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Constructing carbon nanotube junctions by Ar ion beam irradiation

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ABSTRACT

Carbon nanotubes (CNTs) irradiated by Ar ion beams at elevated temperature were studied. The irradiation-induced defects in CNTs are greatly reduced by elevated temperature. Moreover, the two types of CNT junctions, the crossing junction and the parallel junction, were formed. And the CNT networks may be fabricated by the two types of CNT junctions. The formation process and the corresponding mechanism of CNT networks are discussed.

1. Introduction

The quest to improve the miniaturization of devices in integrated circuits industry is one of the main driving forces of the scientific research and technological advance in nanotechnology. The nano-scale interconnections among/inside the building blocks of devices promise the further miniaturization of components for the construction of electronic and optoelectronic devices. The nano-scale interconnections are mainly fabricated by carbon nanotubes (CNTs) (Tans et al., (1998); Javey et al., 2003), metallic and semiconductor nanowires (Gao et al., 2002; Thelander et al., 2003). Among various potential candidates for the nano-scale interconnections, CNTs have become the important conducting wires for the future nano-scale devices due to their unique mechanical and electronic properties. Therefore, it has been one important issue to fabricate the multiple-way CNT junctions and networks.

Until now, the various multiple-way CNT junctions, such as L-junction, Y-junction, and T-junction CNTs, have been synthesized through pyrolysis of carbon-containing precursor (Zhou and Seraphin, 1995; Satishkumar et al., 2000), chemical vapor deposition (CVD) (Li et al., 1999; Cassell et al., 2003; Yang et al., 2005). However, the formation of the CNT junctions was completely random and not easily controlled. In addition, the synthesis of CNT networks was realized through self-organized nanocrystals. Nevertheless, the removal of the nano-particles may result in destruction and even disappearance of the CNT junctions. Recently, the CNT junctions were fabricated by the electron beam irradiation in transmission electron microscopy (TEM) (Banhart, 2001; Terrones et al., 2002; Wang et al., 2005). Especially, Wang et al. (2005) displayed the welding of CNTs and succeeded in fabricating CNT networks by the electron beam equipped in TEM. However, the large-scale fabrication of CNT junctions by electron beam irradiation is still an open issue.

The energetic ion beams, as a powerful tool for driving self-assembly of nanostructures and tuning the properties of CNTs, may potentially be used to fabricate CNT networks to interconnect the building blocks (Gómez-navarro et al., 2005; Ni et al., 2006). In previous work, we have fabricated carbon nanowire networks out of CNTs by ion beam irradiation at room temperature (RT) (Ni et al., 2006; Ni et al., 2008). However, the CNTs were completely transformed into amorphous carbon nanowires due to ion-irradiation-induced damage. Thus, the outstanding properties of CNTs would be lost after formation of amorphous carbon nanowires (Sammalkorpi et al., (2004)). In this paper, we demonstrate two types of multi-walled CNT (MWCNT) junctions simultaneously fabricated by Ar ion beam irradiation at elevated temperature, and the irradiated MWCNTs are not damaged at high temperature. This finally results in the formation of MWCNT networks.

2. Experimental

MWCNTs are synthesized by chemical vapor deposition (CVD) methods in our laboratory (Ni et al., 2006, 2008).The MWCNTs used were dispersed on holey carbon micro-grids and silicon substrates and then the prepared samples were irradiated by Ar ion beam at an elevated temperature in a 100 KV electromagnetic isotope separator (EMIS). The vacuum of the specimen chamber was kept at $\sim 10^{-4}$ Pa. The irradiation dose rate of Ar ions was fixed at $\sim 20\ \mu A/cm^2$. The irradiation energy and dose ranged

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from 40 to 70 KeV and 4×10^{16} to 1×10^{17} ions/cm^2, respectively, which are corresponding to 4.5×10^4–1.5×10^5 Gray for the carbon systems by the calculation of the program SRIM-2003 (Ziegler, 2004). The prepared samples were examined with TEM (JEOL 2010F), scanning electron microscopy (SEM LEO, 1530VP), and micro-Raman (JY LabRam-1B).

