

Investigation of copper deposition in the presence of benzotriazole

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Abstract

The effect of benzotriazole (BTA) on copper electroplating for ultra large-scale integrated circuits interconnection was investigated. BTA exhibited both strong suppressing and brightening effects by modifying the nucleation and growth steps. Electroplating in the presence of BTA followed a random deposition mechanism rather than a selective or preferential deposition mechanism. As a result, the crystal orientation intensity and mean aggregates size of the electroplated copper with BTA were much smaller than those of BTA-free, which resulted in an increase in resistivity. The increased resistivity of the electroplated copper in the presence of BTA was recovered to approximately $2 \mu\Omega\text{-cm}$ through annealing at 400°C in a nitrogen atmosphere by grain growth and recrystallization. The amounts of carbon and nitrogen impurities from the BTA were below the detection limit of Auger electron spectroscopy.

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1. Introduction

The material transition from aluminum alloys to copper as interconnection material for ultra large scale integrated circuits is brought with a new process called damascene for building multilevel interconnections. Electroplating is emerging as a new powerful copper deposition process for high aspect ratio damascene structure due to its relatively lower process cost and process temperature [1,2], especially to excellent gap-filling capability. To achieve the superconformal filling prerequisite to damascene structure formation, the electrolyte for copper electroplating should contain several additives such as a suppressor, a brightener, and an accelerator. Although some of the suppressors and brighteners for metal electroplating have been investigated for some time [3–8], little is known about their mechanisms and even the meanings of the names of three additives are mingled with each other. Suppressors

are known to block the active sites, inhibit the charge transfer from seed layer to copper ions in the electrolyte, and subsequently reduce the deposition rate at the entrance of via or trench. The brightener makes the electroplated copper visually ‘bright’. Kardos and Foulke [9] reported three possible mechanisms for brightening: grain refining; diffusion-control leveling; and random deposition. Since grain refining, random crystal growth, and suppressing are basically affected by ‘adsorption’ of the additive, it is possible that both brightening and suppressing can be embodied from one additive.

Benzotriazole ($\text{C}_6\text{H}_4\text{N}_3\text{H}$, BTA), one of the organic nitrogen compounds that have been widely used as inhibitors of metal corrosion [10–12], is also an important additive for copper plating [13–15]. In particular, the role of BTA as a brightener at concentrations greater than $100 \mu\text{M}$ in a sulfate electrolyte [16] and the structure of adsorbed BTA on the metal surface have been shown [10,17]. The action of BTA on bright copper electrodeposits has been empirically characterized [18,19]. But in order to apply BTA to device fabrication, more fundamental understandings of the effect of BTA

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on copper electroplating in a device-applicable level, which is including the resistivity of the plated copper, is needed. Furthermore, it is important to decrease the amounts of organic additives in the electroplating solution with respect to resistivity. Therefore, BTA action as a suppressor should be investigated. In this work, we demonstrated the efficacy of BTA as an additive for copper electroplating, the electrical properties of the deposits, and the heat treatment effect on electroplated copper in the presence of BTA.

2. Experimental details

A 40-nm-thick TiN film as a barrier metal and a 70-nm-thick Cu film as a seed layer were deposited sequentially on a p-type (100) oriented silicon wafer, using metal organic chemical vapor deposition and physical vapor deposition, respectively. The front side of the wafer was set on a 1×1-cm Cu plate window. The surrounding area of the plate was masked with an insulating Teflon coating that protects the plate from exposure to the electrolyte. After immersion into a 1:200 diluted NH₄OH solution to remove native oxide on the Cu seed layer [20], the surface root mean square (r.m.s.) roughness of Cu seed layer was measured to be 1.44 nm.

The electrolyte was composed of 1 M H₂SO₄, 0.05 M CuSO₄, deionized (DI) water, and various BTA concentrations of 0, 0.05, 0.083, 0.12 and 0.17 g/l. Copper electroplating was carried out at –400 mV for 400 s and the constant potential for Cu electroplating was applied by a PAR 263 potentiostat (EG&G Princeton Applied Research Corporation) with respect to a saturated calomel electrode (SCE) at room temperature. An electronic grade Cu bar (1-mm diameter, 3 cm in length) was used as an anode for copper deposition. All samples after electroplating were rinsed carefully with DI water and dried in a continuous N₂ stream.

