Fabrication of CNTs/Cu composite thin films for interconnects application

Ping Liu, Dong Xu, Zijiong Li, Bo Zhao, Eric Siu-Wai Kong, Yafei Zhang

National Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Institute of Micro/Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200030, PR China

1. Introduction

For many years, copper has been used as a conventional material for interconnects of ultra-large scale integrated circuits (ULSI), due to its excellent electrical conductivity. However, with the feature size of interconnects in ULSI decreasing gradually to nanometer scale [1], it becomes difficult for Cu to work for nano-interconnects due to the effects of electron surface scattering and grain boundary scattering from Cu electrodes. Carbon nanotubes (CNTs) can be considered as an ideal candidate to play the role of “incorporating element” in composite interconnects, because of its one-dimensional structure, as well as unique electrical, mechanical and thermal properties [2–7].

Incorporation techniques play an important role in the performance of CNTs/Cu composites. The electroplating is widely employed for the incorporation of CNTs into metal matrix at room temperature [8]. Chen et al. have reported the tribological behavior of Ni-multiwalled carbon nanotube (MWCNT) composite coatings, fabricated by electroplating [9]. However, the normally obtained samples have non-uniformly dispersed CNTs in the aqueous electrolyte and hardly controlled CNTs content because of aggregation of CNTs into packed ropes or entangled networks induced by strong van der Waals interaction.

In this paper, we report a novel method by combining electrophoresis deposition (EPD) and electroplating techniques to fabricate CNTs/Cu composite films. EPD is an economical and versatile processing technique for the production of novel coatings or films of CNTs on conductive substrates [10]. The electrical properties and the structure of both CNTs/Cu films and pure Cu films after annealing at different temperatures (200–500 °C) were studied. The results indicate that the electrical properties of CNTs/Cu composite thin film fabricated by our method after annealing are much better than that of conventional, pure Cu thin film.

2. Experiment

In order to improve the dispersion of CNTs in ethanol (the EPD solvent), CNTs were firstly undertaken heat treatment (1600 °C, vacuum) and acid treatment (3:1 H2SO4:HNO3, 60 °C, 35 min). Mg(NO3)2(10–4 mol/L) was added to CNT/ethanol suspension as the additive. The CNTs/Mg(NO3)2/ethanol suspension was then ultrasonically agitated for 2 h. The CNTs concentration is 10 mg/L. The suspension was stably placed for two days and then centrifuged to disperse the large-sized CNTs conglomerations. The upper part of the liquid in the suspension was taken out as a solution for electrophoresis procedures. Glass substrates were coated by chromium and copper by magnetron sputtering. The glass/Cr/Cu substrate and stainless steel plate with a constant gap of 2 cm were used as the cathode and anode electrode, respectively. A DC power of 40 V was applied for 4 min. After EPD deposition, electroplating was used to deposit Cu film onto the substrate. The composition of the electroplating bath was 65 g/L CuSO4 · 5H2O + 196 g/L H2SO4 + 50 mg/L HCl. Current density was 15 mA/cm2. The duration time was 2 min. For comparison, pure Cu film was directly deposited onto Cu substrate under the same electroplate condition. Then these films were cleaned with deionized water and dried in a vacuum oven at room temperature. Finally, the CNTs/Cu composite film and pure Cu film were cut into several pieces for annealing treatment at 200, 300, 400 and 500 °C in a vacuum oven for 0.5 h.

Received 28 April 2008
Accepted 28 April 2008
Available online 15 May 2008

Keywords:
Carbon nanotube
Interconnects
Composite film
Annealing

Article info

© 2008 Elsevier B.V. All rights reserved.

Article history:
Available online 15 May 2008

0167-9317/$ - see front matter © 2008 Elsevier B.V. All rights reserved.

The thickness of the sample was measured by STYLUS Profiler. A conventional four-probe technique was used to measure the electrical resistance for the as-prepared sample. The surface morphology and structure of these samples were studied by field-emission-scanning electron microscopy (FE-SEM) and X-ray diffractometer (XRD), respectively.

3. Results and discussion

Figs. 1 and 2 are the SEM images of the as-prepared pure Cu and CNTs/Cu composite films after annealing at different temperatures. It can be observed that there are some differences between annealed Cu film and CNTs/Cu composite film.

