Electrochemical aspects of copper chemical mechanical planarization (CMP) in peroxide based slurries containing BTA and glycine

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Received 22 August 2003; received in revised form 11 November 2003; accepted 15 November 2003

Abstract

The electrochemical behavior of copper was studied in Na₂SO₄ solutions (pH 4), containing peroxide, benzotriazol (BTA) and glycine. The effect of BTA was initially evaluated in sulfate solution without peroxide and it was established that once BTA is present, copper undergoes a strong passivation process in a potential range below 0.2 V (SCE). At potentials above 0.2 V the protective layer of BTA is destroyed and copper suffers from localized corrosion attacks. Positive potentiodynamic sweep of the potential resulted in increase of anodic currents at potentials above 0.2 V and hysteresis appearance resulting in the formation of wide and deep pits on the surface of the copper substrate. The addition of H₂O₂ to BTA containing solutions resulted in a rapid increase of OCP to values significantly higher than 0.2 V, leading to initiation of copper localized corrosion processes.

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Keywords: Potentiodynamic; Mechanical planarization; Saturated calomel reference electrode

1. Introduction

Many types of slurry developed for copper chemical mechanical planarization (CMP) contain hydrogen peroxide [1–15]. Hydrogen peroxide is a powerful oxidizer and can be effectively used in various solutions in a wide range of pH values. Besides, H₂O₂ is a very clean oxidizer, which does not require post-CMP cleaning, because its reactions are accompanied only with oxygen and hydrogen evolution, hydroxide-ions and water formation. This, by itself was one of the main reasons for the development of peroxide based slurries containing only water and hydrogen peroxide [6–15]. H₂O₂ concentration in these solutions is varied from 1 to 30 vol.%, while the pH values of such solutions are in the range of 4.5–3.5, decreasing with any increase in H₂O₂ content [7,8].

Potential–pH diagram [16] predicts active copper dissolution in media at this pH range. Hence, one can expect an increase in copper dissolution rate with an increase in peroxide concentration due to increase in the cathodic reaction acceleration, as was reported for Fe(NO₃)₃ and nitric acid [13]. However, the expected increase in copper dissolution rate with peroxide H₂O₂ content was found only once the peroxide concentration was in the region of 1–3%. Further increase in H₂O₂ concentration resulted in reduction of dissolution rate [3,5]. Many research groups [1–10] suggested that the decrease in copper etch rate with increase in hydrogen peroxide concentration (>3%) was a result of copper passivity.

Similar elucidation was also suggested by Molodov et al. [14], describing copper behavior in HClO₄–H₂O₂ media. It was assumed that copper passivity is provided by OH radicals absorbed on Cu surface [14]. Copper passivation due to formation of oxide film in peroxide solutions was also reported by other researchers [5,15]. However, the values obtained for copper dissolution rate and reported in these works can be hardly attributed to copper passivity. For example, copper dissolution rate of 10 nm/min was recorder in 15% H₂O₂ [9,10]. From corrosion point of view, this dissolution rate is high enough (>5 mm per year), and can be rather attributed to active dissolution than to passivity. The question arises from these studies is what is the role of hydrogen peroxide in reducing copper dissolution rate at such unfavorable conditions (acidic solution with pH values below 4).
In this sense, it was also reported that a rapid copper passivation in peroxide containing solutions can be obtained with the addition of benzenesulfonato (BTA) and glycine [17–20]. This work attempts to provide more insight into the electrochemical behavior of copper in peroxide solutions containing both BTA and glycine, providing more knowledge on the role of hydrogen peroxide and these additives.

2. Experimental

Pencil-type copper electrodes were produced by mounting pure copper metal rod (99.9995 wt. %, ∅, 3.5 mm) in an epoxy resin. The electrodes were freshly wet-abraded to a 1200 grit finish prior to each experiment. The electrochemical measurements were performed in a three electrode electrochemical cell with the use of a potentiostat (273A EG&G). The electrochemical cell was equipped with Pt-wire counter electrode and saturated calomel reference electrode (SCE), connected to the cell through a Luggin–Habber capillary. Previous work by our group demonstrated that solutions of H₂O₂–H₂O are characterized with a very low conductivity [21]. The polarization characteristics of copper measured in such solutions is mainly determined by high IR drop, which make the interpretation of electrochemical behavior of tested metal highly difficult. In order to decrease the role of IR-drop, peroxide solutions were prepared using sodium sulfate (Na₂SO₄) solutions (1 and 10 g/l). H₂O₂ concentration was in the range of 1–15%. BTA concentration was varied between 0.001 and 0.1 M while glycine (C₂H₅NO₂) concentration was set on 0.1 M. Solutions were prepared from DI water and chemically pure reagents without any further purification. The pH value of all solution was 4 and was adjusted by the addition of sulfuric acid. Evaluation of copper electrode morphology in the solutions was conducted with the use of high resolution scanning electron microscopy (HRSEM).