Annealing was performed from 100 to 600 °C for 30 min in a N₂ atmosphere at 20 torr to study the improvement of the electrical properties due to grain growth and recrystallization of the electroplated copper.

Two samples for each concentration of BTA were measured using field emission scanning electron microscopy (FESEM, JEOL, JSM-6330F) and contact mode atomic force microscopy (AFM, Digital Instruments, Dimension 3100 SPM) to get the deposition thickness and surface morphology. The twice-measured thickness and surface morphology at a given BTA concentration were in good agreement within 2% difference. Cyclic voltammetry and double layer capacitance (C_{dl}) measurements were conducted to verify the BTA adsorption and its effect on cathodic deposition. A Pt wire was used as an anode for cyclic voltammetry and an AC signal for double layer capacitance measurements was applied by a PAR 5210 Lock-in amplifier (EG&G

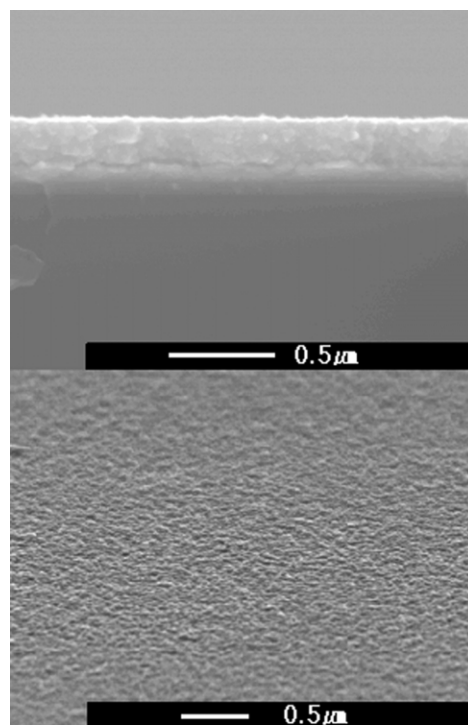


Fig. 1. FESEM micrographs of cross-section and surface morphology of the electroplated copper films in the presence of BTA.

Princeton Applied Research Corporation). Sheet resistance (R_s) measurement was performed using a four-point probe station. Fourier transform infrared (FTIR) spectroscopy was used to investigate the BTA chemisorption sites. X-Ray diffraction (XRD) and Auger electron spectroscopy (AES) were used to analyze the crystallinity and impurities of the electroplated copper.

3. Results and discussion

3.1. BTA as a suppressor and a brightener

Copper was deposited at –400 mV for 400 s with varying the BTA concentration. Without BTA addition, the electroplated copper (standard specimen) had deposition thickness and a surface roughness of 500 nm and 8.63 nm, respectively. Fig. 1 shows a typical SEM picture of the electroplated copper layer with BTA addition. The AFM analysis of the deposits with BTA according to deposition time is shown in Fig. 2. Fig. 2a–e represents the seed surfaces, electroplated copper from electrolyte with 0.17 g/l BTA for 10, 50 and 400 s, and the electroplated copper without BTA addition for 400 s, respectively. Fig. 2e shows three-dimensional hemispherical large aggregates with a relatively low number density of $3.0 \times 10^9/\text{cm}^2$ while (Fig. 2b–d) show small cone-like aggregates with a number density of $1.2 \times 10^{10}/\text{cm}^2$. BTA adsorption accounts for the large number of nuclei and small aggregate size of Fig.