3. Results and discussion

Fig. 1a shows the typical TEM image of as-grown MWCNTs. The diameters of as-grown CNTs range from 18 to 35 nm. The high-resolution TEM (HRTEM) image reveals well-ordered graphitic sheets with some disordered graphitic lattice in the outer walls, as shown in Fig. 1b. The MWCNT junctions cannot be found in the prepared MWCNTs. After the prepared MWCNTs are irradiated by 40 KeV Ar ion beams at elevated temperature, some new structures can be found, as shown in Fig. 1c and d.

The HRTEM images of Fig. 1c and d show the new features of MWCNTs irradiated at the dose of 5×10^{16} ions/cm^2 at the temperature of 800 K. It can be obviously seen that two types of MWCNT junctions have been formed in the joints of the MWCNTs. The first type of junction, which is called the crossing junction, is shown in Fig. 1c. The crossing tubes are connected by some amorphous carbon agglomerating nearby the crossing position of both the MWCNTs, as indicated by the arrow. The formation of the amorphous carbon should be ascribed to the agglomeration of the irradiation-induced sputtered carbon atoms from the MWCNTs. Moreover, the amorphous carbon usually agglomerates nearby the crossing sharp angle position of both the MWCNTs. This should be ascribed to the fact that the sputtered carbon atoms easily deposit the crossing sharp angle position. Here, the crossing junction is connected by amorphous carbon, but it is to be expected that the conductivity of the crossing junction can be enhanced at high annealing temperature and long annealing time since the amorphous carbon can become carbon material with atomic structure such as glassy carbon with sufficient conductivity by annealing at high temperature and long annealing time.

Fig. 1d shows the second type of junction, which is called parallel junction. The parallel junction connects the adjacent parallel parts of both MWCNTs. Moreover, the adjacent part of the two MWCNTs, i.e., as called the parallel junction, shares common graphitic sheets. As mentioned above, the diameters of the as-grown MWCNTs are usually less than 35 nm. According to the calculation of the program SRIM-2003 (Ziegler, 2004), the traverse depth of 40 KeV Ar ions in carbon materials with a density of 2.25 g/cm^2 is 38 nm. These indicate that the most irradiated Ar ions are not absorbed in the MWCNTs. In addition, the Energy Dispersive X-ray analysis (EDX) (equipped in TEM JEOL 2010F) showed no detection of Ar atoms in the irradiated MWCNTs. Therefore, the formation of the parallel junction should be ascribed to the self-organized process from the sputtered carbon atoms and initial disordered graphitic lattice in the outer walls of the two MWCNTs induced by Ar ion beam irradiation at the elevated temperature (Banhart, 1999;Ni et al., 2008). We explain the formation of the parallel junction as follows. The ion beam irradiation produces many defects due to the collision cascade

