Vacuum brazing of carbon nanotube bundles

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A B S T R A C T

We have investigated vacuum brazing of CNTs with a eutectic alloy (Ag_xCu_y) doped with Ti. Bonding is confirmed to involve formation of covalent bonds between Ti and C atoms. The brazing in vacuum leads to the interdiffusion of Ti and C atoms and reaction at the joining interfaces. This joining process is promising for volume production with low cost and a low contact resistance.

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1. Introduction

To realize electronic applications of carbon nanotubes, such as quantum wires [1], ballistic conductors [2], microchip interconnects [3] and transistors [4], reproducible fabrication of joints between individual nano-tubes and -electrodes has been identified as a major impediment [5,6]. Previous studies have shown that electrically conductive connection between nano building blocks is not straight-forward. Instead of desired ohmic contacts, tunnel junctions or weak links of a high contact resistance typically at 200 kΩ [7] for contact regimes on the order of 1 nm^2 [8], are often generated. Obviously, the gap-sensitive contact resistance makes it difficult to join nano building blocks with repeatable performance in nanodevices.

Various methods of joining CNTs to each other or to other materials, such as welding, soldering, and gluing, have been attempted by many groups [9–11]. Terrones et al. [9] used electron beam irradiation to make "X", "Y" and "T" molecular junctions with covalent cross-linking of C atoms between CNTs at high temperatures. Hirayama et al. [11] utilized weak electrostatic attraction (Van der Waals forces) to bring the CNTs together, and then applied Joule heating to produce spot welding between the bundles. While those methods relate to direct bonding between CNTs, Banhart et al. [8] suggest that an electrically conductive material should be added over a larger surface area to form CNT joints with a desired ohmic contact. They produced a "solder" joint between crossing CNTs through electron beam irradiation, using conductive amorphous carbon formed by the decomposition of absorbed hydrocarbons. For joining CNTs to dissimilar materials, Chen et al. [12] was successful in nano-scale joining by using an ultrasonic bonder to connect single wall carbon nano tubes (SWCNT) onto Ti-electrodes. They claimed to achieve mechanically durable low-resistance ohmic contacts with resistances in the range of 8 and 24 kΩ. In their work, Ti_xC was identified by XPS and XRD at the welded junctions.

While almost all the previous work is based on complicated "spot welding" (single shot), which requires exact location of a single carbon nanotube and its manipulation during welding, nano-engineering for devices and commercialization still requires an easier welding method with a low cost. This research develops a novel nanojoining technique, namely "nanoscale brazing" capable of joining dissimilar materials, where the CNTs are bonded in vacuum to a brazing alloy (Ag_xCu_y) doped with Ti, a reactive transition element (other elements such as: Zr, Hf, Ta could also be used) usually added to brazing alloys to aid in bonding under vacuum conditions or in protective atmosphere.

2. Experimental

The double-wall carbon nanotube bundles (DWNTs) used in this experiment were produced using a floating catalytic decomposition method as described in Ref. [13]. A near-eutectic alloy (Ag_xCu_y) doped with Ti was used as a brazing alloy for wetting the CNT bundles at high temperatures in a high vacuum (10^{-6} Torr) furnace. The chemical composition of the alloy is 1.75 wt.% Ti, 63 wt.% Ag, and 35.25 wt.% Cu. It has a melting range from 780 to about 815 °C. The brazing alloy was commercially available from Morgan Advanced Ceramics Inc. This alloy is called active brazing alloy which differs from normal metallic alloy due to the vacant d shell electron of Ti. This vacant electron shell of Ti will greatly increase the ability of the alloy to react with other

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non active materials like ceramic. At the start of joining experiments, the CNTs were fastened to the top of a brazing alloy sample using evaporable glue. Then the experimental rig containing the CNTs and the brazing alloy was delivered into a high vacuum tubular furnace. It was kept there for 9 h until the furnace temperature reached a value of around 1000 °C (which was high enough to melt the brazing alloy), and held for 10 min. And then, the furnace was shut down and allowed to cool to room temperature at a rate of 2 °C/min.

The cross sectional nano/microstructures of the interface area between the CNTs and the brazing alloy were investigated using a Scanning Electron Microscope (SEM) equipped with Energy Dispersive spectroscopy (EDS) and a Focused Ion Beam (FIB). The type of bond between the CNTs and the alloy was analyzed by X-ray Photoelectron Spectroscopy (XPS).

