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Influence of Carbon Nanotubes on the Electrodeposition of Copper Interconnects

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ABSTRACT

The electrochemistry of the co-deposition of Cu with carbon nanotubes, CNTs, is studied by voltammetry and chronoamperometry experiments. Electrochemical data show that CNTs have a slightly accelerating influence on the Cu electrodeposition when nafion was added in the bath as a surfactant of CNTs. The amount of CNTs in the deposit is up to 2% by weight. Kinetic data confirm that the addition of CNTs to the Cu baths increases the Cu exchange current density and decreases the equilibrium potential value. The electrical resistivity results show that at room temperature the resistivity of a Cu/CNT composite film (2.47 μΩ·cm) is close to the resistivity of Cu film (2.15 μΩ·cm). A clear decrease of sample resistivity is observed with increasing anneal temperature up to 315 ºC. The resistivity also increases when the concentration of CNTs is increased from 10 mg/l to 100 mg/l in the bath.

INTRODUCTION

The electrochemical deposition of Cu-based interconnects has facilitated the continuing decrease in feature size of advanced IC's [1, 2]. However, as feature size decreases the conductivity of Cu and electromigration resistance also decrease. Recently carbon nanotubes (CNTs) have received a lot of attention due to their electrical, thermal and mechanical properties [3]. There are still significant engineering challenges to be overcome to make CNTs a potential candidate for interconnect lines and vias. To overcome this reliability problem Cu/CNT composites can be a suitable candidate for the future interconnects and thermal interface material. Addition of Cu increases the contact area between the nanotube (1 D) and substrate (3 D contact) which makes it mechanically a strong material that can sustain high electrical or thermal stress cycling [4, 5]. The co-deposition of CNTs may improve the electromigration resistance of Cu interconnect without significantly decreasing the conductivity [6]. The improved electromigration resistance is expected to result from the location of the alloy element at grain boundaries to prevent movement of Cu at those vulnerable points, which may lead to wiring voids (opens) or hillocks (shorts) during operation. Cu/CNT composites can be prepared by powder metallurgy, electroless plating or electrodeposition techniques. To obtain superior properties of metal-CNT composites, it is necessary to achieve a homogeneous dispersion of CNTs throughout the metal matrix. In this study, nafion was used as a surfactant for dispersion of CNTs. Nafion is a sulfonated tetrafluorethylene co-polymer with ionic properties which bears a polar side chain ($-SO_3H$) and hydrophobic backbone ($-CF_2-CF_2$). The hydrophobic backbone strongly anchored to the hydrophobic side-wall of CNTs. On

the other hand the polar side-chain of the polymer imparts sufficient ionic charge to the CNTs surfaces which enhance the solubility of CNTs in liquid solvent [7-9]. In this work, CNTs were added in the typical Cu sulphate bath to achieve homogeneous Cu/CNT composites. Here, we will report electrochemical analysis and kinetics of electrodeposited Cu when CNTs were added in the bath. The microstructure of the deposits was observed by scanning electron microscopy (SEM) and the resistivity was monitored using a four point probe apparatus.

EXPERIMENTAL

The electrochemical experiments were carried out with a computerized electrochemical system (CH Instruments, model 660 B). A commercial three electrode system was used in the experiment. Cu foil (99.99%) was used as a counter electrode. The working electrodes for the electrochemical analysis were glassy carbon (GC) and Cu disk electrodes. The diameters of these electrodes were 3 mm and 4 mm, respectively. Before experiments, the electrode was polished successively by 0.3 μm, 0.1 μm and 0.05 μm alumina powder (alpha alumina polishing powder supplied by Struers). For each stage of polishing, deionised water, (DI) was added with the alumina powder to make a slurry. Between each stage of polishing, the GC was put in an ultrasonic bath for 2-3 minutes to remove the residue of alumina on the GC. After sonication, the GC was cleaned with DI water and dried with nitrogen. After each of the experiment the deposit was chemically stripped at positive potentials 0.5 V for 10 seconds. The reference electrode was saturated mercury/mercury sulphate (SMSE, E^o = 0.641 V (SHE)). Cu was electrodeposited at room temperature from a bath containing 0.24 mol dm^{-3} $CuSO_4$ (Fisher Scientific) and 1.8 mol dm^{-3} H_2SO_4. Multi Wall Carbon Nanotubes (MWCNTs) from Nanocyl were dispersed by 1 weight % nafion (Sigma-Aldrich) in solution using an ultrasonic bath for 20 minutes.