3. Results and discussion

3.1. The electrochemical behavior of copper in peroxide solution without the addition of BTA and glycine

Fig. 1 presents anodic behavior of copper in 10 g/l Na₂SO₄ solution containing 3 vol.% H₂O₂ (pH 4). Anodic characteristics were measured potentiodynamically at different scan rates subsequent to a cathodic pretreatment (1 min exposure at −1.3 V) of copper electrode, which was conducted in order to reduce native copper oxides covering the electrode surface during its exposure in air and in the solution. Cathodic pretreatment was followed immediately by a positive (anodic) potentiodynamic sweep of the applied potential. The onset of anodic currents at a scan rate of 100 mV/sec occurred at approximately 0.0 V. Positive sweep of the applied potential at this scan rate resulted in a gradual increase in the anodic current, similarly to the results obtained from Na₂SO₄ peroxide-free solution (Fig. 1, inset), which are associated with copper active dissolution. The onset of anodic currents is positively shifted at a scan rate of 25 mV/s and is taking place at 0.03 V. The anodic current peak can be clearly seen in a potential region between 0.4 and 0.5 V. The onset of anodic current is increased with a decrease in the scan rate: onset of 0.1 and 0.3 V were measured at 5 and 1 mV/s, respectively. Current values measured at the anodic current peak markedly decreased while the peak becomes narrower with a decrease in the scan rate (Fig. 1). During further shift of the applied voltage in positive direction (potentials above 0.3 V) we observe a rapid acceleration of the anodic current. Decrease in anodic current along with the formation of anodic peak, detected at slow scan rate, can be attributed to a precipitation of copper oxides/hydroxides.

In addition to potentiodynamic measurements, the anodic behavior of copper in 10 g/l Na₂SO₄ solution with 3 vol.% H₂O₂ was also evaluated potentiostatically. The potentiostatic measurements were conducted at different potentials correlated with the potential range of anodic current peak appearance. The potentials were applied immediately subsequent to a similar cathodic pretreatment as described earlier. The results obtained from the potentiostatic measurements are shown in Fig. 2. As can be seen, exposing the copper at applied potentials below 0.4 V (region of anodic current peak, Fig. 1) is accompanied with a significant current decrease that can be attributed to the formation of protective layer of copper oxides or hydroxides covering the surface. However, at potentials above 0.4 V (region of anodic current increase, Fig. 1) the situation is changed dramatically. Although copper exposure was also accompanied with a current decrease, this decrease in anodic current occurred only for a short period of time (40 s, as can be seen in Fig. 2), while during further exposure, the anodic current begins to increase. It is reasonable to assume that the increase in the applied potential from 0.3 to 0.4 V results in the initiation of other electrochemical processes.
In order to clarify the differences in electrochemical behavior of copper at potentials below and above 0.4 V, we evaluated copper surface subsequent to exposure at these potentials. Fig. 3 presents SEM micrographs illustrating polished copper surface prior to immersion in the solution (Fig. 3a) and after 5 min of exposure at 0.3 and 0.4 V (Figs. 3b and 3c, respectively). The potentials were applied potentiostatically subsequent to cathodic pre-treatment as described earlier.

As can be seen, the surface of the copper substrates exposed at 0.3 V was covered with a layer composed of copper oxide or hydroxide precipitations (Fig. 3b). However, the morphology of copper oxides precipitation covering the electrode surface at 0.4 V (Fig. 3c) was markedly different, compared with the surface morphology obtained at 0.3 V. The layer covered electrode surface after exposure at 0.4 V appears as being defected. The numerous small pits (black dots in HRSEM micrograph) with a diameter of 10–50 nm were detected at the copper surface (Fig. 3c).

The formation of a dense deposition film of copper oxides at potentials below 0.4 V may be attributed to increase in the solution pH at the electrode-electrolyte interface to values above pH 5.5, where copper oxides remain thermodynamically stable. Increase in pH value at the electrode interface can occur as a result of peroxide cathodic reduction:

\[ \text{H}_2\text{O}_2 + \text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

The formation of this deposit layer covering the copper surface is apparently responsible for the reduction in the observed anodic current at potentials below 0.4 V. Positive shift in the applied potential decreases the cathodic reduction rate of \( \text{H}_2\text{O}_2 \), leading to a decrease in pH values at the electrode/electrolyte interface. This leads to a decrease in the formation rate of copper oxide/hydroxide deposits covering the copper surface. In this case, copper would dissolve rapidly, compared with deposit layer formation rate, at potentials above 0.3 V.