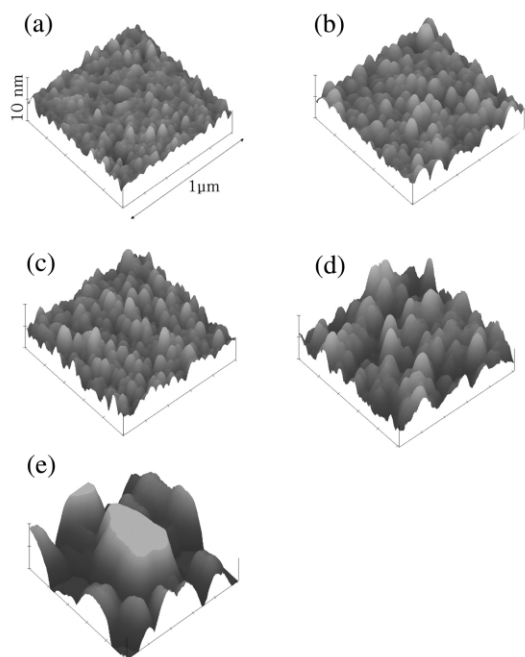


Fig. 2. AFM images of the electroplated copper films from an electrolyte containing 0.17 g/l BTA for various deposition times of (a) 0, (b) 10, (c) 50, (d) 400, and (e) 400 s, no BTA. The deposition potential is -400 mV (vs. SCE). For all images, the scan size is $1 \times 1 \mu\text{m}^2$ and the z -range is 10 nm.

2b–d. BTA possibly adsorbs at the active sites of the copper surface and this results in a relatively uniform surface energy distribution [18], that is, there are few preferential active sites available for deposition. Since the active sites are blocked by BTA adsorbates, copper deposition occurs at the randomly distributed surface sites. Consequently, random deposition with a nucleation rate four times higher than that of the BTA free is observed (Fig. 2d,e). The adsorbed BTA also inhibits the lateral diffusion of copper adions [18], thus lateral growth, which is indispensable for three-dimensional growth, is blocked and two-dimensional small aggregates dominate [21]. This phenomenon is seen in Fig. 2b–d, which shows only slight vertical growth of aggregates with increasing deposition time. Fig. 3a shows that both the deposition thickness and surface roughness reduce with increasing BTA concentration. Generally, the decrease in deposition thickness results in the decrease in surface roughness. In this case, however, the decrease in roughness with BTA addition is not the result of the decrease in deposition thickness, since the surface r.m.s. roughness of a 700-nm-thick copper film electroplated with 0.17 g/l BTA is 5.2 nm (not shown here). This value is much smaller than that of a standard specimen (8.63 nm) which is 200 nm thinner in thickness. The significant decrease in both thickness and surface roughness of the deposits in the presence of

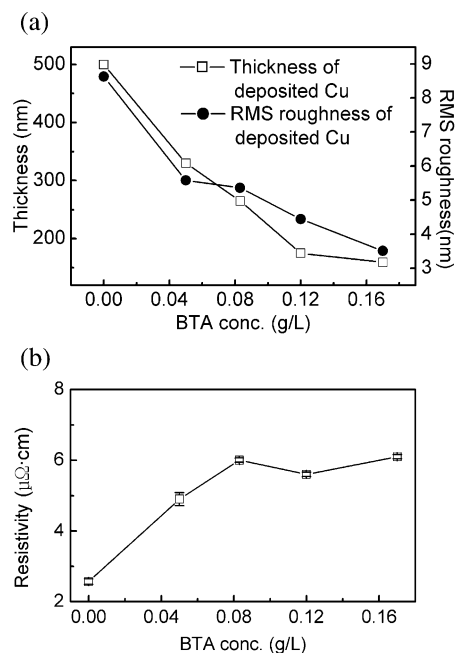


Fig. 3. (a) Deposition thickness, r.m.s. surface roughness and (b) resistivity change of the electroplated copper in the presence of various BTA concentrations. All electroplating were carried out at -400 mV (vs. SCE) for 400 s.

BTA suggests the possibility that BTA acts as both a suppressor and a brightener in copper electroplating.

