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Characterization of TMAH based cleaning solution for post Cu-CMP application

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ABSTRACT

The cleaning of copper surface after chemical mechanical planarization (CMP) process is a critical step since the surface would be contaminated by a large number of slurry particles such as silica or alumina and organic residues such as benzo triazole (BTA). The presence of organic residues results in a hydrophobic surface, which leads to problems in particle removal and drying. A major function of a post copper CMP cleaning solution is to remove these organic contaminants without significant increase in the surface roughness. Alkaline or acidic cleaning solutions are usually preferred over neutral solutions since they can remove organic residues better. The objective of this work is to formulate an alkaline cleaning solution and characterize its efficiency on particle and BTA removal. The cleaning solution studied consists of tetra methyl ammonium hydroxide (TMAH) as the cleaning agent and arginine as the chelating agent. The removal of BTA is characterized using contact angle measurements and electrochemical techniques. The proposed cleaning solution showed good ability in removing BTA and silica particles from the copper surface and also yielded a lower surface roughness. Arginine facilitates complexing of Cu ions thereby preventing redeposition.

1. Introduction

Apart from the adherence of slurry particles, the attachment of organic residues to the copper surface after chemical mechanical planarization (CMP) process is an important problem. Benzo triazole (BTA) which is used as corrosion inhibitor in the copper CMP slurry is the primary source for the formation of organic residues [1–3]. BTA molecules tend to chemisorb onto the copper surface to form $[Cu–BTA]_n$ polymeric film [4–6]. Using quartz crystal microbalance studies it was shown that a thin chemisorbed BTA layer forms on the Cu surface in the pH of 11.6, while a thick physisorbed layer forms at pH of 2 [1]. The interaction of BTA with Cu surface depends on the immersion time [1,5,7,8], concentration of BTA [7,8], the nature of the Cu surface [8,9] and the pH [1,8–11]. BTA prevents corrosion by stabilizing the Cu_2O underlayer [10]. The thickness of BTA layer depends on the thickness of Cu_2O [9]. Notoya et al. [11] measured the Cu corrosion inhibition efficiency at various pH values using potentiodynamic polarization studies and reported that the corrosion inhibition efficiency is very high at pH of 6, good at pH of 13 while it is low at pH values of 1, 3 and 9 [11]. In the same report, they found that Cu(I)–BTA film forms as short polymer structure in the neutral pH while it is only a monomer or dimer in acidic or alkaline solution. Thus while BTA is used as a corrosion inhibitor in Cu CMP slurries, its interaction with the Cu and its oxides strongly depends on pH.

To remove the particles after CMP, nitric acid based solutions with BTA as corrosion inhibitor were suggested [12]. The major issue is that BTA covered Cu surface is hydrophobic which leads to the problems of particle attachment and wafer drying issues [1,2,13]. The particles on Cu surface can be removed by using suitable chemistry of cleaning solution and sometimes in combination with megasonics and/or brush scrubbing [14]. The particle removal can occur by selective dissolution of the particles or by undercutting the particles by etching of the wafer, lifting of particle by mechanical forces, prevention of redeposition and transporting them away from the wafer [14]. Thus the cleaning chemistry should create an environment such that the lifted particles and the wafer surface should have the same sign of zeta potential so as the particle and the wafer surface electrostatically repel each other. An effective cleaning solution should also remove the organics and particles completely without increasing the surface roughness and should leave the Cu surface passivated. Thus, later studies focused on removing the particles and BTA while leaving a hydrophilic surface.

Several reports are available in the literature on various cleaning formulations employed to remove the organic residues and particles from copper surface, and they are summarized below. Murakami and Ishikawa suggested that the pH of the Cu–BTA cleaning solution must be less than 3 or more than 10 to remove the BTA effectively since the potential-pH diagram of Cu–BTA system shows that the Cu–BTA complex is absent in this pH range [15,16]. They further reported that acidic cleaning solution of pH 2.4 showed better performance than the conventional cleaning

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solution of pH 4.2 to remove Cu–BTA as well as to suppress the metallic contamination [15]. On the other hand, Lin et al. reported that citric acid based solution at pH 5 is a suitable candidate for removing the organics [3]. This is because the formation of Cu–BTA complex not only depends on the pH value but also on the corrosion potential value. In addition to organic residue removal, the particle removal could also be facilitated in citric acid based cleaning solution with the addition of ammonium hydroxide [17]. Yeh et al. [2] proposed post CMP cleaning for Cu using buffer hydrofluoric (BHF) solution and ozone (O_3) water cleaning and reported that the roughness is better than that achieved with a citric acid based cleaning solution. Organic acids such as citric, glycolic, phthalic, DL Malic, acetic and oxalic acids were considered for post Cu CMP cleaning and among them, oxalic acid was reported to show the least Cu etch rate [18]. Otake et al. evaluated the effectiveness of various chelating agents to remove BTA using contact angle measurements [19]. It was reported that all of them showed relatively more Cu etch rate than DI water. Alkaline cleaning solutions are also of interest for post Cu CMP cleaning [20,21]. One of the advantages of alkaline cleaning solutions is that high pH chemistry dissolves only CuO on the surface and leaves Cu_2O thereby passivating the surface while low pH chemistry dissolves both Cu_2O and CuO [22]. Moreover, the negative charge on the slurry particles is also expected to increase in alkaline regime which eventually results in higher particle removal efficiency. In addition, Cu Pourbaix diagram [23] reveals that the attack on Cu is less in the alkaline regime due to the formation of oxides. Thus at high pH, good cleaning performance and low surface roughness could be achieved. Few alkaline based solutions such as ammonium hydroxide and tetra methyl ammonium hydroxide (TMAH) have been evaluated for post Cu CMP. However, it was shown that the etch rate of Cu in NH_4OH is high, especially in dense patterned wafers, and hence ammonium hydroxide is not considered as a potential candidate for post Cu cleaning [24].