RESULTS AND DISCUSSION

Figure 1 shows the comparison cyclic voltammograms of Cu deposition with/without nafion in the bath. It can be seen that the cathodic peak potential shifts to a more negative value by addition of nafion in $CuSO_4$ bath which represent a suppressor influence on Cu electrodeposition.

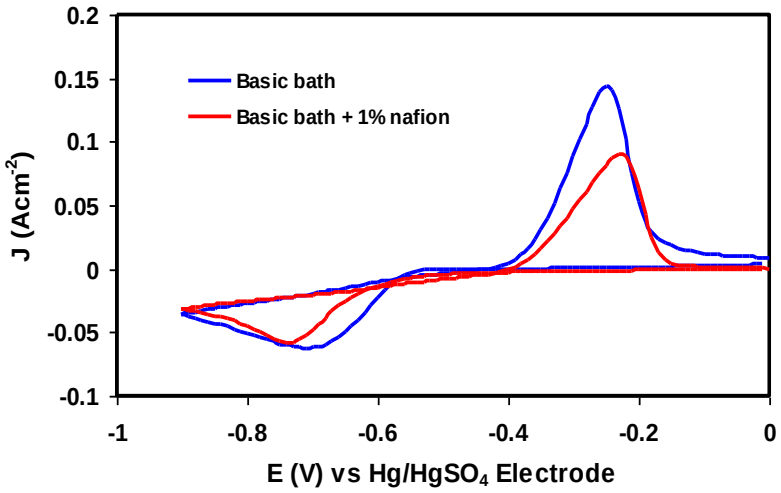


Figure 1. Comparison of cyclic voltammetry plots for Cu deposition from 0.24 mol dm^{-3} $CuSO_4$ + 1.8 mol dm^{-3} H_2SO_4 with and without nafion on a glassy carbon electrode (initial potential: 0 V; scan rate: 0.1 V/s).

Figure 2 shows the comparison cyclic voltammograms of Cu deposition with/without nafion and CNTs. Unlike the case represented in figure 1 above with the addition of CNTs to the bath containing nafion and Cu, the cathodic peak was shifted to less negative potential which represents an accelerator effect on Cu deposition.

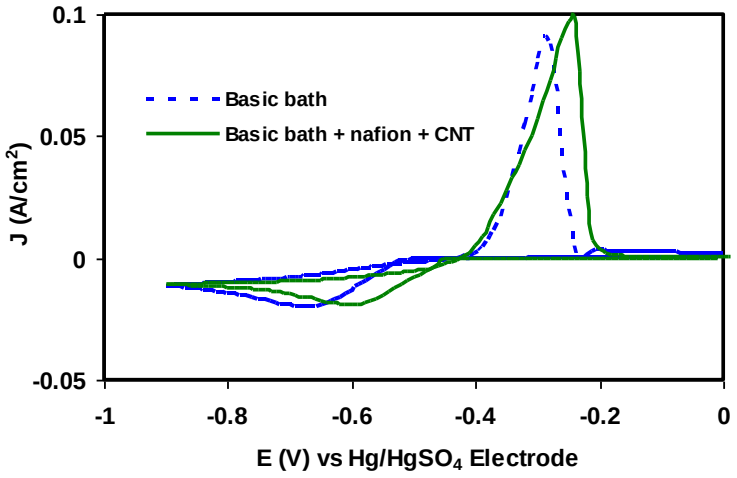


Figure 2. Comparison of cyclic voltammetry plots for Cu deposition from 0.24 mol dm^{-3} $CuSO_4$ + 1.8 mol dm^{-3} H_2SO_4 with and without CNTs on a glassy carbon electrode (initial potential: 0 V; scan rate: 0.01 V/s).