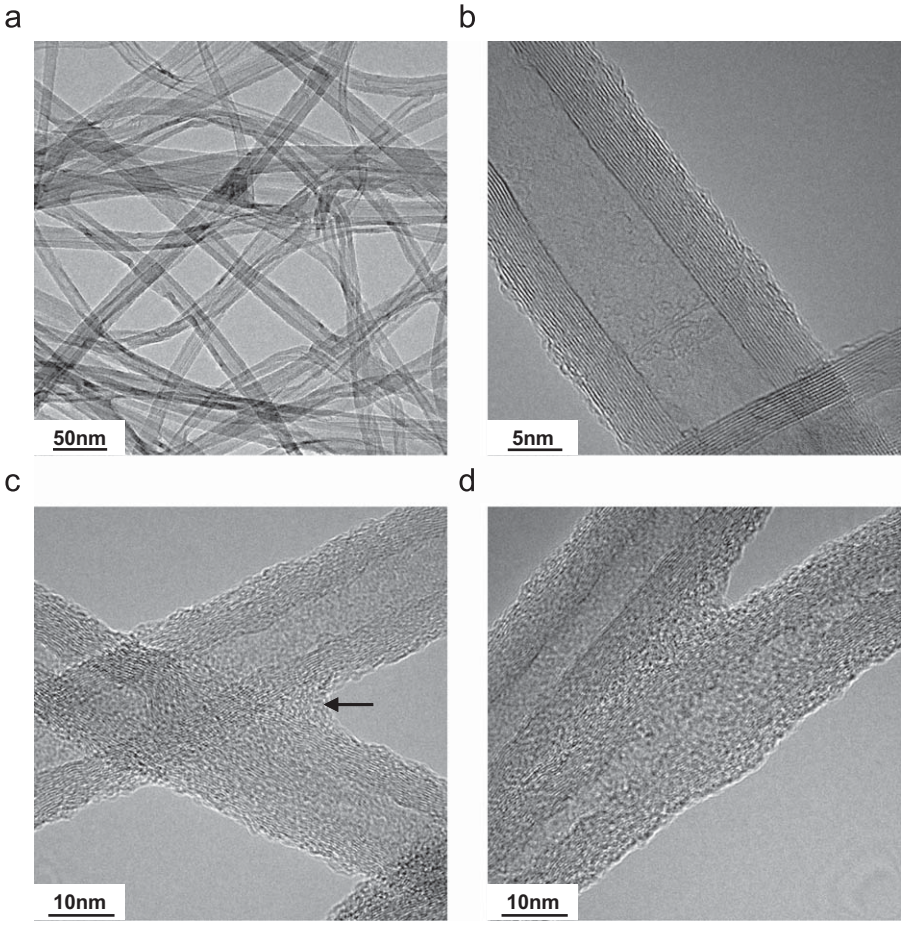

Fig. 1. TEM image (a) and HRTEM (b) of the as-grown MWCNTs. HRTEM images of a crossing MWCNT junction (a) and a parallel MWCNT junction (b), which are irradiated at the dose of 5×10^{16} ions/cm^2 at the temperature of 800 K. The irradiation energy is 40 KeV.

effect and sputtering of a substantial amount of atoms from the MWCNTs (Krasheninnikov et al., 2002; Krasheninnikov and Nordlund, 2004). Nevertheless, heating can give rise to a substantial drop in the defect number due to the migration of carbon atoms (Terrones et al., 2002; Krasheninnikov et al., 2002). For the inter-contacted parts between both MWCNTs, the dangling bonds of the carbon atoms around the two tubes produced by irradiation can serve as bridges to form inter-tube covalent bonds (Salonen et al., 2002). Moreover, the elevated temperature can accelerate the creation of interlinks and the formation of the common graphitic sheets in the inter-contacted parts between both the MWCNTs, which can result in the formation of the parallel junction.

Here, it should be noted that the graphitic structure of the irradiated MWCNTs keep very well even in comparison with the as-grown MWCNT though some defects indeed are produced in the irradiated MWCNTs. This should be caused by the high defect recombination rate of the irradiated MWCNTs in the heating condition, which greatly decrease the formation of amorphous structures of the irradiated MWCNTs. Note that a 40 KeV Ar ion can transfer the energy of 2000 eV to the carbon system. When the heat capacity of MWCNTs is set to 2000 J kg^{-1} K^{-1} (Huang et al., 2005), the Ar ion bombardment can heat the MWCNT to a temperature of 200 K. Nevertheless, the temperature cannot prevent the formation of amorphous structures of the irradiated MWCNTs (Banhart, 2001; Ni et al., 2008). The high-temperature heating is prerequisite for the high defect recombination of the irradiated MWCNTs. As has been widely confirmed, the high-temperature annealing is one of the most efficient methods for the structural revolution from disordered structure to ordered structure in CNTs. Moreover, the structural alterations of the CNTs under the electron beam irradiation could be avoided above ~600 K (Banhart, 2001; Terrones et al., 2002). We also compared the results of irradiated MWCNTs in different temperatures. We found that in the range 600–1000 K, the irradiation effect has not obvious difference at the same irradiation dose. However, below 600 K, the irradiated MWCNTs are greatly destroyed even at low irradiation dose. In addition, we also take notice of some amorphous structure in the outer walls. The amorphous structure should be attended by Ar ion irradiation-induced sputtering of the MWCNTs, which plays a key role in the formation of MWCNT junctions.

