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Nitric acid-based slurry with citric acid as an inhibitor for copper chemical mechanical polishing

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Abstract

A novel inhibitor, citric acid, was introduced in the HNO_3-based slurry for copper chemical mechanical polishing. It was anticipated that a passivation layer could be formed on the copper surface in the presence of citric acid. In a 3 vol.% HNO_3 solution, the passivation effect derived from citric acid saturated as the citric acid concentration reached ca. 0.01 M. The polishing rate was found to decrease with the addition of citric acid. The results showed that the HNO_3-based slurry with citric acid as an inhibitor could achieve good surface planarity for copper chemical mechanical polishing. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Chemical mechanical polishing; Inhibitor; Copper; Citric acid; Nitric acid

1. Introduction

The chemical mechanical polishing (CMP) of copper has been generally recognized as a viable technique to delineate copper patterns in the deep sub-micron integrated circuits (ICs). Recently, several studies reported that copper CMP (Cu-CMP) has achieved multilevel interconnections with low electrical resistance, and excellent electromigration for high performance ICs [1,2]. As reported, Cu-CMP can be performed in either acidic or neutral or alkaline media [3–8]. Chemical effects have also been shown to be particularly important in Cu-CMP due to the presence of the polish media (slurry). In the acidic media, nitric acid is commonly used due to its benefits of high solubility and dissolution rates of copper and copper oxides, by which the redeposition of the abraded copper species onto the surface can be strongly suppressed. However, in using a HNO_3-based slurry, a corrosion inhibitor, benzotriazole (BTA), is frequently used to decrease the etch rate and thus avoid isotropic etching for insuring good surface planarization.

In this article, the authors proposed a novel inhibitor, critic acid, used for the HNO_3-based slurries in the process of Cu-CMP. Similar to the inhibitive action of BTA, citric acid, was also capable of reducing etch rate of copper in nitric acid. However, citric acid exhibits rather competitive for use in Cu-CMP relative to BTA, since citric acid not only is a more common and cheaper chemical substance compared with BTA but also can act as a chelating agent to inhibit the redeposition of copper. In this work, the polishing rate was found to decrease with the addition of citric acid. The results also showed that the use of citric acid as an inhibitor for the HNO_3-based slurries could achieve good surface planarity.

2. Experimental

The copper film was a stacked Cu/Ta layer structure with a combination thickness of 900/50 nm which was sputter deposited onto the 6-in (150-mm) diameter Si wafer covered with a 500-nm thick thermally grown SiO_2. The wafer was cut into 2×2 cm^2 pieces for the static etching experiments, in which the pieces were dipped in various solutions without intentional stirring for 30 s. After immersion, the samples were cleaned in deionized water and blown dry.

To investigate the effect of citric acid on the etching rate of copper film in HNO_3 solution, two kinds of solutions were prepared: (i) 0.01 M citric acid solution to which were added various volume percentages of HNO_3 ranging from 1% to 8%; (ii) 3 vol.% HNO_3 dilute solution to which were added various concentrations of citric acid ranging from 0.0005 to 0.5 M.

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Table 1
Experimental parameters and conditions used for Cu-CMP

Controlled parameters	Values
Platen/carrier speed	20/42 rpm
Down pressure	3.0 psi
Back pressure	1.5 psi
Slurry flow rate	150 ml/min
Temperature	37°C
Pad	Politex Regular E. pad

Polarization curve scans of copper in the prepared solution being studied were carried out on an EG&G Potentiostat Model 273. The working electrode was 99.9% copper foil (0.05 mm in thickness), with an area of 0.64 cm^2 exposed to the solution. The reference and conductor electrode were SCE (standard calomel electrode) and Pt, respectively. The potentiodynamic scans were performed at a rate of 1 mV/s, beginning at 0.2 V below the open circuit potential. Nitrogen gas was purged before testing. The corrosion current and potential were calculated by QuickCalc Tafel Analysis, in which the tafel region was ±50 mV centered around the open circuit potential.

To determine the etching rate/polishing rate of copper film, a four-point probe was used to measure the sheet resistance before and after the static etching measurement or CMP process. Cu-CMP was performed with a Westech Model 372 M polisher using a Politex Regular E. pad. Table 1 given the experimental parameters and conditions used for Cu-CMP process. The polishing rate of Cu-CMP was measured at 13 points across a 150-mm diameter (10-mm edge exclusion). Nonuniformity of polishing rate is defined as follows:

$$\text{Nonuniformity}\,(\%) = 100\% \times \frac{(\text{Max} - \text{Min})\ \text{polishing rate}}{2 \times \text{mean value}}$$

3. Results and discussion

In the metal CMP, formation of a passivation layer is critical in the planarization of metal surface. The passivation layer protects the low regions from removal while the pad abrades the surface in the high regions. These repetitive actions proceed until the pad contacts the entire surface every time, which ensures the success of good surface planarization. In the static etching experiments, as shown in Fig. 1, without addition of citric acid, the etching rate increases linearly as the HNO_3 volume percentage increases. In contrast, with addition of citric acid, the lower etching rates are obtained. From 9 to 15 vol.% HNO_3 the etching rate increases, but over 15 vol.% the etching rate decreases with the volume percentage of HNO_3. Therefore, with addition of citric acid to HNO_3 solution, a non-native surface film may form which inhibits etching. This copper surface passivation layer is thus suggested due to the formation of citrate complexes [9]. In Fig. 2, the static etching rate of copper film is presented as a function of citric acid concentration in a 3 vol.% HNO_3 solution. The etching rate of copper decreases with increasing the citric acid concentration. However, the passivation effect derived from citric acid saturates as the citric acid concentration reaches ca. 0.01 M.