Tetra methyl ammonium hydroxide (TMAH) has wide range of applications in the post CMP cleaning process for Poly Si [25], W [17] and Cu [1,17,20,21,26]. TMAH has the ability to remove particles from various surfaces due to change in the surface charges of the particles [25,26]. It does not form complexes with Cu [17] and hence will not lead to rapid corrosion. On the other hand, it is important to ensure that the Cu dissolved during the undercutting does not redeposit on the wafer leading defects [26]. Hence chelating agents in limited quantities should be used in the cleaning solutions [20]. Arginine is an alkaline amino acid, which can complex with Cu [27–29]. Although TMAH has been employed as an ingredient for post Cu CMP cleaning solutions, a systematic evaluation of the effect of TMAH on organic removal has not been reported yet. In this work, the performance of TMAH as a cleaning agent in removing the BTA molecules and that of and arginine as a Cu chelating were tested using contact angle measurements and electrochemical studies. The particle removal efficiency was also evaluated using FE-SEM analysis. The roughness of the cleaned surface area was measured using atomic force microscopy (AFM). The structures of BTA, TMAH and Arginine are given in Fig. 1. The results show that TMAH is very effective in removing the BTA and the abrasive particles from the Cu surface and that it's cleaning effect can be improved by using L-arginine as a complexing agent. A mechanistic model is presented to explain the action of TMAH and arginine.

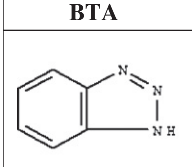
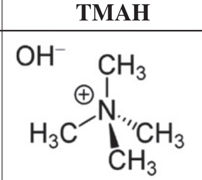
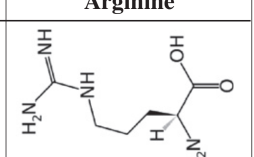
BTA	TMAH	Arginine
		

Fig. 1. Structure of BTA, TMAH and arginine.

2. Experimental

Cu coupons (2 × 2 cm) cut from 200 mm blanket Cu wafer were used for all the experiments. Prior to the experiments, the Cu coupons were cleaned in iso-propyl-alcohol (IPA) solution with ultrasonication for 3 min and dried by blowing N_2 gas. This is taken as the reference and defined as the fresh Cu. The following chemicals were used for the experiments: BTA (Sigma–Aldrich, USA), TMAH (Alfa Aesar, Korea), arginine (Junsei, Japan), uric acid (Acros, USA) and $NaClO_4$ (Sigma–Aldrich, USA). Different concentrations of BTA (0.01, 0.05, 0.1 wt.%), TMAH (0.1, 0.5 and 1.0 wt.%), 1 wt.% of arginine and 0.01 M of uric acid were used. The contact angle of Cu surface was measured using a static contact angle analyzer (Phoenix 300, SEO, Korea). For contact angle measurement, the copper coupons were dipped in solution under investigation for 1 min and then rinsed in the DI water twice in separate beakers (the first rinse for 10 s and the second rinse for 20 s). After the rinse, the sample was dried with N_2. Each experiment was repeated three times and the average and standard deviations are reported. The formation of BTA complex on Cu is very rapid [30] and it forms a monolayer within a second. Thus, the time of 1 min used in the present experiments is sufficient to attain equilibrium. The electrochemical experiments were conducted in a standard three electrode quartz cell and the data was acquired using a potentiostat (VersaSTAT 3, Princeton Applied Research, USA). A Cu coupon was used as the working electrode, Ag/AgCl (Satd. KCl) was used as the reference electrode and a Pt mesh was used as the counter electrode. 0.1 M $NaClO_4$ was used as supporting electrolyte. The potentiodynamic polarization curves were obtained in the range of −500 to +500 mV with respect to the open circuit potential (OCP) in the positive direction with a scan rate of 1 mV/s. A commercial slurry (Starplanar 4000, by Cheil Industries, Korea) containing 12.5 wt.% silica abrasives of primary particle size 100 nm was used for the slurry contamination experiments. The zeta potential of silica particles in various chemistries and the particle size distribution were measured using Zeta analyzer (ELS-Z, Otsuka Electronics Japan). Field Emission-Scanning Electron Microscope (FE-SEM) images (MIRA3 model, TESCAN) were used for the estimating the particle contamination. The surface roughness of Cu was measured by using AFM (Park Systems, Korea). To compare the performance of our new alkaline cleaning solution with commercial solutions, two alkaline based commercial solutions A and B of pH 10.5 were also tested for its effectiveness in removing organics and particles.

3. Results and discussion

Fig. 2 shows the contact angle values of DI water on Cu surface dipped in solutions with different concentrations of BTA for 1 min. The Cu samples were dipped in four different concentrations of BTA solutions viz. 0.01, 0.05, 0.1 and 0.15 wt.% and the respective pH values were 6.6, 6.5, 6.2 and 6.1. The dipping process was used to create adsorbed BTA film on Cu and simulate the effect of BTA adsorption from Cu slurries during CMP. The contact angle can be used as a measure of hydrophobicity of a surface [19,31]. A higher contact angle implies that the surface is hydrophobic. It is seen from Fig. 2 that addition of 0.01 wt.% of BTA increases the contact angle from about 20° to 55°. Further addition of BTA does not change the contact angle significantly. The interaction between Cu and BTA is strongly dependent on the pH [1,8–11]. Finsgar and