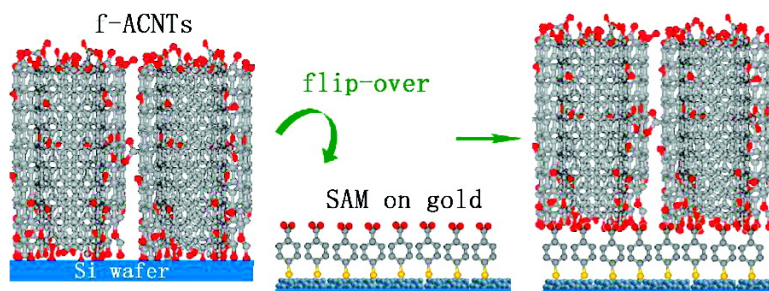Communication

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Self-Assembled Monolayer-Assisted Chemical Transfer of In Situ Functionalized Carbon Nanotubes

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Carbon nanotubes (CNTs) have attracted much interest due to their extraordinary electrical, thermal, and mechanical properties and their wide range of potential applications.[1–3] Aligned CNT (ACNT) structures make the best use of the 1-D transport properties of individual CNTs and have been proposed as the promising candidate for thermal interface materials (TIMs),[4,5] electrical interconnect materials,[6] gas sensors,[7,8] and electrodes,[9–11] and more. However, the problems with the chemical vapor deposition (CVD) process for ACNT growth, such as high growth temperature and few substrate materials suitable for the CVD growth, become barriers for ACNT applications. To circumvent these problems, great efforts have been made to separate the CVD process and the ACNT assembly by various ACNT transfer technology[9–12] with moderate success. For the wet chemical process,[9–11] pristine CNTs are functionalized in acids and then assembled onto the substrate in a solution. The functionalization process usually truncates the CNTs randomly and introduces high defect density to the lateral walls of the CNTs, which greatly degrades the intrinsic electrical and thermal properties of the 1-D structure of the CNTs. Furthermore, big challenges exist in selective patterning, length control, and quality control of functionalized ACNTs. In this study, we propose a new transfer technology for ACNT assembly, named "chemical transfer", which promises to bypass the problems associated with the wet chemical process and allow ACNTs to be used with various substrates. Chemical transfer is a two-step assembly process, similar to the flip-chip assembly technique (Figure 1): (1) well-aligned CNTs are in situ functionalized (f-ACNTs) during the CVD growth; (2) f-ACNTs are then anchored onto the gold-coated substrate by forming covalent bonding between the f-ACNTs and the self-assembled monolayer of conjugated thiol molecules on the gold surface. The in situ functionalization process allows for precise length control of ACNT assembly without randomly damaging the CNT structures and, equally importantly, renders the ACNT surface, especially the opened ends, chemically reactive to certain functional groups. Compared to the solder−reflow transfer technology introduced previously by our research group,[12] the chemical transfer technique is a low-temperature solder-free process and is easily implemented on a wide variety of substrate materials including metals, polymers, and semiconductors. In this study, silicon wafers with 5−10 nm Ti (as adhesion layer) and 60−100 nm Au (as top layer) were used. ACNTs could be chemically transferred onto other gold-coated smooth substrates, such as glass (or quartz slides).

The ACNTs were grown on SiO_2/Si with 10 nm thick Al_2O_3 and 2 nm thick iron films deposited by an e-beam evaporation. The CVD growth was carried out at 750 °C, with gas flow rate
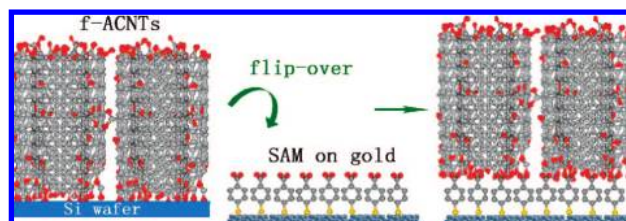

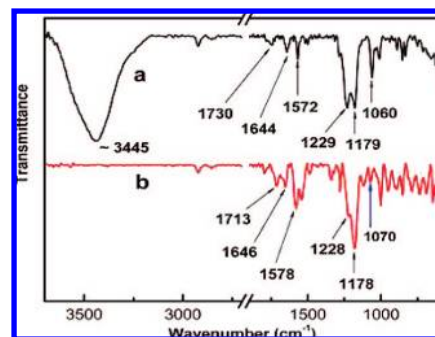**Figure 1.** Schematic illustration of the chemical transfer process.

Figure 2. FTIR spectra of the f-ACNTs (a) and the s-CNTs (b).

ratio as $Ar/H_2/C_2H_4 = 380/150/150$ standard cubic cm/min (sccm). The in situ functionalization of the ACNT surface was realized by bubbling a small amount of Ar through H_2O_2 (10−30 wt %) into the furnace chamber during the CVD growth. X-ray photoelectron spectroscopy (XPS) survey (SSX-100, in the Supporting Information) carried out on the top of the f-ACNT shows an asymmetric C1s peak and an oxygen peak, indicating the existence of oxygen-involved functional groups. Consistent with the XPS results, the FTIR spectrum (Nicolet, Magna IR 560, 4 cm^{-1} resolution, 5000 scans) in Figure 2 (trace a) shows the presence of O−H, C−O, and C−O−C at 3445, 1229, and 1179 cm^{-1}, respectively. The weak and wide band at ~1730 cm^{-1} consists of various carbonyl functional groups. These surface functional groups result in a relatively small contact angle of DI water droplet on the f-ACNT film (125−135°) with respect to the superhydrophobic surface of the pristine ACNT film (>150°). To test the chemical reactivity of the surface functional groups, f-ACNTs were immersed in $SOCl_2$ for 24 h, and the FTIR spectrum of the resultant product (s-CNT) is shown in Figure 2 (trace b). The disappearance of the band at 3445 cm^{-1} indicates that the hydroxyl groups on f-ACNTs react with $SOCl_2$. Correspondingly, the absorptions below 1100 cm^{-1} become complex. The peaks at 1070 cm^{-1} are probably attributed to the S=O stretching.

