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Fabrication of copper/carbon nanotube composite thin films by periodic pulse reverse electroplating using nanodiamond as a dispersing agent

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ABSTRACT

A method for forming a carbon nanotube (CNT) reinforced copper (Cu) composite by an electrodeposition process has been developed. Nanoscale diamond particles were introduced as a dispersing agent to prevent aggregation of carbon nanotubes while performing electrodeposition, or what is commonly referred to as electroplating. The technique involves co-deposition of Cu and CNTs in an electroplating process that uses both direct current and a sequence of forward and reverse pulses. Reverse pulse times were varied in order to examine parameters for dispersion of carbon nanotubes in the resultant composite material. Electrical resistivity, surface morphology, and composite structure were investigated using a probe station, scanning electron microscopy, and x-ray diffraction, respectively. Experimental results show carbon nanotubes can be dispersed uniformly in a Cu/CNT composite due to the role played by the nanodiamond particles in CNT de-aggregation. Direct current electrodeposition yields high deposition rates while reverse pulse electrodeposition is a slower process although necessary for providing a higher percentage of CNTs integrated into the composite.

1. Introduction

One dimensional carbon nanotubes (CNTs) and two dimensional graphene are some of the most well-known carbon materials [1–3], in which their exceptional properties make them ideal candidates for carbon and metal matrix composites [4]. In the past decade, carbon reinforced composite materials have attracted great attention due to their enhanced electrical and mechanical properties leading to a variety of applications. For example, nickel (Ni)/CNT composites can be used in scanning micromirrors [5], antimony/tin/CNT anodes in Li^+ batteries [6], and copper (Cu)/CNTs in electronic packaging [7,8]. Silver/CNT hybrid nanoparticles can be used in antimicrobial applications [9], Cu/graphene along with Ni/graphene can be used in applications relying on improved strength [10]. Cu/CNTs (multiwalled) exhibit improved frictional properties compared to pure Cu [11].

The extraordinary reinforcement of these composites is attributed to the metal grain refinement and homogeneous dispersion of carbon nanomaterial [12,13]. In order to obtain fine grains in the composites, control during the fabrication process is critical. Several methods have been reported for dispersing carbon materials in the metal matrix; examples include: ball milling [14], squeeze casting [15], spark plasma sintering [16], and electrodeposition [17,18]. Electrochemical co-deposition has proven to be an effective way for obtaining metal/carbon composites, since this technique results in good interfacial bonding [19]. Both direct current (DC) electroplating and periodic pulse reverse (PPR) electroplating have been used for depositing composites. PPR plating involves a series of forward currents with an off time followed by reverse currents with an additional off time for electroplating bath stabilization. PPR electroplating produces films with a finer grain size and lower porosity than films obtained by DC electroplating [20]. In addition to grain size and porosity, dispersion of the nanomaterials is important since CNTs have a tendency to form agglomerates due to high surface area to volume ratio, electrostatic interactions, and a strong Van der Waals attraction. A uniform dispersion of carbon is required for reinforcement in metal/carbon composites.

Conventional methods of preventing agglomeration in a composite involves agitation of the carbon materials or functionalizing the carbon materials with a surfactant. In this paper, nanodiamond (ND) particles were used to aid the dispersion of CNTs to prevent introduction of unwanted agglomerates in the composites; NDs are simply additional nano-scale carbon materials. The NDs allow the formation of stable colloidal suspensions of CNTs/NDs [21], which enables an extensive array of applications due to their excellent mechanical and optical properties, high surface area, and tunable surface structure [22]. Nanostructured

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materials consisting of CNTs and NDs possess a combination of outstanding functional properties with just the two constituents or in combination with other materials [23].

Cu is a common metal deposited by electrodeposition. In the fields of thermal management and electronic packaging, investigation of Cu/CNT composites has experienced rapid growth due to the hybrid material's low coefficient of thermal expansion, high thermal conductivity, and high carrier density [24–28]. CNTs suppress electromigration in Cu at high temperatures, reduce the skin effect in Cu interconnects, lower the thermal mismatch between Cu and a silicon wafer. Thus the Cu/CNT composites are studied as a possible alternative solution to problems encountered with Cu-based interconnects. In this work, CNT/ND is used in the formation of Cu/CNT composites and reported. A sulfuric acid-based Cu electroplating solution was used to study the colloidal stability of CNT/NDs introduced into the plating solution at varying concentrations. A series of Cu/CNT composite films were prepared on planar surfaces by DC electroplating and by PPR electroplating to determine the relationship between experimentally measured electrical resistivity and electroplating process conditions. Based on these results, future work will involve fabrication of vertical interconnects filled with the Cu/CNT composite using NDs as a dispersing agent.