The suppressing and brightening effects of BTA are basically due to BTA adsorbates. Fig. 4a,b shows the

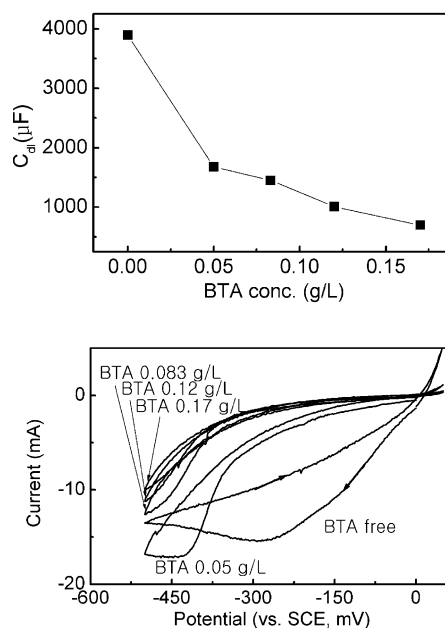


Fig. 4. (a) Double layer capacitance and (b) cyclic voltammogram for the electroplated copper as a function of the BTA concentration. Double layer capacitance measurement was performed at -400 mV (vs. SCE) DC potential superimposed by 5 mV AC signal and the scan rate of cyclic voltammetry was 20 mV/s.

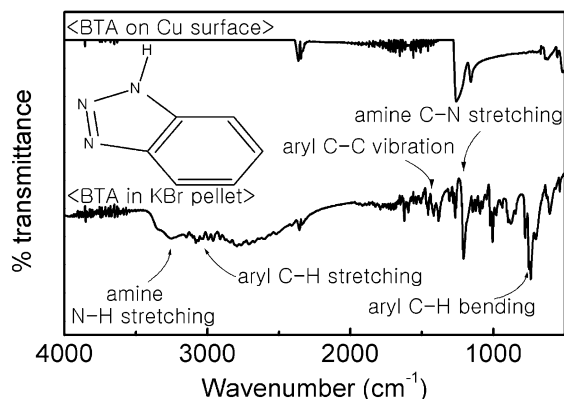


Fig. 5. FTIR spectra of pure BTA powder (transmittance) and a Cu-BTA film on copper (reflection).

change in the double layer capacitance and cyclic voltammogram as a function of BTA concentration, respectively. The figure shows that the double layer capacitance decreases with increasing BTA concentration. The double layer capacitance change shown in Fig. 4a agrees very well with the deposition thickness and surface roughness trend shown in Fig. 3a. Furthermore, the cyclic voltammetry results presented in Fig. 4b suggest three aspects. First, the very small amount of added BTA alters the I - V relation. As the BTA concentration is increased, the cathodic deposition peak moves further in the cathodic direction indicating that the consumption rate of copper ions at the cathode surface is retarded. This is important indirect evidence for charge transfer inhibition by BTA adsorbates. Secondly, the current density at the same potential is reduced when BTA is added. The amount of reduction in current density depends on the BTA concentration, which is possibly due to the active sites occupation by BTA adsorbates. Finally, BTA adsorption is not a faradaic process, which means no electrons are transferred between BTA and the electrode and no structural change in BTA occurs.

In summary, when BTA is used as an additive, additional nucleation sites are produced by the applied current and the reduced mean free path of adions along the surface follows two-dimensional growth. Both the reduced current density and the two-dimensional growth of deposits are the suggested mechanisms for the suppressing action of BTA and the small aggregates that are caused by inhibited surface diffusion are a key feature of the bright deposits.

