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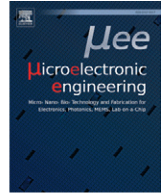

Research paper

Sodium hypochlorite as an oxidizing agent in silica based ruthenium chemical mechanical planarization slurry

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ABSTRACT

In the present work, Ru as well as Cu chemical mechanical planarization (CMP) with slurry containing fumed silica as abrasive and sodium hypochlorite as oxidizer was investigated. Benzotriazole (BTA) was used as a corrosion inhibitor for the proposed slurry. The results reveal that for CMP runs with only sodium hypochlorite, Ru RR was found to be higher at pH 7 and decreases as the pH decreases or increases, while Cu RR decreases with the increase in pH. Addition of BTA to the slurry resulted in a slight decrease in the removal rate. The polishing selectivity between Cu and Ru was found to be ~1 at pH 9, which is desired for the microelectronic industries. RuO_4 is formed in the acidic pH whereas RuO_4^- and RuO_4^{2-} were formed between pH 7 and 14 in the presence of sodium hypochlorite. RuO_4/RuO_4^- species assist in forming RuO_3/RuO_2 which is porous in nature and maintains the removal rate. Polishing selectivity obtained using the proposed slurry was found to be less sensitive to any changes in pressure and table speed.

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1. Introduction

Ruthenium (Ru) is used as a barrier layer for future devices due its high melting point (2334 °C), low resistivity (~7 μΩ cm) and negligible solid solubility with copper (Cu) [1,2,3]. Earlier, tantalum (Ta), tantalum nitride (TaN) and titanium nitride (TiN) were used as barrier layer and a thin copper (Cu) seed layer is grown on the top through physical vapor deposition (PVD) followed by electrodeposition of Cu. However, with ruthenium barrier layer, Cu seed layer is not required as it allows the direct electrodeposition of Cu [4,5].

During fabrication of integrated circuits, chemical mechanical planarization (CMP) is employed to remove the excess material [6,7]. Polishing of Ru is challenging due to its inherent hardness, hence by modifying the chemical composition of slurry using abrasive and oxidizer, the removal rate (RR) of Ru can be enhanced. Since RuO_4 is a soluble oxide in an aqueous solution, it would be possible to formulate slurry for Ru CMP by using oxidizer which can form RuO_4 or $RuO_2 \cdot 2H_2O$ on the Ru surface [8,9]. Several oxidizers were investigated and Ru removal rates over wide pH range of the slurry were reported [3–15]. Ceric ammonium nitrate (CAN) was proposed as an oxidizer in acidic slurry for Ru CMP [16]. Sodium/potassium periodate salts were used as oxidizer to enhance the Ru RR in alkaline conditions to avoid the formation of RuO_4 which is toxic in nature [17–19]. Cui et al. investigated the Ru CMP using several oxidizers (like potassium ferricyanide, potassium perchlorate, potassium persulfate, hydrogen peroxide, sodium periodate and sodium hypochlorite) at neutral pH of the slurry [20]. It was reported that the formation of soft and porous layer of RuO_3/RuO_2 improved the Ru polishing rate. In integration of Ru barrier layer with Cu, galvanic corrosion may take place. Since most of the CMP slurries favor strong ionic conduction, Ru forms strong galvanic couple with Cu which leads to corrosion of Cu lines of Ru-Cu structures due to coupling [17,18]. BTA, a commonly used anodic inhibitor for Cu forms a protective layer on the surface [18,21,22].

In the microelectronic industries, ruthenium as well as copper needs to be polished during the damascene processing of interconnects, at the same rate (i.e., selectivity of 1) with the aim of obtaining the desired surface quality [17]. Polishing selectivity between ruthenium and copper of 1:1 is preferred in the semiconductor industry [17,23,24]. Though there are many literatures available for the Ru CMP, very few types of slurry were tested for both Cu and Ru CMP. Peethala et al. [17] studied using 0.015 M KIO_4 as an oxidizing agent and 5 wt% colloidal silica as abrasives for Ru CMP which yielded Ru:Cu RR selectivity of ~1. According to Jiang et al. [24], the material removal rate selectivity of Ru vs. Cu was found to be >1.0 by increasing the K^+ source with the help of KNO_3 in the formulated slurry of 2 wt% colloidal silica (abrasive) and 3 wt% hydrogen peroxide (oxidizer).

In this paper, effect of sodium hypochlorite (NaOCl) and fumed silica on Ru as well as Cu CMP RR has been investigated. The static etch rate (ER) of Ru and Cu was studied as a function of pH and temperature. Effect of temperature on ruthenium and copper etch rate was used to determine the thermodynamic properties. Ruthenium and copper CMP experiments were performed as a function of pH, polishing pressure

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and table speed. Polishing experiments were also carried out using fumed silica based slurry containing sodium hypochlorite as oxidizer and BTA as corrosion inhibitor. X-ray diffraction (XRD) study of the ruthenium coupons was performed to understand the changes happening during etching.

2. Experimental

2.1. Static etch rate experiments

A vacuum melted 3 N (99.9% pure) Ru ingot (0.75″ diameter × 0.5″ tall) within 99% of true density was purchased from Rare World Metals Mint, Cincinnati, USA [25] and Cu coupon (1″ diameter × 0.5″ tall) 99.9% purity, purchased from Industrial Engineering Store, India were used for the polishing and etching experiments. Etching experiments of the above mentioned coupons were performed to determine the Ru and Cu static etch rate as a function of pH and temperature. The pH of the solution was measured using a pH meter (Eutech Cyberscan pH tutor) [26] and was adjusted using either potassium hydroxide (KOH) or nitric acid (HNO_3). The disk was immersed in a beaker containing 100 ml of etchant solution for 30 min. Coupons were weighed before and after the immersion in the solution, using an analytical balance (Sartorius Model BSA224S-CW) of 0.0001 g readability [27]. Subsequently, the disk was washed thoroughly with distilled water and dried. At least three experimental runs were performed for each case and the average rate was reported along with the standard deviation.

