterize the solution based on the benzotriazole (organic residue) removal and particle removal efficiency. Cesium hydroxide and potassium hydroxide were used as cleaning agents and ethylene glycol was used as a corrosion inhibitor. Ethylene glycol acts as a chelating agent as well in the cleaning composition. BTA removal was characterized using contact angle measurements, X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy (EIS) techniques. The corrosion protection ability of the cleaning solutions was quantified by potentiodynamic polarization studies. Both potassium hydroxide- and cesium hydroxide-based solutions exhibited high BTA and silica particle removal. When compared to a potassium hydroxide based cleaning solution, cesium hydroxide based cleaning solutions were found to be more effective in terms of low surface roughness and low etch rate.

1. Introduction

Copper is widely used as an interconnecting material to replace aluminum in integrated circuits due to its useful properties, such as low resistivity and high electromigration resistance [1,2]. Copper is deposited by means of an electrochemical deposition process. Excess copper in the dual damascene process has to be removed by means of chemical mechanical planarization (CMP). In general, a Cu CMP slurry consists of abrasive particles, an oxidizing agent, a chelating agent and a corrosion inhibitor. Benzotriazole (BTA) is the most common corrosion inhibitor used in Cu CMP slurries [3]. However, the CMP process leaves lot of residual contaminants such as organic residues, abrasive particles and metallic contaminants on the copper surface. The organic residue is mostly BTA, while abrasive particles are generally silica [4]. BTA makes the surface highly hydrophobic in nature, which causes severe drying issues and also poor adhesion of the stacking layers. In addition to these contaminants, the CMP process also creates process induced defects such as scratches. Hence post-Cu CMP cleaning of the wafer using an efficient cleaning solution is necessary. BTA can exist in one of three forms, depending on the pH of the slurry [5]. BTA can exist in a protonated form ($BTAH^+$) in strongly acidic media, while in weakly acidic, neutral or weakly alkaline media it exists in the form of BTA; in strongly alkaline media it exists as BTA^- [5]. Tromans constructed a potential pH diagram for the Cu–BTA complex and indicated the type of species for a given set of conditions [6]. Copper forms a stable Cu–BTA complex in the pH range 4–10 [6–9]. In other words, the Cu–BTA complex is highly insoluble in this pH range [10]. Copper forms two different types of oxides, cuprous oxide and cupric oxide, and the acidic-based post-Cu CMP cleaning solution dissolves both types of oxides from the copper surface, while an alkaline-based post-Cu CMP cleaning solution selectively dissolves the cupric oxide leaving the cuprous oxide to passivate the surface [4]. Hence, alkaline-based cleaning chemistry is preferred to an acidic-based

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cleaning solution, as the copper surface is less damaged, according to the Cu Pourbaix diagram [11].

Ammonium hydroxide and tetra methyl ammonium hydroxide (TMAH) have been examined for use of alkaline-based post-Cu CMP cleaning solutions. Severe material loss was encountered for the ammonium hydroxide-based cleaning solution, as ammonia etches the copper surface at higher rates [12]. Thus, a TMAH-based cleaning solution has been used widely for post Cu CMP applications [13,14]. Both the ammonium hydroxide and TMAH are classified as amine-based cleaning agents.

In addition to either one of these compounds, the cleaning solution also consists of a chelating/complexing agent, and a corrosion inhibitor. The corrosion inhibitor should be hydrophilic to overcome the previously mentioned problems associated with hydrophobic surfaces. As amine-based compounds possess high vapor pressures, they can easily evaporate to the environment. Furthermore, amine species can deteriorate the lithography process in semiconductor fabrication units [15,16]. As such, expensive filters are needed to remove these species from clean room air in industrial applications, leading to higher cost and increased maintenance. In addition, TMAH may cause severe health issues if inhaled or absorbed through skin [17,18]. Hence, the semiconductor industry prefers to use non-amine-based chemistries for all applications. Recently, Barnes et al. proposed a non-amine alkaline cleaning solution, which is devoid of amine and ammonium-containing compounds. The cleaning solution consists of cesium hydroxide, glycerine and iminodiacetic acid [19]. However, the exact role of each compound was not reported. Though amine-based alkaline chemistry has been extensively studied, non-amine-based alkaline chemistry has not been comprehensively studied yet. In this work, cesium hydroxide and potassium hydroxide are evaluated as candidates in Cu CMP cleaning solution. Ethylene glycol is commonly used as a corrosion inhibitor in CMP slurries as well as in cleaning chemistry [20,21]. Ethylene glycol can also act as a chelating agent in cleaning chemistry [22]. Contact angle measurements, X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) techniques were used to confirm BTA removal. Potentiodynamic polarization studies were performed to evaluate the corrosion protection ability of the copper surface cleaned with the proposed cleaning solution. Atomic force microscopy (AFM) was used to monitor the surface quality of copper and field-emission scanning electron microscope (FESEM) was used to quantify the number of particles.