3. Results and discussion

The SEM micrographs (Fig. 1) show a uniform solidified brazing alloy (due to a slow furnace cooling rate at 2 °C/min) connecting two bundles of CNTs in a smooth way. Shown in the inset is the magnified micrograph of entangled carbon nanotubes at the top of the wetted bundles. It can be seen that the brazing alloy melted and spread over the roots of the CNT bundles. It is worth noting that the CNT bundles are embedded into the brazing alloy, giving an indication of good wetting.

Fig. 2a shows the cross sectional view of a joining region cut by the focused ion beam (FIB) in situ. Five elemental maps are also presented corresponding to oxygen, carbon, Ti, Ag, and Cu respectively. It is easy to see that oxygen spread evenly all over the region. This indicates lack of a preferential oxide layer in the brazing area. The cross in the electron image is placed at the periphery of the black region. Accordingly, in the Ti, C elemental maps, the cross locates at the edge of the region rich in Ti, C respectively. This could be understood, as the Ti is the active element with a relatively higher diffusivity, and easy to react with carbon to form a carbide layer. The simultaneous appearance of the cross at the same position rich in Ti, and C is an indication of the formation of C–Ti bonds. The Ag and Cu in the brazing alloy are spread out acting as the carriers to transport Ti to the vicinity of the DWCNT tubes and also to form compounds with the carbide layer induced by Ti and C. The darker and lighter contrast areas are Cu and Ag elements respectively from the mapping. Comparing these elemental maps, the region rich in Ti element is also rich in C with adjacent regions full of Ag or Cu.

The bonding mechanism was confirmed to be due to the formation of covalent and metallic bonds among Ti and C, and among Ti, Ag and Cu atoms, respectively, using the XPS analysis to identify the chemical stoichiometry of the elements in the wetted regions (highlighted region inside the dashed circle in Fig. 1.). Two major peaks shown in Fig. 3b at 532.1 eV and 284.1 eV correspond to the oxygen and the carbon peak.

While carbon is obviously from the CNTs, the oxygen peak comes from an amorphous oxide layer covering the surface of the brazed CNTs, which was formed likely during the exposure of the CNT bundles to the air after vacuum brazing. The Ti peaks observed in Fig. 3a and b (taken from the wetted region) at 454.9 eV and 461.0 eV, are of good fit with the values of 454.8 eV and 460.8 eV, the characteristic Ti $2p_{3/2}$ and Ti $2p_{1/2}$ shells of the Ti-carbide (Ti_xC) crystals[14]. Additional evidence of the formation of Ti_xC include the peaks of C 1 s at 281.9 eV (Fig. 3a) and Ti 3p at 34.0 eV (Fig. 3b). Those peaks correspond to 281.6 eV and 33.8 eV, the energy peaks of Ti_xC crystals given in Ref. [15]. It should be noted that the C 1 s peak of the Ti_xC crystals shifted towards lower energies (281.9 eV) compared to published values of the elemental C 1 s level. This indicates a higher tendency to the formation of covalent bonds between Ti and C atoms due to an increase in the electronegativity of Ti–C bonds. The difference between the
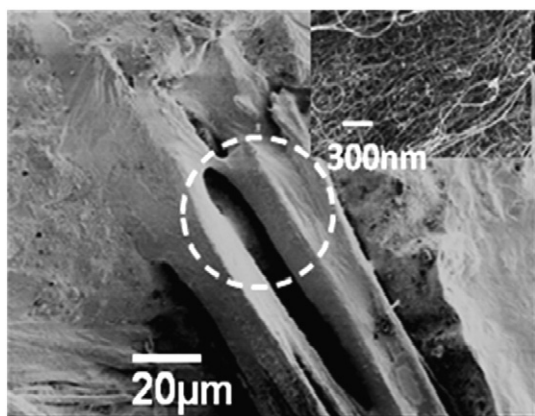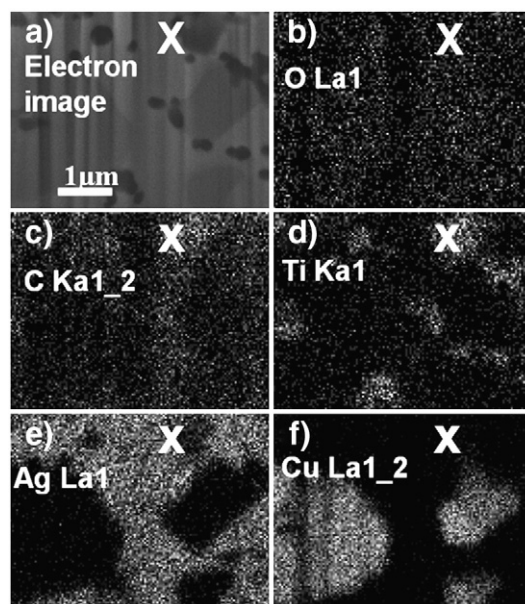