The diffusion coefficient of Cu was calculated from chronoamperometry data using the Cottrell equation and the value was found to be 4.54 x 10^{-6} cm^2/s. This value is close to literature value, 5.4 x 10^{-6} cm^2/s to 9.7 x 10^{-6} cm^2/s [10-12]. Upon addition of nafion in the bath, the diffusion coefficient value of Cu slightly decreases to 4.48 x 10^{-6} cm^2/s and addition of CNTs in the bath, the diffusion coefficient value of Cu slightly increases to 5.13 x 10^{-6} cm^2/s. It is clear that nafion and CNTs in the Cu bath do not have a significant

influence on the diffusion coefficient of Cu. The above results confirm that the Cu/CNT bath is compatible with the Cu bath.

Figure 3 shows the comparison of linear sweep voltammograms of Cu and Cu/CNT composites deposition from Cu based sulphate bath with and without nafion and CNTs using a Cu disk electrode rotating at 2000 rpm. The corresponding Tafel plot is shown in figure 4. The approximate exchange current density, i_0 and the equilibrium potential E_0 values measured for the basic $CuSO_4$ bath are 7.24 mA/cm^2 and - 406 mV, respectively. The addition of nafion has a minor suppressor type behaviour on the Cu deposition as it slightly decreases the exchange current density, i_0 to 7.07 mA/cm^2 and increases the E_0-value to - 410.5 mV. On the other hand, the addition of CNTs has an accelerator influence on Cu deposition as it increases the exchange current density, i_0 to 10.23 mA/cm^2 and decreases the E_0-value to - 403.5 mV.

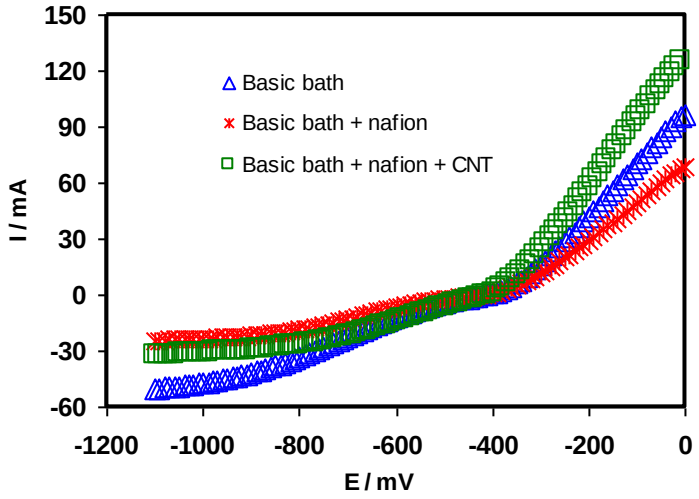


Figure 3. Comparison of cyclic voltammetry plots for Cu deposition from 0.24 mol dm^{-3} $CuSO_4$ + 1.8 mol dm^{-3} H_2SO_4 with and without CNTs on a Cu disk electrode rotating at 2000 rpm (initial potential: 0 V; scan rate: 0.1 V/s).

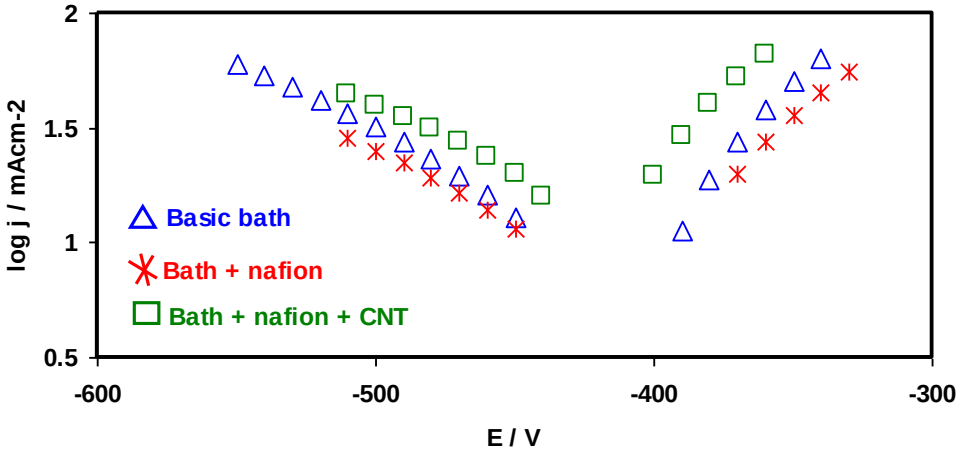


Figure 4. Comparison of Tafel plots for Cu deposition with and without additives using a rotating disk electrode.