3.2. Adsorbate molecular structure

To investigate both the exact chemisorption sites in BTA molecule and the structure of BTA adsorbates, FTIR analysis was done, with the results shown in Fig. 5. The transmittance spectra of pure BTA were obtained

using KBr pellets and the reflection spectra of the BTA interaction with the surface copper atoms were obtained from the electrodeposits with 0.17 g/l BTA. Due to the thin layer of the deposits, the incident angle of the reflection spectra was set at 80° . In the BTA transmittance spectra, N-H and C-N peaks corresponding to the amine stretch (3300 and 1250 cm^{-1}), aryl C-H stretching and bending peaks, and aryl C-C vibration peaks (3030 , 800 and 1400 cm^{-1} , respectively) can be observed. However, all but the C-N stretching peak disappeared in the reflection spectra. This implies that both the $\text{Cu}_{\text{surf}}\text{-N}$ (nitrogen previously bonded with hydrogen) and the $\text{Cu}_{\text{surf}}\text{-phenyl}$ (possibly with delocalized electrons in benzene ring) bonds are involved. Previous researches suggested the perpendicular orientation of the adsorbed BTA through $\text{Cu}_{\text{surf}}\text{-N}$ bonding and the flat adsorption geometry [10,17]. But from this FTIR study, it can be easily postulated that BTA adsorbates show a flat orientation through the participation of benzene ring in the surface adsorption and that the copper ions are connected by doubly bonded nitrogen. BTA was known to adsorb at the copper surface in a Cu(I)-BTA complex form when Cu ions exist in the electrolyte [13,22]. The Cu ions were suggested to form a bond with a doubly bonded nitrogen in theazole ring of BTA and eachazole ring was also known to be bonded to two Cu ions forming a continuous polymer-like chain connected by a $\text{N-Cu}^+\text{-N}$ bond. The thin Cu-BTA complex layer may act as a grain refiner rather than as a physical barrier for electron transfer.

3.3. Properties of electroplated copper with BTA

Fig. 3b shows the resistivity of the deposits with varying BTA concentration. In contrast to the low resistivity of deposits without BTA, 2.6 $\mu\Omega\text{-cm}$, the resistivity of the deposits increases with increasing BTA concentration up to maximum value of 6 $\mu\Omega\text{-cm}$. Two explanations for the increased resistivity are proposed: small aggregate size and relatively undeveloped (111) texture. As we mentioned above, the BTA adsorbates inhibit surface migration of Cu adions. Subsequent small grains result in an increase in the number density of grain boundaries [23]. According to the Mayadas-Shatzkes model [24], the resistivity is inversely proportional to the grain size, which is directly proportional to the number density of grain boundaries due to the electron scattering. This relationship concurs with the comparison between experimental observations of aggregate size and resistivity. The decreasing tendency of aggregate size, shown in Fig. 6, due to the increased amounts of BTA adsorption agrees very well with the trend of increasing resistivity with BTA concentration (Fig. 3b).

Fig. 7 shows the XRD analysis of the seed layer, as-deposited, and 400 $^\circ\text{C}$ annealed specimens both with

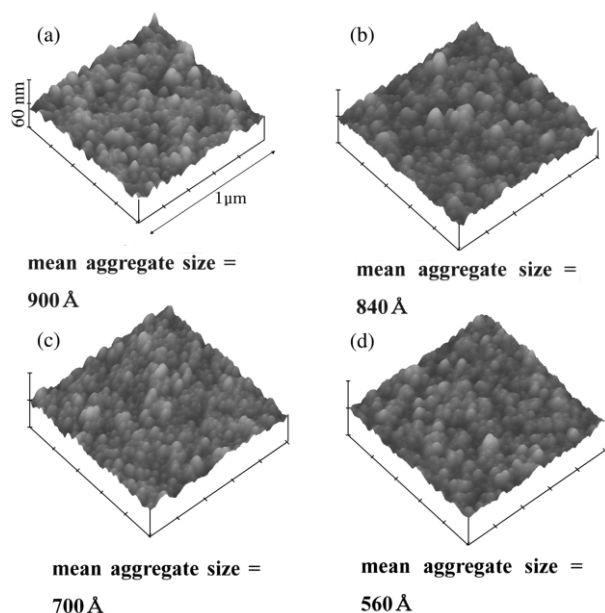


Fig. 6. AFM images of the electroplated copper films from an electrolyte containing (a) 0.05, (b) 0.083, (c) 0.12, and (d) 0.17 g/l BTA. For all images, the scan size is $1 \times 1 \mu\text{m}^2$ and the z-range is 60 nm.