2. Experimental

Copper wafer (Buysemi, Korea) coupons of 2 × 2 cm^2 were cut from 8 in. blanket copper wafers and were used for all the experiments. The Cu wafers were pre-cleaned in iso propyl alcohol for 1 min. Benzotriazole (BTA) from Aldrich, ethylene glycol (EG) and sodium perchlorate ($NaClO_4$) from Sigma Aldrich, potassium hydroxide from Samchun, and cesium hydroxide from Alfa Aesar were used for the experiments. Organic contaminant removal from copper coupons was characterized using a static contact angle analyzer (Phoenix 300, SEO Korea). Prior to the contact angle measurements, copper coupons were treated with a 0.1 wt.% BTA solution. BTA-treated copper coupons were treated with 200 ml of an alkaline solution of various concentrations. Unless mentioned otherwise, the duration of the cleaning experiment was 1 min. Finally, the copper coupons were rinsed with de-ionized water (DIW) followed by drying using nitrogen gas.

The electrochemical experiments were conducted in a standard three-electrode quartz cell, and the data were acquired using a potentiostat (VersaSTAT 3, Princeton Applied Research, USA). Ag/AgCl (saturated. KCl) was used as the reference electrode, a treated copper coupon was used as the working electrode, and a platinum mesh was used as the counter electrode; 0.1 M $NaClO_4$ was used as the supporting electrolyte. Electrochemical experiments were also conducted with untreated copper coupons in 0.1 M $NaClO_4$. Potentiodynamic polarization curves were obtained in the range of -250 to +500 mV with respect to the open circuit potential (OCP), at a scan rate of 1 mV/s. EIS measurements of treated copper coupons were conducted at an open circuit potential in a solution containing only 0.1 M $NaClO_4$. EIS spectra were acquired in the frequency range of 10 kHz–0.1 Hz with a potential amplitude of 10 mV rms.

XPS (Sigma Probe, Thermo VG, UK) was operated at a base pressure of 3×10^{-9} mbar. The photoelectron spectra were excited by an Al-Kα (1486.6 eV) anode operating at a constant power of 100 W. During the spectra acquisition, a constant analyzer energy (CAE) mode was employed at a pass energy of 20 eV and a step of 0.1 eV. XPS spectra were obtained using copper coupons treated with various solutions.

A commercial colloidal silica-based slurry with a solid concentration of 6 wt.% was used to contaminate the wafer for the polishing experiments. The primary particle size of the abrasive was 60 nm, and the pH value of the slurry was 9.5. A constant slurry flow rate of 200 ml/min was maintained for the polishing experiments. The wafers were polished with a down pressure of 0.85 psi. The platen and carrier head were rotated at a speed of 60 rpm, and a Politex polishing pad was used for the polishing experiments. The duration of the polishing run was 1 min. The cleaning experiments were performed in a Class-10 clean room. Contaminated coupons were cleaned using the developed cleaning solution for a fixed cleaning time of 1 min. Coupons contaminated by silica particles were captured by FE-SEM (Mira3, TESCAN, Czech Republic). Particle removal efficiency, that is, the ratio of the average number of particles removed during cleaning to the total number of particles before cleaning, was calculated based on the particle counts obtained from the FESEM image using a software package (Image Pro).

The zeta potentials of silica particles dispersed in DIW and various solutions were measured using a zeta analyzer (ELS-Z, Otsuka Electronics, Japan). For static etch rate experiments, the copper coupons were treated with a cleaning solution for 10 min. The pre- and post-cleaning of copper film thicknesses were measured using a four-point probe (Advanced Technology Instruments, CMT SR5000, Korea). An AFM (Park Systems, Korea) was used to measure the surface roughness of the wafer coupons.

3. Results and discussion

Fig. 1 shows the contact angles of DIW on the BTA treated copper coupons dipped in various concentrations of CsOH and KOH solutions for 1 min. Hydrophobicity and hydrophilicity of a surface can be measured using contact angle measurements [23,24]. The contact angle of water on a fresh copper surface was ~30°, which shows it is hydrophilic, and it was taken as reference for this study. The contact angle on a BTA-treated copper coupon was found to be ~64°. Copper coupons became hydrophobic after treatment with 0.1 wt.% of BTA for 1 min [25]. The stability of the Cu–BTA complex strongly depends on the pH of the slurry used for polishing. The Cu–BTA complex is unstable in the higher alkaline ranges. Both the CsOH and KOH solutions are capable of removing the BTA layer from the copper coupons. The addition of 0.25 wt.% of alkali reduces the contact angle to about 25° and further addition of CsOH decreases the contact angle even further while in case of KOH, it decreases only slightly. A solution of 1 wt.% of alkali corresponds to 0.067 M CsOH and 0.2 M KOH. CsOH is a stronger base compared to KOH and this may explain the observed results. The contact angle of Cu surface treated with BTA and then 1 wt.% alkali is