Figure 5 shows the SEM image of a Cu/CNT film deposited on a Cu coated Si wafer coupon. In the early study the length of CNTs was less than a micron and the diameter was 10 to 12 nm. The size was too small to resolve under SEM. To solve this issue, large CNTs (length 5-9 µm, diameter 110-170 nm) were added in the bath instead of short CNTs. The large CNTs were dispersing in the Cu bath with the aid of nafion using a similar procedure as short CNTs. In the SEM image, CNTs were clearly observed in the Cu matrix.

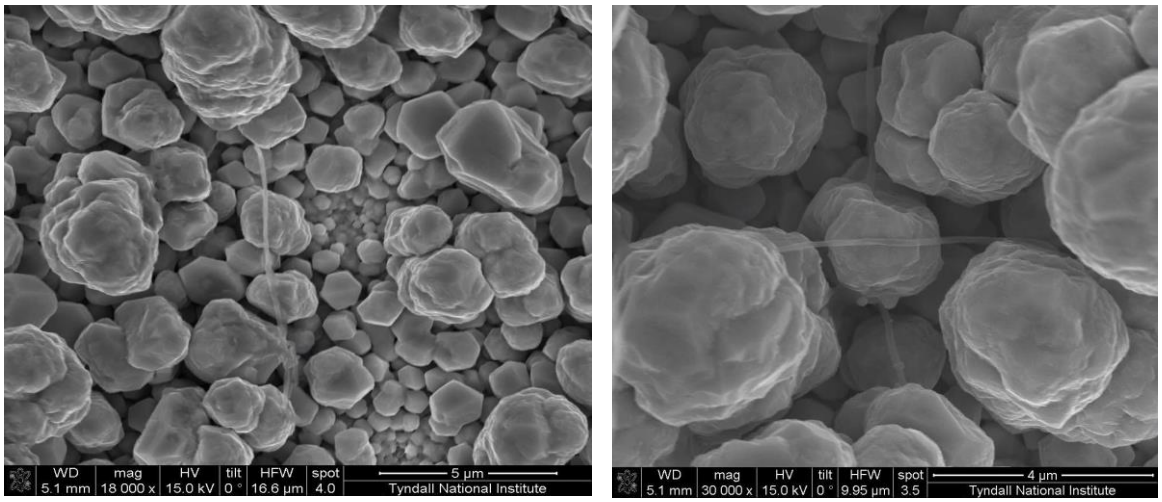


Figure 5. SEM images of a Cu/CNT composite film, deposited at 50 mA/cm^2 for 20 minutes. Bath composition was 0.24 mol·dm^{-3} $CuSO_4$ + 1.8 mol·dm^{-3} H_2SO_4 + 1% nafion + 0.01 gm/l CNT.

Figure 6 shows the XRD peaks of a Cu/CNT film deposited on a Cu-coated Si sample. Besides the Cu (111) and Cu (200) peaks, a (220) Si peak was also observed in the XRD.

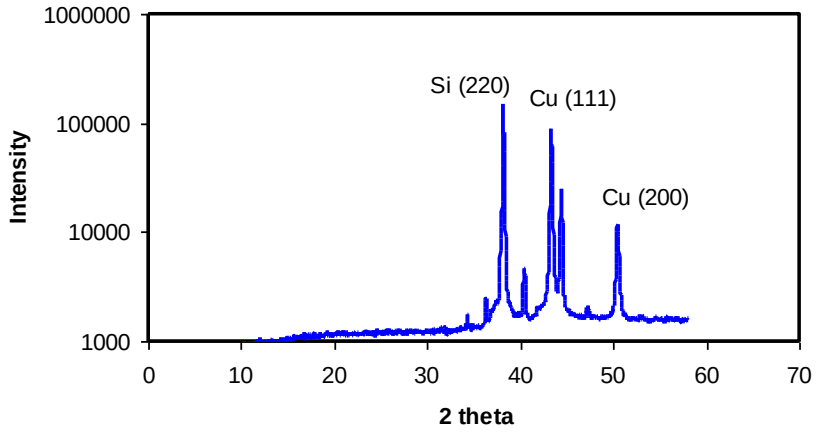


Figure 6. XRD pattern for the Cu/CNT composite film, deposited at 50 mAcm^{-2} for 20 minutes. Bath composition was 0.24 mol dm^{-3} $CuSO_4$ + 1.8 mol dm^{-3} H_2SO_4 + 1% nafion + 0.01 gm/l CNT.