and without BTA. As presented in Fig. 7, the electroplated copper without BTA (standard specimen) shows a dominant (111) orientation as well as a small (200) peak. However, the (111) orientation intensity of the deposits with BTA is much smaller when compared to the standard specimen. This relative small (111) intensity is due to the generation of additional nucleation sites followed by random deposition caused by the BTA adsorbates. When the surface is covered with large amounts of adsorbates, random deposition is preferred to selective deposition [25]. As deposition progresses, this random deposition is intensified by both the accumulated randomness of the underlayer and the inhibited growth of the (111) texture by BTA adsorbates. Thus, the poorly developed (111) texture can also explain the increase in resistivity.

Impurity incorporation in the electroplated copper with 0.17 g/l BTA was characterized by AES depth profiling analysis and is shown in Fig. 8. The C and N atoms of the BTA molecule, Cu and Ti atoms of the wafer, and O atoms were analyzed along the depth direction. As shown in Fig. 8, the amounts of C and N incorporation in the deposits are far below the detection limit of the AES analysis and an almost pure copper film is observed.

3.4. Annealing effect

High temperature furnace annealing at 200–600 °C was performed to improve the electrical properties. Fig. 9a shows the reduction ratio of the R_s vs. annealing temperature for both deposits with (0.17 g/l) and

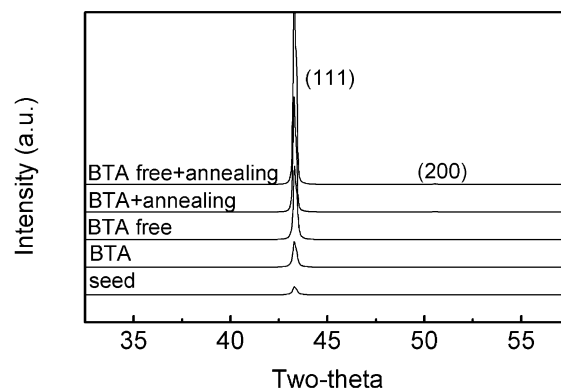


Fig. 7. XRD patterns of the seed layer, as-deposited, and annealed specimens of both with and without BTA. BTA concentration is 0.17 g/l and anneal condition is 400 °C, 30 min in N_2 .

without BTA. The R_s reduction ratio is defined as $(R_{si} - R_{sf})/R_{si}$, where the R_{si} is the R_s of as-deposited copper and R_{sf} is the R_s of annealed copper. All specimens show a maximum R_s reduction ratio at 400 °C. On the assumption that the reduction in sheet resistance is mainly the result of grain boundary elimination due to grain growth, the relatively steep slope of R_s reduction of the deposits with BTA (below 400 °C) results from the higher grain growth activation energy of this deposit due to its small grain size. Furthermore, electroplated copper with BTA exhibits random deposition (see Fig. 7), in which the grain boundary energy is relatively high due to randomly oriented boundaries [26]. Thus the released energy after grain growth, which is the driving force for crystal growth, is much higher than in selective deposition. This higher released energy results in a higher recrystallization rate of the deposits with BTA, as shown in Fig. 9a. Accelerated grain growth at higher temperature, over 500 °C in this case, can cause the agglomeration of grains [27]. By this agglomeration, increase in surface roughness [28], partial decrease in

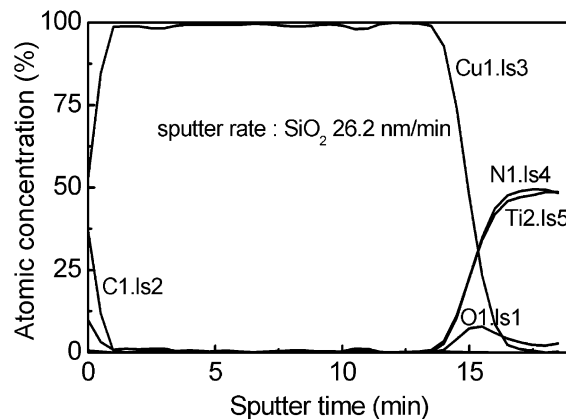


Fig. 8. AES depth profile of the electroplated copper from an electrolyte containing 0.17 g/l BTA. Deposition thickness is 1600 Å.