2. Experimental details

A schematic showing the experimental setup used for electroplating is shown in Fig. 1(a). The suspension contains acid treated NDs with a zeta potential of −45 mV and carboxylated CNTs (MWCNT-COOH) purchased from Cheap Tubes, Inc. (Brattleboro, VT). The multi-walled carbon nanotubes (MWCNTs) have a length of 1–2 μm and a diameter of 10–20 nm. The NDs have an average volumetric aggregate size of 60–70 nm. MWCNTs and NDs were mixed in deionized (DI) water at a weight ratio of 1:10:100 (MWCNTs:NDs:DI water). This mixture forms a suspension that is dark in color. It was added to Enthone's Cu electroplating solution, MICROFAB DVF 200. The proportions for the bath were 1 part suspension to 100 parts Cu plating solution. This gave the mixture a concentration of approximately 0.01 wt.% CNTs and 0.1 wt.% NDs. A layer of titanium (~17 nm thick) and Cu (~200 nm thick) were deposited by electron beam evaporation on a silicon wafer to act as an adhesion and electroplating seed layer, respectively. A window in a thin polymer layer with an area of 1 cm^2 was formed on each diced silicon piece through which electrodeposition occurred. The polymer masking enabled samples with the same area to be prepared for comparative testing. The electrodeposition was carried out with agitation using magnetic stirring. DC and PPR currents were applied by a Wafer Power Technology power supply. PPR electroplating was performed by applying periodic pulsed power with current cycles as shown in Fig. 1(b). When using the PPR method, the forward pulse current density, J_f, was 50 mA/cm^2 and power ON time, T_{fON}, was 50 ms. The reverse pulse current density, J_r, was 10 mA/cm^2 and power ON time, T_{rON}, was in the range of 10–75 ms. The forward pulse OFF time, T_{fOFF}, and reverse pulse OFF time, T_{rOFF}, were both 100 ms. The films resulting from co-electrodeposition of Cu/CNTs were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), and 4-point probe measurements. The SEM is a JEOL 7000 field emission SEM. We used it in secondary electron mode at an operating voltage of 10–25 kV. XRD data were collected at an ambient temperature on a Philips X'Pert MRP diffractometer (Cu Kα X-radiation, λ = 1.54060 Å), in a Bragg-Brentano para-focusing optics configuration (40 kV, 40 mA). The 4-point probe electrical measurements were performed on a probe station with two Keithley meters, a 6220 current source meter and a 2182 A nanovoltmeter.

3. Results and discussion

Fig. 2(a) shows a top view of the Cu seed layer after electron beam deposition illustrating film morphology. The Cu covered the wafer surface homogenously while tiny wrinkles can be observed with an appearance similar to water ripples; the origin of the ripples is unknown. However, the roughness can be neglected when compared to the size of the electroplated Cu grains. Low current density DC (4 mA/cm^2) was initially applied for co-deposition of Cu and CNT/NDs for 30 min. The concentration of CNTs and NDs in the electroplating bath was around 0.01 wt.% and 0.1 wt.%, respectively. This low current density was used to determine potential electroplating parameters for performing an experimental investigation of Cu/CNT composites at various process conditions. Fig. 2(b–d) are SEM images that show the morphology of the composite films that result from co-electrodeposition. Though the CNTs did not aggregate, the electrodeposition process step did not produce uniform films. Besides covering the wafer surface, protrusions of electroplated Cu with a snow flake appearance were distributed over the planar sample surface. Fig. 2(c) is a zoomed-in image of the snow flake-like shape. Fig. 2(d) more clearly shows the NDs distributed over Cu branches. The NDs had an average volumetric aggregate size of 60–70 nm. The CNTs were not apparent or visible in the images. Thus optimizing DC plating parameters was necessary to continue the investigation.

It is well known that electroplated microstructures can be affected by current density. Several properties can benefit from low current density deposition for electroplated metals. For example, an optimal current density of 2 mA/cm^2 was found when electroplating stress-free thin metal films [29] while other researchers found a uniform thickness distribution and microstructures with flat profiles could be obtained at an optimal plating condition of 8 mA/cm^2 [30]. Compared to reported results, our electroplating at low current density did not produce homogenous composites. One possible reason is that corrosion occurred in the Cu seed layer in the presence of the sulfuric acid-based Cu electroplating bath [31]. Furthermore, the existence of NDs may have contributed to nonuniform corrosion. The NDs attached to the Cu seed layer could

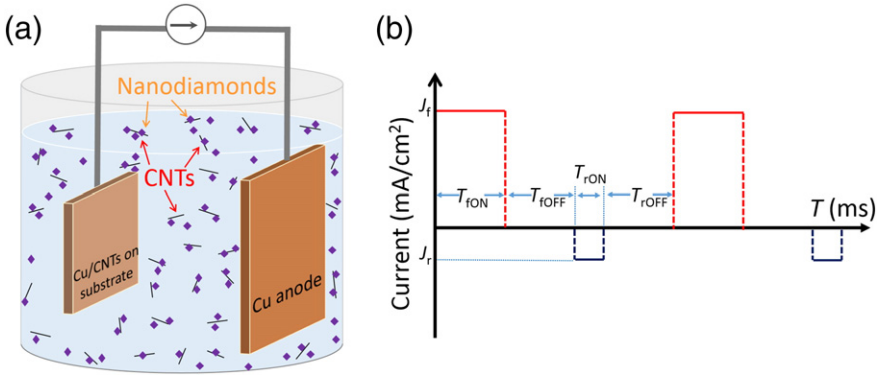

Fig. 1. Schematic of (a) experimental setup for co-deposition of Cu and CNTs and (b) the current waveform for depositing Cu/CNT composites using periodic pulse reverse (PPR) co-electrodeposition.