The amount of CNTs in the deposit was determined by dissolving the deposit in a HNO_3 solution. The Cu/CNT film was deposited on a 1 x 1 cm^2 Cu foil at a current of 1 A for 1 hour. The concentration of CNTs in the bath was 100 mg/l. After deposition, the

sample was dipped in a hot acidic solution (65 % HNO_3, at 65 °C). The acid solution was then vacuum filtered using PTFE filter paper. The filtration process was repeated at least 5 times to ensure all CNTs were left as a residue on the filter. After filtration, the PTFE membrane was dried in an oven at 80 °C for at least 30 minutes to ensure the membrane was completely dried. The weight difference of the PTFE membrane before and after filtration gives the amount of CNTs in the deposit. Figure 7 shows a SEM image of CNTs on a PTFE membrane after filtration of the Cu/CNT deposit. The amount of CNTs in the deposit was 1.12 % by weight when long CNTs (length 5-9 μm, diameter 110-170 nm) were added in the bath. On the other hand, the amount of CNTs in the deposit was 1.56 % when short CNTs (length < 1 μm, diameter 9.5 nm) were added in the bath. The density of CNTs is close to 1.3 gm/cm^3 and pure Cu is 8.89 gm/cm^3 which indicates the CNTs in the deposit are up to 12 % by volume.

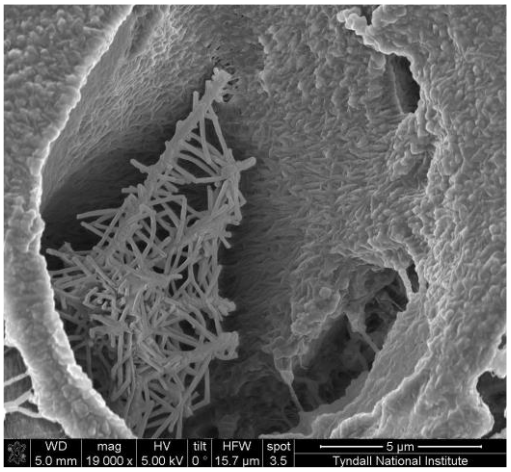


Figure 7. SEM image of CNTs on a PTFE membrane after filtration of dissolved Cu/CNT composites deposited on a Cu foil.

Figure 8 shows the comparison of the resistivity changes of Cu and Cu/CNT over time at room temperature. The film was electrodeposited on a sputter Cu-coated Si substrate. The deposition current density was 15 mA cm^{-2} and deposition time was 2 minutes. The film thickness as measured by using surface profilometry was approximately 660 nm. The resistivity of the sample was monitored using a four point probe apparatus. We also compared the resistivity change of Cu/CNT composites obtained from a Cu/CNT bath using cetyl trimethyl ammonium bromide (CTAB). CTAB is a cationic surfactant and is widely used to disperse CNTs in suitable solvents [13-15]. In each case we took 4 samples and recorded the average resistivity. It can be seen from the analysis at room temperature over time that the resistivity did not change significantly. The electrical resistivity results showed that at room temperature the resistivity of the Cu/CNT composite film is 2.43 μΩ·m. When nafion was used as a surfactant of CNT the resistivity is close to the resistivity of a Cu film deposited (2.17 μΩ·cm). The resistivity of the Cu/CNT composite film was higher when CTAB was used instead of nafion as a surfactant.