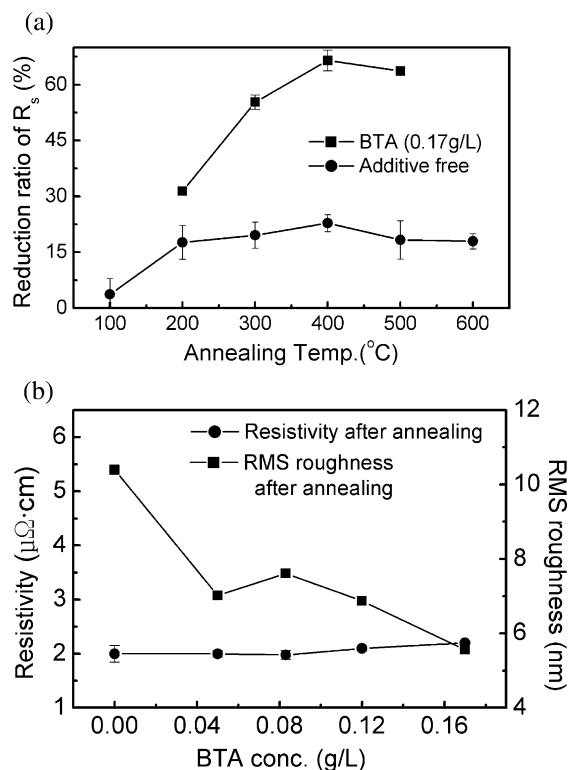


Fig. 9. (a) Reduction rate of the sheet resistance vs. annealing temperature and (b) resistivity and r.m.s. roughness change of 400 °C, 30-min annealed specimens as a function of the BTA concentration.

effective film thickness for electron flow, and even the breakdown of film continuity [27] can occur. Therefore, the agglomeration of grains, resulting in the increase of electron flow resistance, is responsible for the decreased R_s reduction ratio above 500 °C, compared to the 400 °C anneal.

Fig. 9b shows the resistivity and the surface roughness of the annealed specimens with BTA concentration. Though the surface roughness of the deposits with BTA after annealing is approximately 20–60% higher than that of the as-deposited copper, it is still better than that of the BTA-free specimen. It is notable that the resistivity of the annealed specimens is reduced by 59–67% and approaches 2.0–2.2 $\mu\Omega\cdot\text{cm}$, which is the resistivity of the annealed standard specimen. The grain growth and the strong increase in (111) texture after annealing (Fig. 7) account for the decrease in resistivity.

From the simple monitoring of R_s of electrodeposits with BTA (not shown here), it was evident that no self-annealing phenomenon in room temperature occurred. This may be due to the AES-undetected small amounts of impurities that play an important role of pinning of grain boundaries [23], though the AES threshold in sensitivity is somewhat high.

4. Conclusions

The effects of BTA in the electroplating solution on the properties of the deposited copper films were investigated. BTA was found to strongly adsorb on the copper surface as a Cu–BTA complex form, which results in strong inhibition of the surface diffusion of copper ions, lowering the current density and subsequent randomly oriented copper film having two-dimensional small aggregates. This suppressing behavior makes the plated copper quite thin and smooth. High resistivity of the electroplated copper film caused by BTA was recovered to 2 $\mu\Omega\cdot\text{cm}$ as a result of grain growth and recrystallization during annealing at 400 °C in a nitrogen atmosphere. During annealing, the promoted dependency on temperature and the increased amounts of the sheet resistance reduction ratio of the electroplated copper with BTA were the result of randomly oriented high-energy grain boundaries and a small grain size of the deposits. The amounts of carbon and nitrogen impurities from the BTA were below the detection limit of AES.

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