Co-Deposition of Carbon Nanotubes with Copper

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Carbon nanotubes (CNTs) are known for their unique structures and excellent electrical and thermal properties. This makes them good potential candidate for reinforcement and improvement of other properties of metals. Extensive investigation had been conducted on this subject. [1~3]. Dai et al [4] used a simple effective-medium model and showed that at room temperature 50% lowering of resistivity of Cu may be achievable, because of the ballistic conduction of carbon nanotubes which have mean free path which is orders of magnitude longer than that of copper.

One of the present author previously studied [5, 6] copper and CNTs' co-deposited using pulse reverse plating. Ultra high tensile strength was achieved. Most of the previous work was done on thick blanket films or large features using chemistry without additives. CD co-deposited CNTs with Cu without additives are very rough. Pulse reverse plating gives smoother surface morphology, but small voids were observed in 200nm trenches (figure 1). The present day, electronic feature dimensions are in nanometer range and have high aspect ratios. In order to fill such small trenches and vias, Cu plating bath with organic additives are used. These additives may be expected to change the CNTs behavior in solution. We have developed a technique which permits us to use a commercial damascene copper plating bath from which we co-deposited CNTs with copper under DC condition and achieve smooth surfaces. In this paper, we report electroplating of Cu/CNTs composites using commercial chemistry which include organic additives such as suppressor, accelerator and levelers. Feature size of 50nm to 2µm is used for the experiments. A 200mm Si wafers with test structures was plated to evaluate the possibility of extendibility of this technology to standard semiconductor practice. The plating results will be shown. The electrical conductivity characterization was performed.

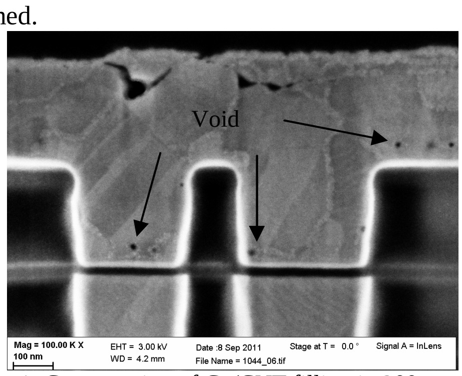

Figure 1: Cross section of Cu/CNT filling in 200nm trench

In our study, carbon nanotubes were pretreated with nitric acid and rinsed with DI water and copper containing solution. Carbon nanotubes were positively charged in this process and were able to be co-deposited with copper. Three additives used in our make-up Cu electrolyte are Chemistry C, same as IBM production. By adjusting the concentration of CNTs and additives, Cu/CNT composites were successfully plated into features down to 50nm. (Figure 2) Fracture surface of composite film showed very unique structure. The "pointy" structure indicated the existence of carbon nanotube inside the deposit and good interfacial adhesion between copper and carbon nanotubes [5].

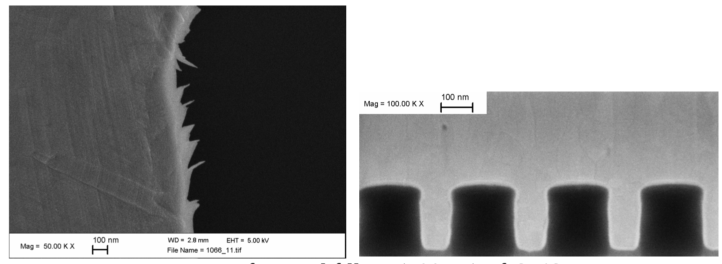

Figure 2: Fracture surface and filling (100nm) of Cu/CNTs

The plated blank films were analyzed by SIMS [Figure 3]. The result showed that carbon signal in composite is 2~3 order higher than in pure copper which was plated at exactly same condition, which correspond to 0.11wt% of carbon (1100ppm) in the film. We also dissolved the plated film in solution and the UV-Vis analysis showed the carbon peak of 0.1wt% by calculation.

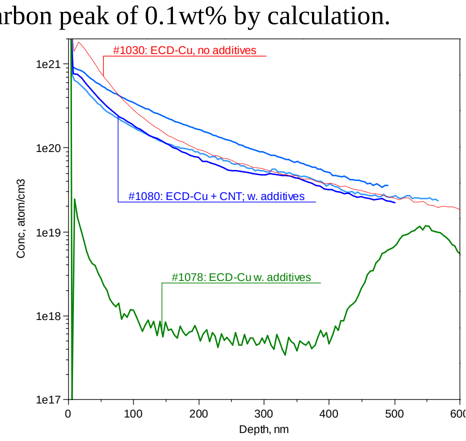

Figure 3: SIMS analysis on Cu and Cu/CNTs composites.

Electrical resistance of the material was measured by four-point probe on blanket wafer. The film thickness was measured by combining FIB and SEM analysis. After annealing, the average resistivity of 1.6 µOhm-cm was measured. There is a 10% decrease compared with pure copper plated under the same condition (1.8 µOhm-cm). The electrical resistance was also characterized in our test structure on 200mm wafers. After deposition, samples were CMP-ed first and also annealed after NBLoK cap deposition. Among 11 test chips, the average resistance was 22.1Ohm and 21.09Ohm for pure copper and Cu/CNTs composites respectively. And composites also showed a tighter resistance distribution.

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