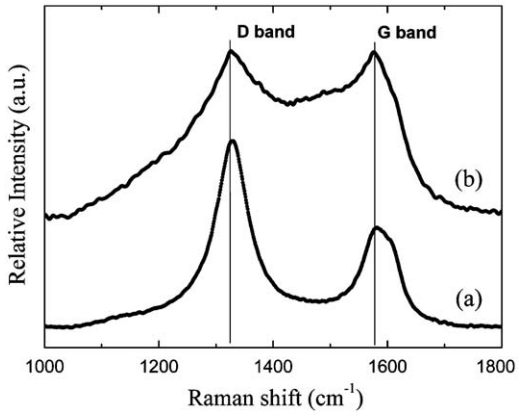

Fig. 2. Raman spectra of the MWCNTs irradiated with a dose of 5×10^{16} ion/cm^2 at 800 K (a) and RT (b). The excitation wavelength is 632.8 nm.

Furthermore, the Raman spectrum can distinguish the graphitization of the MWCNTs in large area. Fig. 2 shows the Raman spectra of MWCNTs irradiated at the dose of 5×10^{16} ions/cm^2 at different temperatures. The irradiation energy is fixed at 40 KeV. There are two bands between 1000 and 2000 cm^{-1} corresponding to the typical Raman peaks of MWCNTs. The peak centered at 1578 cm^{-1} (G band) is corresponding to an E_{2g} mode of graphite. The G mode can occur at all sp^2 sites (Ferrari and Robertson, 2000). The peak centered at 1327 cm^{-1} (D band) is associated with the vibration of carbon atoms with disordered graphite, such as, dangling bonds in plane terminations, defect, grain boundaries, etc. From Fig. 2, it can be seen that at 800 K, the G peak is not dispersive though the intensity of D peak is stronger than that of the G peak. This indicates that the graphite and nanocrystalline graphite structure of irradiated MWCNTs at 80 K are dominant (Ferrari and Robertson, 2000). For the Raman spectrum of the irradiated MWCNTs at RT, the G peak becomes very dispersive. This indicates the formation of amorphous carbon with sp^3 bonding in the irradiated MWCNTs (Ferrari and Robertson, 2000). Our previous results also prove that the irradiated MWCNTs at RT were completely transformed into amorphous carbon nanowires (Ni et al., 2006; Ni et al., 2008). Therefore, the heating of the MWCNTs can improve the defect recombination of the irradiated MWCNTs and reduce the disorder of the irradiated MWCNTs.

Actually, the two types of MWCNT junctions can be obtained at a certain range of irradiation energy and dose at the temperature of 800 K. Fig. 3a shows the typical TEM image of MWCNTs irradiated at the dose of 4×10^{16} ions/cm^2 and irradiation energy of 70 KeV at the temperature of 800 K. Both the types of MWCNT junctions, the crossing junction and the parallel junction have

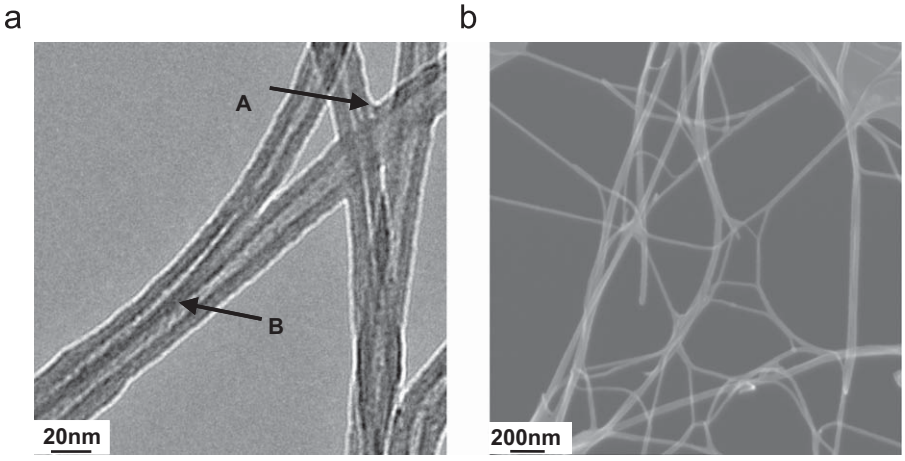

Fig. 3. (a) TEM image of the MWCNT networks. The crossing MWCNT junction and the parallel MWCNT junction indicated by arrows A and B. (b) The SEM image of the MWCNT networks at large scale. The MWCNTs are irradiated at 4×10^{16} Ar ions/cm^2 at the temperature of 800 K and the irradiation energy is 70 KeV.