2.2. X-ray diffraction (XRD)

X-ray diffraction analysis of ruthenium coupon was performed using a PANalytical 3 kW X'pert Powder – Multifunctional, Netherlands [28]. X-ray source was Cu high resolution X-ray tube, which gives Cu kα with a wavelength of 1.54 Å. XRD pattern of the Ru disk before the etching experiments were taken as the reference. XRD analysis of the Ru disk, etched using oxidizer maintained at pH 3, 7 and 11, were performed to determine the modification happening on the surface during etching.

2.3. Chemical mechanical polishing (CMP)

Polishing experiments were carried out using a bench top polisher (Struers, Denmark) [29]. Pad made up of polyurethane (SUBA IV, Eminess Technologies, USA) [30] was adhered on the turntable of the polishing machine. The abrasive (CAB-O-SIL® M5 Fumed silica) was purchased from Cabot India Limited, India [31] and the oxidizer (sodium hypochlorite) was obtained from Fisher Scientific, India. Corrosion inhibitor used was benzotriazole (BTA), purchased from Loba Chemie Private Limited, India. Polishing of Ru as well as Cu was performed to determine the selectivity. All the CMP experiments were carried out at room temperature. The slurry was prepared using fumed silica particle as an abrasive and sodium hypochlorite as an oxidizer. Slurry was dispensed over the pad at a constant flow rate of 100 ml/min using a peristaltic pump (Ravel Hitek, India) [32]. Unless mentioned otherwise, a down pressure of 3.51 psi was applied on the surface. Unless mentioned otherwise, turn table and the specimen holder speed was kept as 150 rpm and 250 rpm respectively. A dummy run was conducted with the slurry before the experiments to restore the pad surface condition. For each polishing experiment, at least three experimental runs were performed. Each CMP run was conducted for a min followed by conditioning of the pad for a min. The disk was washed and subsequently dried. Pre- and post-polish weight of the coupons were noted. Removal rate was calculated using the weight lost by the coupon, density and area of the coupon and immersion time. The pH of the slurry was adjusted using either KOH or HNO_3. Few polishing experiments were performed using the formulated slurry with benzotriazole as a corrosion inhibitor.

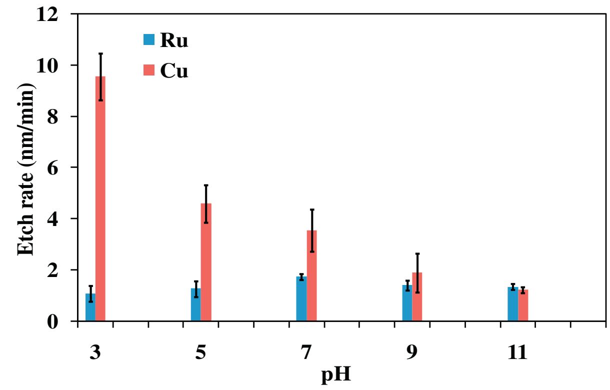

Fig. 1. Effect of pH on etch rate of Ru and Cu in presence of 0.5 wt% NaOCl.

3. Results and discussion

3.1. Dissolution experiments

Static etch rates of Ru and Cu were studied using NaOCl for odd pH range (3 − 11) at room temperature and at different temperatures (30–50 °C) for pH 7. Fig. 1 shows the etch rate as a function of pH using 0.5 wt% NaOCl for the Ru and Cu disks. The etch rate of Ru increases in the presence of oxidizer in the acidic region and decreases in the alkaline region. The maximum Ru etch rate was obtained at pH 7 using 0.5 wt% NaOCl. A similar trend for the etch rate of ruthenium with the pH was reported in the literature [8,9]. Cu etch rate decreases with increase in the pH of the etchant solution, which is in line with the reported literature [33].

Fig. 2 shows the effect of temperature on Ru and Cu etch rate, in a solution with 0.5 wt% oxidizer at neutral pH. The etch rate of both Ru as well as Cu increases with increase in the temperature. During this measurements in solutions containing oxidizer, a black film i.e., $RuO_2 \cdot 2H_2O$ was formed on the surface of the Ru [34,35] and the solution turned yellow due to the formation of RuO_4, especially in acidic range [36,37]. In case of Cu, it was observed that blue layer was formed on the surface might be due to the formation of cupric oxide (CuO/Cu_2O) on the surface and consequently, the solution turned blue slowly [18]. This can be attributed to the increased rate of chemical reaction between the metal surface and the medium with temperature. As a result, metal etches at a faster rate.

The activation energy (E_a) for the proposed system was calculated using Arrhenius equation given by Eq. 1 [38]

$$\log(ER) = A - \frac{E_a}{2.303RT} \tag{1}$$

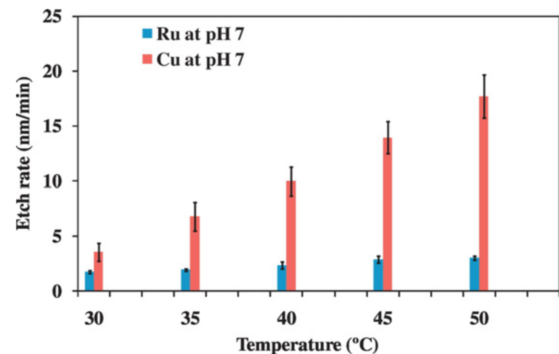

Fig. 2. Effect of temperature on etch rate of Ru and Cu in presence of 0.5 wt% NaOCl at pH 7.

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