Fig. 2. Cross section view of (a) joined area (×10,000) image and corresponding element mapping (b–f) of brazing DWNT with FIB-SEM.

values of the energy peaks (281.6 eV) presented in Ref. [15] and those found here may result from an experimental error. However, it may also be due to the difference in the valence of the Ti cations in the Ti_xC phases of the other studies.

Note that the lattice structure of the brazing alloy (Ag_xCu_y) utilized in this research is face-centered cubic (FCC), and the added (doped) Ti atoms which have a native hexagonal close packed structure reside in substitutional sites. For this reason they are in a very unstable position and ready to diffuse out towards more open regions at the interface between the CNTs and the brazing alloy when they are excited by high temperature. They are able to make bonds of mixed character between the metal matrix atoms and the covalent carbon lattice of the CNTs hexagons. The melting of the brazing alloy helps to improve the contact of the alloy with the CNTs, and the high temperature helps to improve diffusion of Ti into the interface with CNTs. This contrasts to the behavior of solid-state ultrasonic nano-welding of CNTs to Ti [12], in which external forces and ultrasonic energy were required to produce plastic deformation of Ti electrodes to aid the contact between Ti and the CNTs, and to provide energy to the C atoms to covalently bond to the Ti (matrix) atoms.

In comparison to the "spot welding" techniques in the literature, nano-brazing is well suited for volume production in which multiple nano-joints could be made in a single operation by preassembling multiple junctions coated/deposited with brazing alloys. Furthermore, brazed nano-joints provide better mechanical durability versus soldered joints with amorphous carbon [8].

It is important to mention that although DWCNT is used in the present study SWCNT and MWCNT would be also applicable to this brazing method since a CNT bundle is used here. The brazing will not be influenced by a certain nanotube with the given structure. Besides, similar to Ti, transition metals, V and Nb are popular active elements adding to the brazing alloy. It is also interesting to investigate the effect of these active brazing materials. Regarding the electronic application, one would expect limited joint size which would require remove the excess brazing alloy. A possible way to do this is the

Fig. 1. SEM image (×300) of the roots of wetted CNT bundles surrounded by the brazing eutectic alloy (Ag_xCu_y) doped with Ti. Inset: high resolution image of the top of wetted CNT bundles.
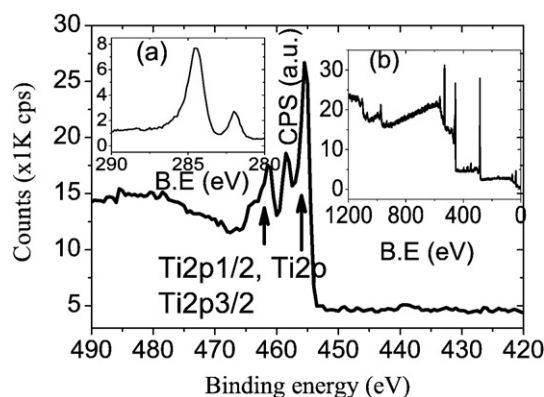

Fig. 3. XPS spectra near the Ti binding energy of 454 eV on the wetted region of brazing DWCNT. Inset: a) XPS spectra of C1 s core-level. Inset: b) XPS survey spectra.

surface corrosion of joints in diluted aqua regia (royal water, HNO_3:HCl = 1:3). While Ag and Cu, Ti are all soluble in aqua regia, CNT and TiC are not. The microstructure and property of joints can be well remained. Such an investigation is under way.

4. Conclusions

Nanoscale joining of CNTs using vacuum brazing with intermetallic alloy formed through the addition of transition element Ti to an alloy (Ag_xCu_y) was successfully developed. The basis for successful nanoscale brazing between the CNT bundles and the brazing alloy is the formation of strong covalent Ti–C bonds. The vacuum is essential to reduce the rate of unwanted reactions with oxygen and promotes bonding of Ti with C atoms. The Ti atoms act as the electron reservoir required to form metallic and covalent bonds among the atoms of the metal matrix and the CNT bundles.

Acknowledgement

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