A self-assembled monolayer of conjugated thiol molecules was employed as the molecular wire junctions[13] at the f-ACNT/gold

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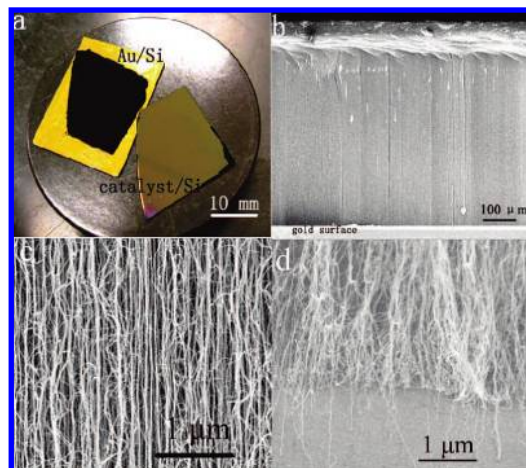‡ School of Material Science & Engineering.

Figure 3. Chemically transferred f-ACNT film on the gold surface: (a) photograph; (b) the side-view SEM image (by 0.5 N/cm^2 of compressive force during transfer); (c) further enlargement of the CNT alignment after chemical transfer; (d) the anchored f-ACNT/gold interface after part of the transferred ACNTs was removed.

interface. The gold/Si substrate was cleaned with UV ozone (0.75 L/min flow rate of the oxygen for 3 min) and subsequently immersed in 1 mM ethanol solution of 4-mercaptobenzoic acid (MBA) for 48 h in nitrogen atmosphere. After such treatment, the gold surfaces were thoroughly rinsed with ethanol to remove the excess thiol molecules and dried with an Ar flow. The XPS survey shows the existence of MBA molecules on the gold surface (Supporting Information). Then thionyl chloride was used to treat the MBA monolayer to make it reactive with the f-ACNTs. The f-ACNT film was flipped and held onto the as-treated gold surface and kept at 110 °C in nitrogen for 4 h. Then the Si growth substrate was separated from the f-ACNTs, leaving all the f-ACNTs attached to the gold surface. Figure 3 shows the chemically transferred ACNT film on the gold surface.

Interfacial strength was tested in Die Shear Equipment (Dage series 4000, 10 kg load cell). For the chemically transferred f-ACNT ($\sim$200 μm thick)/gold interface, the shear strength is 3.1−3.8 N/cm^2, $\sim$2 times stronger than that of the pristine ACNT/Si interface (1.5−2.1 N/cm^2) with ACNT film of the same thickness. When compressive force (in Instron 5548 Microtester) was applied during the transfer process, the shear strength could reach 30−110 N/cm^2, depending on the thickness of the ACNT film and the external compression force. Although it is not recommended that the value reported here be compared directly with those obtained by different testing methods,[14,15] we note that this interface is much stronger than what has been reported so far. We postulate that the compression force ensures more contact between the ACNTs and the gold surface,[15] as can be seen from Figure 3b, so that more covalent bonds can be formed between f-ACNTs and the gold surface, as well as higher van der Waals forces.

The current−voltage (I−V) response of the f-ACNT interconnect was conducted on a Keithley 2000 multimeter equipped with a four-point probe station. The upper gold electrodes (150 nm thick, diameter: $\sim$2.1 mm) were deposited on the top of the f-ACNT films. Figure 4 shows the I−V curve of the chemically transferred f-ACNT structure measured at room temperature. The curve is linear, suggesting that the electrical transport and the contacts are Ohmic, which is in stark contrast to the result shown in ref 16. The resistance of a compact CNT bundle with a diameter of $\sim$2.1 mm is $\sim$0.02 Ω. From the length and estimated area density and the
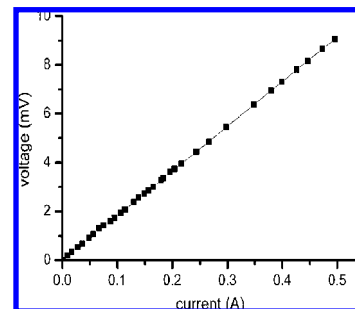

Figure 4. The room temperature I−V curve of the f-ACNT/interconnect via the chemical transfer.

average diameter of f-ACNTs, the resistivity of the individual ACNT is $\sim$3.0 × 10^{-4} $\Omega \cdot$cm. This order of magnitude is smaller than that reported in ref 16 but consistent with that in ref 17. The Ohmic contact and low resistance of the f-ACNT interconnect is probably attributed to two factors: (1) conjugated SAM-assisted bonding at the interface of $\sim$1 nm thick, which facilitates the electron transport; (2) relatively low defect density along the f-ACNT walls as compared to the functionalized CNTs by the wet chemical method.

In summary, the in situ functionalization is a simple way to functionalize CNTs and simultaneously maintain the well-aligned structure and uniform thickness of the ACNT film. A self-assembled monolayer of conjugated thiol molecules at the f-ACNT/gold interface serves both as the bonding ligand and as the path for electron transport or tunneling, as well as for phonon transport (thermal testing is in progress). Therefore, this process may offer a new paradigm to applications of ACNTs in electrical interconnect, thermal interfacial management, and electrodes for sensors.

Supporting Information Available: XPS survey results of the f-ACNT film and the SAM−gold surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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