Low Temperature Carbon Nanotube Film Transfer via Conductive Adhesives

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Abstract
A low temperature process for transferring carbon nanotube (CNT) film from a silicon wafer to a copper surface via conductive adhesives is proposed. Both the close- and open-ended CNT films were successfully transferred to a desirable substrate. The morphologies and electrical properties of the transferred CNT films were studied. An ohmic contact was formed between a CNT film and a highly conductive adhesive, while a semiconductor joint was formed between a CNT film and a high resistivity adhesive.

Introduction
The discovery of carbon nanotubes (CNTs) has prompted an increasing number of investigations on their properties and applications. In particular, CNTs offer many promising characteristics for future electronic and device applications [1, 2] due to their extremely high thermal conductivities [3], outstanding mechanical properties [4] and very high electrical conductivities by the ballistic effect. Although the ballistic transport in a multwalled CNT (MWCNT) displays an electrical resistance of 12.9 KΩ [5], an array or film with thousands of well aligned parallel CNTs can be used as a promising interconnect material in electronic and photonic devices. Till now, several chemical vapor deposition (CVD) methods have been developed to produce well aligned CNT films and arrays [6-8]. In these methods, each catalytic particle can produce a nanotube, and bundling of these neighboring tubes leads to collective vertical growth due to the Van der Walls force among them. Recently, the synthesis of well aligned open-ended CNT films was reported by our group [6]. The open-ended CNT films can improve the electrical conductance of MWCNTs because recent studies have demonstrated that the internal walls of MWCNTs can participate in the electrical transport as well, therefore enabling larger current carrying capability [9].

However, some technical issues hinder the full utilization of the CNTs in microelectronic and photonic manufacturing, which include high processing temperature and poor CNT interfacial adhesion: First, the typical CVD is carried out at 700–900 °C, at which many electronic or photonic devices cannot withstand. Second, the adhesion between the silicon substrate and CNTs is very poor and the low adhesion strength limits the application of CNTs as interconnect materials in the microelectronic packaging due to high contact resistance and the long term reliability issue. Consequently, a novel CNT transfer technology is needed, rather than growing CNTs directly on the devices.

A CNT transfer technology was first proposed by which an open-ended CNT film was transferred to a copper surface via eutectic tin/lead (Sn/Pb) solder [10]. The hollow cavity of the open-ended CNTs will allow the wicking of solder due to the capillary force after the solder melts. This process could overcome the serious obstacles of integration of CNTs into integrated circuits and microelectronic device packages by offering low processing temperatures and improved adhesion of CNTs to substrates. The transferred CNTs can be used to simultaneously form electrical and mechanical connections between chips and substrates. However, the close ended CNT films cannot be successfully transferred by the Sn/Pb solders. Moreover, the solder has technical barriers as CNT transfer medium, such as limited options of substrate surfaces for wetting, adhering and low flexibility in design.

Silver pastes [11] and 70 nm thickness of gold layer [12] were also used to transfer the CNT bundles or films to conductive substrates. However, the process temperatures used are 530 °C and 800 °C, respectively, which are too high to be compatible with microelectronic processes.

Recently, we have demonstrated an ultra highly conductive adhesive for the lead-free interconnect applications, which was composed of nano sized Ag particles, micron sized Ag flakes and an epoxy resin [13]. The resistivity of this adhesive could be achieved as low as 5 × 10⁻⁶ Ω cm, which was even lower than that of eutectic Sn/Pb solder (2 × 10⁻⁵ Ω cm). In this study, this ultra highly conductive adhesive was used as a transfer medium instead of Sn/Pb, which transfers the aligned CNT films to a copper surface. This process can take advantage of certain properties of polymers, such as low processing temperature, better compatibility on substrates and flexible design, etc. The morphologies of the joint structures were investigated and the electrical properties of CNT films transferred via the conductive adhesives were studied.

Experimental
Synthesis of aligned CNT films
The CVD was performed in a horizontal alumina tube (3.8 cm diameter, 92 cm long) housed in a Lindberg Blue furnace. The substrates used in this study were silicon wafers coated with a thin layer of SiO₂ formed by thermal oxidation. The thin support layer of Al₂O₃ and a Fe catalyst were deposited onto the silicon wafer by sequential e-beam evaporation. CVD growth of the open-ended CNTs was carried out with ethylene as the carbon source, hydrogen and argon as carrier gases. The water vapor concentration in the CVD chamber was controlled by bubbling a small amount of argon gas through water held at 22 °C. In all experiments, the water concentration in the furnace tube was maintained at <0.1% until the CVD process was terminated. In addition, close-ended CNTs were synthesized without introduction of aqueous H₂O with the similar process.

Preparation of conductive adhesives
The Ag nanoparticles with an average diameter of 20 nm were first surface functionalized with surfactants [13]. The as-prepared surface functionalized silver nanoparticles and micron sized silver flakes (6:4) were incorporated into a
mixture of bisphenol-A epoxy and hexahydro-4-methylphthalic anhydride (weight ratio: 1.0:75) to form the adhesive. The adhesive was then sonicated for one hour to disperse the fillers in the epoxy resin. Thereafter, an imidazole type catalyst (0.5% weight to the polymers) was incorporated and the mixture was sonicated again for 5 mins. The resistivity of the as-prepared highly conductive adhesive in this study is $3.1 \times 10^{-5} \text{Q.cm}$. As a reference, a high resistance Ag-epoxy formulation was created by dispersing 50 wt% Ag nanoparticles without any surface functionalization into the epoxy resin, the resistivity of which was $58.6 \text{Q.cm}$.