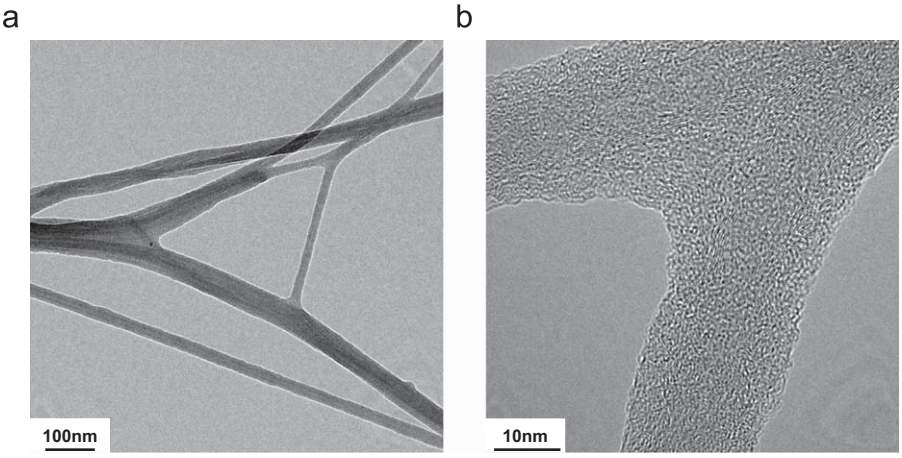

Fig. 4. TEM image (a) and HRTEM image (b) of the irradiated MWCNTs with the dose of 1×10^{17} ions/cm^2 at the temperature of 800 K. The irradiation energy is 70 KeV.

simultaneously been formed, as indicated by arrows A and B. The two types of junctions are usually the basic forms of the MWCNT junctions. Thus, the CNT networks could be fabricated by the two types of junctions. Fig. 3b exhibits the corresponding SEM image of the CNT networks at large scale. It can be seen that the most of the MWCNTs have been connected by the two types of junctions. That is, the CNT network has been fabricated. It should be noted that for as-grown MWCNTs prepared on the holey carbon micro-grids, the crossed MWCNTs should be well contacted, which is prerequisite to form MWCNT junctions by irradiation. Here, although the crossing junction is connected by amorphous carbon, it is to be expected that the conductivity of the crossing junction can be enhanced at high annealing temperature and long annealing time since the amorphous carbon can become carbon material with atomic structure such as glassy carbon with sufficient conductivity by annealing at high temperature and long annealing time (Banhart, 2001).

According to the above discussion, the two types of MWCNT junctions can be formed at the irradiation energy range of 40–70 KeV at the dose range of 4×10^{16}–5×10^{16} ions/cm^2. Moreover, our irradiation experiments also reveal that the irradiation effect is vital to the structure change of the MWCNTs. Fig. 4a shows the TEM images of the MWCNTS at the dose of 1×10^{17} ions/cm^2 and irradiation energy of 70 KeV at the temperature of 800 K. It can be seen that the typical hollow structure of the MWCNTs has disappeared. The HRTEM image exhibits that the irradiated MWCNTs are greatly destroyed and the formed junctions also become amorphous structure, as shown in Fig. 4b. This is similar to our previous results at RT (Ni et al., 2006, 2008). The difference is that the higher irradiation dose can damage the MWCNTs at the elevated temperature than that at RT.

4. Conclusions

In conclusion, the two types of CNT junctions, the crossing junctions and the parallel junction, can be formed by Ar ion beam irradiation at elevated temperature, and the structural evolution process and mechanism are discussed. Using the two types of CNT junctions, we have displayed a new approach for the construction of CNT networks. Moreover, the electrical conductive properties of CNT networks irradiated by Ar ion beams can be improved at the high temperature. The fabrication of the CNT networks by ion irradiation technology may be an available method for interconnection in nano-electronic and optoelectronic devices.

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