Fig. 1 shows that the grain size of pure Cu becomes larger as the annealing temperature increases. Compared with pure Cu film, the grain size of CNTs/Cu film becomes much larger as the annealing temperature increases as shown in Fig. 2. And the adherence between CNTs and Cu matrix becomes stronger. Some small particles appear on the surface of Cu film and CNTs/Cu composite film at the annealing temperature of 500 °C. Furthermore, some narrow grooves can be found to appear on the surface of CNTs/Cu film at the annealing temperature of 400 °C. These particles and grooves increase the surface area of films.

The Cu film and CNTs/Cu composite films without annealing treatment were patterned into resistance stripe (Fig. 3) by lithography to measure the thickness of samples. The average thicknesses of original Cu film and CNTs/Cu composite film are 1.087 μm and 1.133 μm, respectively.

The annealing temperature dependence of the sheet electrical resistance for as-deposited CNTs/Cu films and pure Cu films is shown in Fig. 4. The sheet electrical resistance at 25 °C is the sheet resistance of initial sample without annealing treatment.

Fig. 4 shows that the sheet electrical resistance of CNTs/Cu composite film decreases linearly as the annealing temperature increases and reaches the minimum value at 300 °C, it then increases as the annealing temperature increases. Comparison shows that the variation trend of sheet resistance of Cu film is similar to that of CNTs/Cu composite film, but the resistance reaches minimum value at the annealing temperature of 400 °C. The resistance of Cu film increases abruptly at 500 °C and that of CNTs/Cu film increases at 400 °C, due to the increase in surface area, i.e., an increase in surface scattering of electrons [11]. The resistance of CNTs/Cu films decreases much faster than that of pure Cu films, as the annealing temperature increases. Therefore, it is indicated that the electrical conductivity of Cu has been improved due to the incorporation of CNTs after annealing.

![Fig. 1. SEM images of Cu film after annealing at different temperatures: (a) room temperature, (b) 200 °C, (c) 300 °C, (d) 400 °C and (e) 500 °C.](image-url)
XRD patterns of as-prepared pure Cu film (Fig. 5) and CNTs/Cu film (Fig. 6) after different annealing temperature reveal the structure of the samples. The crystallization of CNTs is not extensive enough to show XRD peaks, so only XRD peaks for Cu in CNTs/Cu composite film are observed. The patterns show that the intensities of Cu peaks become stronger as the annealing temperature increases. Cu (111) plane reaches its maximum peak value at 300 °C for CNTs/Cu film, but Cu (111) plane reaches its maximum peak value at 400 °C for pure Cu film. It is worth noting that the relative peak intensity of Cu (111) plane in CNTs/Cu film was even stronger than that of pure Cu film at the same annealing temperature. However, the relative peak intensity of Cu (200) plane in pure Cu film becomes much stronger than that of CNTs/Cu film. The result indicates that Cu (111) plane is more preferred orientation in composite with CNTs than Cu (200) plane by using our method after annealing.

According to the results above, the CNTs/Cu composite thin film after annealing has larger mean grain sizes and better...
preferred-oriented grains than that of conventional pure Cu thin film. Large mean grain sizes and preferred-oriented grains can improve the electromigration reliability of thin films [12,13].

4. Conclusion

CNTs/Cu composite thin films were successfully prepared by combining electrophoresis and electroplating techniques. The sheet electrical resistance of CNTs/Cu films decreases faster than that of pure Cu films, as the annealing temperature increases. The grain size of CNTs/Cu film becomes much larger than that of Cu film at the same annealing temperature. The peak intensity of Cu (111) plane in CNTs/Cu film was stronger than that of pure Cu film. Our results verify that the CNTs/Cu composite thin film fabricated by electrophoresis and electroplating deposition techniques after annealing has obviously better electrical properties than that of conventional pure Cu thin film. We have demonstrated that the combination of electrophoresis and electroplating techniques provide a new method for interconnects.

Acknowledgements

This work is supported by Hi-Tech Research and Development Program of China No. 2007AA03Z300, Shanghai-Applied Materials Research and Development fund No. 07SA10, National Natural Science Foundation of China No. 50730008, Shanghai Science and Technology Grant No: 0752nm015 and National Basic Research Program of China No. 2006CB300406.

References