**Characterization Method**

Scanning electron microscopy (SEM) was used to characterize the morphologies of the as-synthesized CNTs and the conductive adhesive transferred CNTs. The SEM is a JEOL 1530 equipped with a thermally assisted field emission gun operating at 10 KeV. To measure the electrical performance of CNT film transferred by the conductive adhesives, the copper top electrodes were deposited on the surface of CNT film with a diameter of 2.1 mm. This test coupon was measured by a four probe method. A Keithley 2000 multimeter equipped with a probe station was used to measure the current-voltage response of CNT film by contacting with the bottom and top electrodes.

Figure 1. SEM images of (a) CNT films grown at a temperature of 750 °C, (b) high magnification SEM image of CNT film in (a).

**Results and Discussion**

Figure 1 showed the SEM images of the as-synthesized aligned CNT film. Due to the high density of the catalyst layer, the CNTs formed a dense film with good alignment. No other residual particles were observed on the CNT walls, as shown in the high magnification SEM image of CNTs (Figure 1 (b)). The surfaces of the CNTs were smooth, and the diameter of each tube was approximately 10 nm.

![CNTs Si Flip Si CNTs Ag filled adhesive Substrate](image)

Figure 2. Schematic diagram of CNT films transferred via conductive adhesives.

The substrate used in this study was a flame retardant level-4 (FR-4) printed wiring board coated by a laminated copper foil. The conductive adhesive was stencil-printed on the FR-4 board. The silicon substrate with a CNT film was flipped over and the aligned CNTs were penetrated through the adhesives with an applied pressure. The adhesive was cured at 150 °C for one and a half hours. Thereafter, the silicon substrate was removed (Figure 2). Thus, the CNT film can form the electrical and mechanical connections onto the copper substrate surface by the conductive adhesive. This process enables CNTs to be transferred and implemented into integrated circuits and microelectronic device packages at a low temperature (150 °C) and with improved adhesion of CNT films or arrays to the substrates.

Figure 3. Photograph of a CNT film transferred onto the copper surface via conductive adhesives.

Figure 3 shows a CNT film transferred onto a Cu-clad FR-4 substrate via a conductive adhesive. This figure indicates that the entire CNT film was successfully transferred onto the substrate because no trace amount of CNTs was observed on the silicon substrate. A cross-sectional SEM image (Figure 4...
clearly shows that the aligned CNT film was bonded to the conductive adhesive. CNTs in the form of bundles were observed after the adhesive curing due to the polymer wetting along the CNT surfaces by capillary force in/between tubes. In the higher magnification SEM image (Figure 4 (b)), it can be observed that the nanotubes inside the bundles still maintain their original aligned structures.

For the electrical measurement of CNT films, the Cu surface of the substrate was used as bottom electrode and Cu top electrodes with a 2.1 mm diameter were DC-sputtered after the transfer process, where four Pt coated probes with tip sizes around 6 μm were used for the four-probe measurement. The configuration of the four-probe experiment is shown in Figure 5. The resistance between two electrodes can be directly obtained from the applied current and the measured voltage.

Figure 4. (a) A cross-sectional SEM image of the well aligned CNT film transferred by conductive adhesives. (b) The higher magnification image of CNT film after the transfer process.

Figure 5. Schematic setup for the I-V curve measurement.

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The I-V characteristics of the as-transferred CNT films via an ultra highly conductive adhesive are shown in Figure 6 (a). A linear relationship between current and voltage for both the open- and close-ended CNT films was obtained, which indicated that an ohmic contact was formed between the CNT
films and the highly conductive adhesive. The resistance of the as transferred open- and close-ended CNT films was 0.024 and 0.090 Ω, respectively. This indicates that both the open- and close-ended CNT films can be successfully transferred by the conductive adhesives. A relatively high resistivity adhesive (ρ = 58.6 Ω·cm) was also used to transfer the open-ended CNT films to copper surface. Figure 6 (b) shows the I-V characteristics of the CNT film transferred by the high resistivity adhesive, where a nonlinear I-V behavior was observed which can be typically found at non-ohmic contacts such as a joint between a semiconductor and a metal connection. Therefore, the electrical properties of the whole device can be altered by the delivery medium (conductive adhesives). Ohmic or non-ohmic joints can be easily formed by just changing the resistivity of the conductive adhesives.

Conclusions

Both the open- and close-ended CNT films were successfully transferred to the copper surface via conductive adhesives at a low temperature (150 °C). The CNT films formed bundles due to the polymer wetting along the tubes by capillary force in/between tubes. The nanotubes inside the bundles still maintained the aligned structures. An ohmic contact was formed between a CNT film and a highly conductive adhesive. The resistance of the as-transferred open- and close-ended CNT films was 0.024 and 0.090 Ω, respectively. The significance of the transfer method in this study is not only to provide a low temperature CNT transfer technique, but also a highly conductive CNT film or array for lead-free interconnect applications. At the same time, the polymer materials can provide a flexible design and can easily wet many surfaces, which enable transferring CNTs to different kinds of substrates.

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References

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