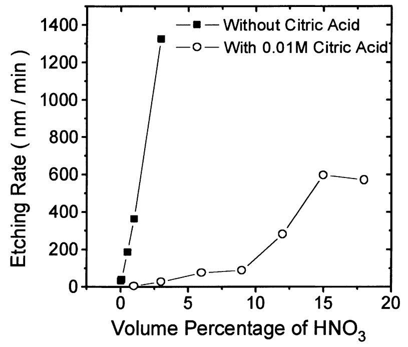

Fig. 1. Etching rate of copper film versus HNO_3 volume percentage with and without citric acid.

Fig. 3 shows the polarization curves of the copper films in the 3 vol.% HNO_3 solution, 0.5 M citric acid solution, and their combination solution (i.e. 3 vol.% HNO_3 + 0.5 M citric acid solution), respectively. As noted in this figure, the curve shape does not change between 0.5 M citric acid with and without 3 vol.% HNO_3. With addition of citric acid to the 3 vol.% HNO_3 solution, the corrosion potential changes from −81.22 mV for 3 vol.% HNO_3 to −60.53 mV for the combination solution, while the corrosion potential is −40.72 mV for 0.5 M citric acid. This difference in the corrosion potential caused by addition of citric acid evidently indicates the formation of a passivation layer. Also, the corrosion current of 3 vol.% HNO_3 is ca. 2110 nA/cm^2. As the addition of 0.5 M citric acid to 3 vol.% HNO_3, the corrosion current becomes 260 nA/cm^2. It indicates that the presence of citric acid inhibits copper corrosion in HNO_3 solution.

Fig. 4 shows the polishing rate of the copper film as a function of citric acid concentration using a 3 vol.% HNO_3 with 0.0005–0.5 M citric acid and 3 wt% Al_2O_3 abrasive

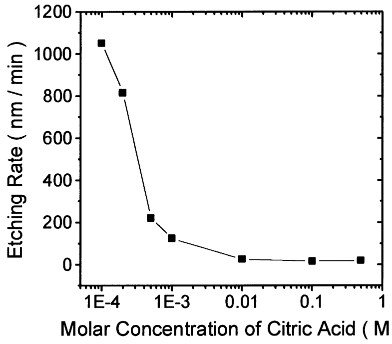

Fig. 2. Etching rate of copper film in 3 vol.% HNO_3 solution with various molar concentration of citric acid.

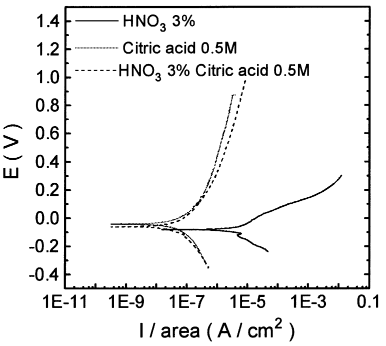

Fig. 3. Polarization curves of copper in 3 vol.% HNO_3 solution, 0.5 M citric acid, and their combination solution.

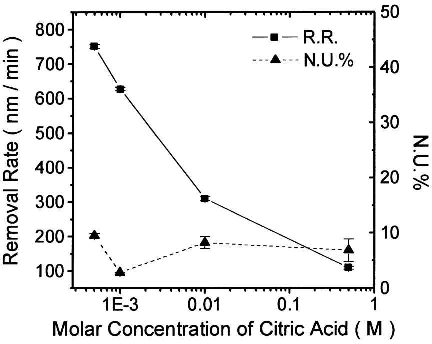

Fig. 4. Removal rate and nonuniformity of copper film as a function of citric acid concentration using a 3 vol.% HNO_3, 0.0005–0.5 M citric acid, and 3 wt% Al_2O_3 abrasive slurry.

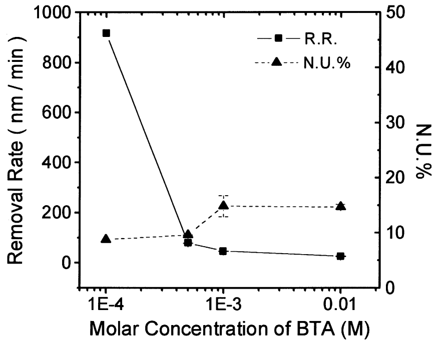

Fig. 5. Removal rate and nonuniformity of copper film as a function of BTA concentration using a 3 vol.% HNO_3, 0.0001–0.01 M BTA, and 3 wt% Al_2O_3 abrasive slurry.

slurry. As noted in this figure, the polishing rate decreases with the addition of citric acid and the across-wafer nonuniformity remains below 10%. In contrast, Fig. 5 shows the polishing rate of the copper film as a function of BTA concentration using a 3 vol.% HNO_3 with 0.0001–0.01 M citric acid and 3 wt% Al_2O_3 abrasive slurry. As shown, the polishing rate of the copper film decreases with addition of BTA, but the across-wafer nonuniformity shows close to 10% or higher than 10%. Clearly, the HNO_3-based slurry using citric acid as an inhibitor gets the better polishing rate and nonuniformity than that using BTA as an inhibitor. Accordingly, during Cu-CMP using HNO_3-based slurry, citric acid can play a successful role as a corrosion inhibitor in forming a passivation layer tightly adhered to the copper surface.

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