3.2. The effect of BTA and glycine additives on the electrochemical behavior of copper in peroxide based solutions

The addition of BTA to peroxide solutions is suggested as a rapid route for production of instant passive film on the freshly abraded copper surface. The effect of copper protection by BTA addition to peroxide containing solution was also studied by means of potentiodynamic measurements.
Fig. 4. Potentiodynamic (1 mV/s) profiles of copper in Na₂SO₄ solution (pH 4) with (a) BTA and (b) glycine additives; (1) 10 g/l Na₂SO₄ peroxide-free solution; (2) Na₂SO₄ solution containing 0.01 M BTA; (3) Na₂SO₄ solution containing both 0.01 M BTA and 3 vol.% H₂O₂; (4) Na₂SO₄ solution containing 0.01 M glycine; (5) Na₂SO₄ solution containing both 0.01 M BTA and 0.1 M glycine; (6) Na₂SO₄ solution containing 0.01 M BTA, 0.1 M glycine and 3 vol.% H₂O₂.

As can be seen, the addition of BTA to Na₂SO₄ solution (profile 2) significantly decreases the anodic current at potentials below 0.2 V, indicating the formation of a protective layer. During further positive sweep, we observe a slow increase of the anodic currents up to ∼0.4 V and rapid current increase at potentials above 0.4 V. The addition of peroxide to the Na₂SO₄–BTA solution results in a strong increase of the anodic current onset up to 0.4 V. Fig. 4a shows that any shift of the potential in a positive direction is accompanied with a gradual increase of anodic current immediately from OCP. Unlike BTA, the addition of glycine to Na₂SO₄ solution without (profile 4) and with the addition of BTA (profile 5) and H₂O₂ (profile 6) additives practically did not affect the electrochemical behavior of copper. The inhibition properties of BTA are ascribed to the formation of a protective polymeric matrix in the form of [Cu–BTA]n [22–25], while glycine (being the simplest amino acid, exist as zwitterions, or inner salt, in the peroxide solution) apparently does not have the ability to inhibit copper corrosion via the formation of a protective film.

The effect of BTA addition on copper protection capabilities in different potential regions was studied with the use of cyclic polarization. The results obtained from Na₂SO₄ containing 0.01 M BTA are shown in Fig. 5. The figure presents potentiodynamic curves obtained from positive potential scan and backscan. The potential sweep was reversed immediately when specific reverse potential values were achieved at the positive potential sweep. The reverse potential values were in the range of 0.1 and 0.7 V. Reversing the scan at potentials below 0.2 V results in a decrease in the anodic current, compared with values obtained at positive potential scan. This indicates that the copper surface was covered with a stable protective film at potentials below 0.2 V. The marked hysteresis between current values measured at positive potential scan and backscan was detected when the reverse potential was above 0.2 V, indicating that any layer formed at the copper surface is not fully protective at potentials above 0.2 V. Thus, the copper electrode surface suffers from localized corrosion attacks. Similar experiments were conducted in Na₂SO₄ solution containing both BTA (0.01 M) and 3 vol.% H₂O₂ (Fig. 6). Scan reversing was performed at 0.45, 0.47 and 0.52 V. It is evident that at reverse scan potentials above Ecorr the drawn currents are increased.

Fig. 5. Potentiodynamic profile (1 mV/s) of copper in 10 g/l Na₂SO₄ containing 0.001 M BTA.

Fig. 6. Potentiodynamic profile (1 mV/s) of copper in 10 g/l Na₂SO₄ containing both 0.001 M BTA and 3 vol.% H₂O₂.
indicating the poor protective characteristics of BTA layer covering the copper surface.

Fig. 7 presents results obtained with the use of HRSEM evaluating copper substrates previously potentiostatically exposed in 10 g/l Na₂SO₄ solution containing 0.001 M BTA at applied potentials of 0.1, 0.3 and 0.4 V. No corrosion attacks were detected on the copper surface exposed at 0.1 V (Fig. 7a), while at potentials of 0.3 and 0.4 V, the copper surface suffers from localized corrosion attacks, indicated by the numerous pits detected.

4. Conclusions

Copper surface electrode exposed in Na₂SO₄ solutions containing H₂O₂ are covered with precipitation of copper oxides/hydroxides. At potentials below 0.4 V, precipitated copper oxide produces a dense deposition layer that provides efficient copper protection. The formation of this layer can be attributed to a pH increase at the electrode-electrolyte interface as a result of peroxide cathodic reduction. At potentials above 0.4 V, cathodic reduction rate of H₂O₂ decreased, leading to a reduction in pH values at the electrode/electrolyte interface. Consequently, protective characteristics of copper oxide layer are damaged. This results in the formation of nano-scale pitting at the copper surface. BTA provides effective protection of copper in peroxide-free sulfate solution only in a potential region below 0.2 V. At potentials above 0.4 V copper surface suffers from localized corrosion attacks. Peroxide added to sulfate solution containing BTA shifts the potential towards more positive region, above 0.2 V, leading to the development of pitting corrosion processes. Moreover, glycine does not affect the electrochemical behavior of copper in peroxide solutions containing both sulfate and BTA.

Acknowledgements

This research was supported by the Technion-Israel Institute of Technology and by a joint grant from the Center for Absorption in Science of the Ministry of Immigrant Absorption and the Committee for Planning and Budgeting of the Council for Higher Education under the framework of the KAMEA Program.

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