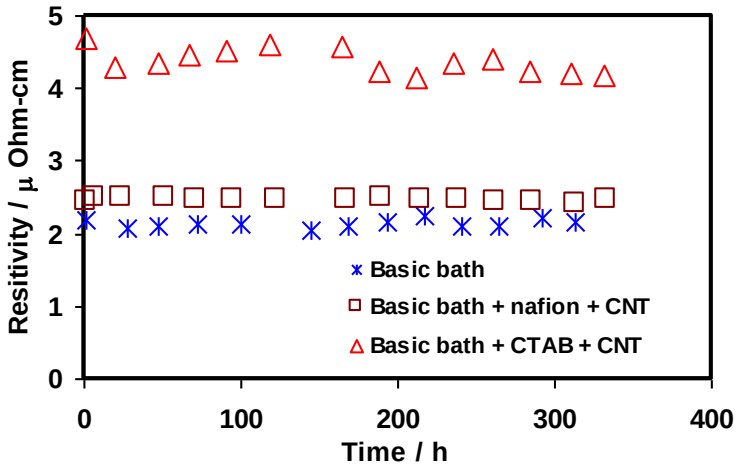


Figure 8. Comparison of the resistivity changes of Cu vs. Cu/CNT composites on planar substrate at room temperature over time using different surfactants in the bath.

Figure 9 shows the microstructure of Cu/CNT composites film on a Cu-coated Si substrate before and after annealing at 315 ºC in nitrogen. It can be seen that the room temperature microstructure of the Cu composite was rough. The samples were annealed at 315 ºC with a hold at the peak temperature for 20 minutes. It is clear from SEM images that due to the anneal at higher temperature the surface became finer. The possible cause of the fine surface is due to grain refinement at high temperature annealing. It can be seen that a clear decrease of sample resistivity was observed with increasing annealing temperature which is shown in figure 10. The resistivity value of Cu film approaches that of bulk Cu value (1.67 μΩ·cm) after annealing at 315°C for 20 minutes. Also the resistivity of Cu/CNT composites film decreased with increasing annealing temperature. The electrical resistivity of the Cu/CNT composites film became 1.89 μΩ·cm when the sample was annealed at 315 °C for the case of the composite film which was deposited from a nafion containing bath. The conductivity increase of the composite film was probably due to a decrease in the interface resistance between CNTs and Cu matrix at the higher temperature.

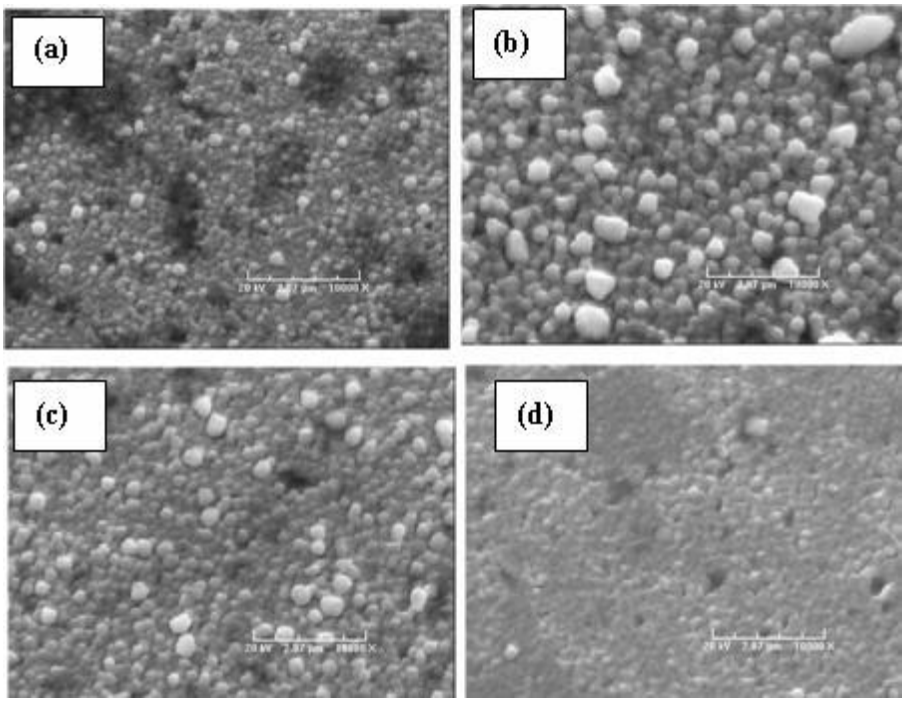


Figure 9. SEM microstructure of Cu/CNT composite films at (a) room temperature, and after annealing at (b) 215 ºC, (c) 265 ºC and (d) 315 ºC for 20 minutes in nitrogen. The bath contained nafion and CNT. Deposition condition was 15 mA/cm^2 for 2 minutes.

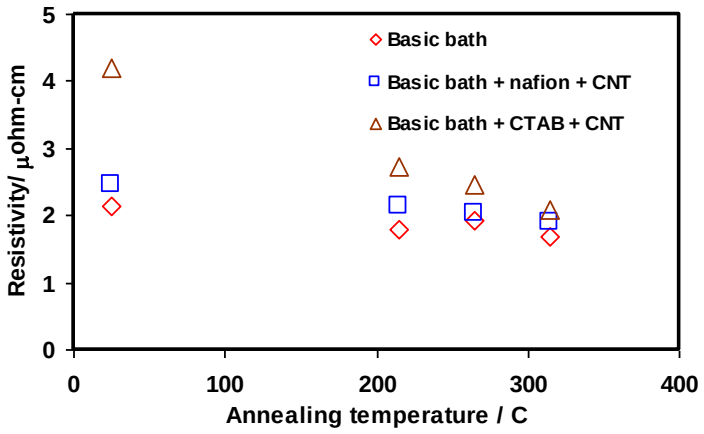


Figure 10. Comparison of the resistivity changes due to annealing for 20 minutes at various temperatures for Cu vs. Cu/CNT composites on planar substrate using different surfactants in the bath.

Higher electrical resistivity was observed when the concentration of CNT was increased from 10 mg/l to 100 mg/l in the bath. It can be seen from figure 11 that when the samples were annealed at higher temperatures up to 315 ºC for 20 minutes, the resistivity decreased from 2.46 µΩ·cm to 1.89 µΩ·cm for 10 mg/l CNTs and 2.7 µΩ·cm to 2.19 µΩ·cm for 100 mg/l CNTs in the bath. The resistivity increase of the higher CNTs content deposit is probably due to the increased CNTs content which increases the interface resistance between CNTs and Cu in the composites.

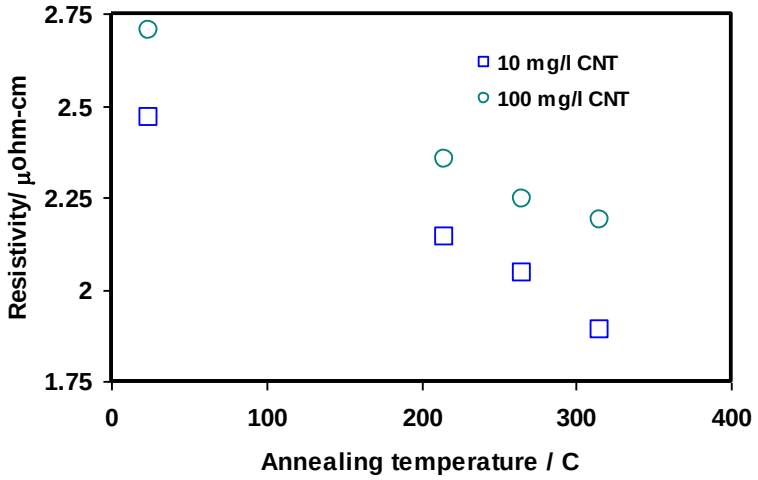


Figure 11. Comparison of the resistivity change of Cu/CNT composites after annealing for 20 minutes at higher temperature using 10 mg/l and 100 mg/l CNTs in the bath.

CONCLUSIONS

The electrochemistry of the codeposition of Cu with CNTs was studied by voltammetry and chronoamperometry. Electrochemical data show CNTs have a slight accelerator influence on the Cu electrodeposition when nafion was added in the bath as a surfactant for CNTs. The amount of CNTs in the deposit is close to 2 % by weight. Kinetic data confirm that the addition of CNTs to the Cu baths increases the Cu exchange current density slightly and decreases the equilibrium potential value. The electrochemical data confirm that the Cu/CNT bath is compatible with the Cu bath. The electrical resistivity results shows that at room temperature the resistivity of Cu/CNT composites film (2.47 μΩ·cm) is close to the resistivity of Cu film (2.15 μΩ·cm). A clear decrease in sample resistivity is observed with increasing annealing temperature. The resistivity also increases when the concentration of CNTs is increased from 10 mg/l to 100 mg/l in the bath.

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