Welding of multi-walled carbon nanotubes by ion beam irradiation

Carbon nanotubes (CNTs), due to their unique mechanical and electronic properties, have been parts of versatile nano-scale building blocks or conducting wires incorporated into a variety of nanodevices [1,2]. The realization of circuits on the nanodevices based on CNTs requires a technique that is able to connect the tubes electrically with each other and with their periphery. Therefore, much research work has been devoted to the fabrication of various multiple-way CNT junctions [3,4]. The different multi-way CNT junctions have been synthesized by chemical vapor deposition (CVD) [3]. Furthermore, the connection of CNTs could be realized by the connection of particles with the CNTs [4]. Recently, it has been known that the electron beams in transmission electron microscopy (TEM) can be used to fabricate CNT junctions [5–7]. However, the large-scale fabrication of CNT junctions by electron beam irradiation is still an open question.

Similar to the electron beam irradiation, the ion beam irradiation is also a powerful tool for driving self-assembly of nanostructures and may be used to fabricate CNT junctions [8]. Moreover, the large-scale fabrication can be easily realized by the present ion beam irradiation techniques. In our previous study, the carbon nanowire networks have been realized by Si ion beam irradiation at room temperature (RT) [9]. Nevertheless, the irradiated CNTs are transformed into amorphous carbon nanowires (ACNs). It is well known that the defects in CNTs can deteriorate some unique properties of CNTs. Recently, the theoretical simulation indicated that CNT junctions could be formed by ion beam irradiation under the heating conditions [8]. Here, we demonstrate the formation of multi-walled CNT (MWCNT) junctions through the ion beam irradiation at elevated temperature.

The MWCNTs synthesized by thermal CVD were dispersed on holey carbon micro-grids and irradiated by 40 keV Si ion beam with different doses in a 100 kV electromagnetic isotope separator (EMIS). The vacuum of the specimen chamber was kept at $\sim 10^{-4}$ Pa. The temperature was ranged from 300 to 850 K. The irradiation dose was ranged from 1×10^{16} to 5×10^{17} ions/cm^2. The irradiated MWCNTs were investigated by TEM (JEOL 2010F) operated at 200 kV. The energy dispersive X-ray analysis of the MWCNTs irradiated at the dose of 5×10^{16} ions/cm^2 shows that the quantity of the Si atoms incorporated into the MWCNTs is less than 1%.

Fig. 1 shows typical TEM and high-resolution TEM (HRTEM) images of MWCNTs irradiated at the dose of 5×10^{16} ions/cm^2 at the temperature of 550 K and 600 K. At 550 K, the irradiated MWCNTs and the formed MWCNT junctions have hollow structure, as shown in Fig. 1a. However, the corresponding HRTEM observation exhibits many amorphous carbon structures in the irradiated MWCNTs and only some graphitic layer structures can be observed in the MWCNTs and formed junctions (see Fig. 1b). At 600 K, the irradiated MWCNTs and the formed MWCNT junctions have not only evident hollow structure but also well-ordered graphitic layer structures, as shown in Fig. 1c and d. Even compared with the as-grown MWCNTs (see the inset of Fig. 1c), the irradiated MWCNTs also do not have obvious damage. Therefore, it can be seen that temperature plays a key role in keeping the well-ordered graphite structure of the irradiated MWCNTs and the formed junctions. This should be ascribed to the fact that the heating of the MWCNTs can improve the rate of the defect recombination and avoid the formation of ACNs. Actually, the temperature induced defect recombination effect of CNTs has been widely investigated. For example, Huang et al. exhibited tubule formation from ACNs under high-bias Joule heating, which confirmed the defect recombination process of ACNs induced by heating [10].

The detailed structure of the formed MWCNT junction can be investigated by the HRTEM in Fig. 1d. The adjacent parts of the two MWCNTs share common graphitic sheets. Thus, the MWCNT junction is formed. Furthermore, the sum of the width of the wall A (5.5 ± 0.1 nm) and the width of the wall B (4.5 ± 0.1 nm) is smaller than the width of the junction (11.0 ± 0.1 nm) in the conjoint area of the both MWCNTs as indicated by the lines I, II, III. Therefore, the formation of the MWCNT junction is a self-assembly process from the sputtered carbon atoms and initial disordered graphite lattice to the ordered structure in the outer walls of the two MWCNTs under the ion beam irradiation at the elevated temperature. In addition, the irradiation induced sputtering may also lead to the reduction of the well-ordered graphitic layers of the isolated MWCNTs. This can be confirmed by the amorphous carbon structure nearby the conjoint area of the both MWCNTs, as indicated by the arrow. On the whole, the interconnection of the MWCNTs is a self-assembly process of structural transformation in the MWCNT system induced by Si ion beam irradiation at the elevated temperature, which is similar to some structural transformation from amorphous carbon structure to ordered carbon structure by electron beam irradiation [10]. Our experimental results also show that the welding of the MWCNTs with well-ordered graphitic layer structures can be always realized at the temperature range of 600–850 K.

It should be noted that the irradiation effect is vital to the welding of the MWCNTs. Therefore, we turn to investigate the effect of irradiation dose on the structures of MWCNTs and formed MWCNT junctions. The temperature was fixed at 600 K. Fig. 2 shows typical TEM and HRTEM images of the MWCNTs irradiated by Si ion beam with different doses. No junctions are observed in the MWCNTs irradiated at the dose of 1×10^{16} ions/cm^2 (see Fig. 2a). Even for the two adjacent MWCNTs, the interconnection has never been realized, as shown in Fig. 2b. However, with increasing irradiation dose to 5×10^{17} ions/cm^2, the typical hollow structure of the MWCNTs has disappeared (see Fig. 2c). The corresponding HRTEM observation exhibits that both the irradiated

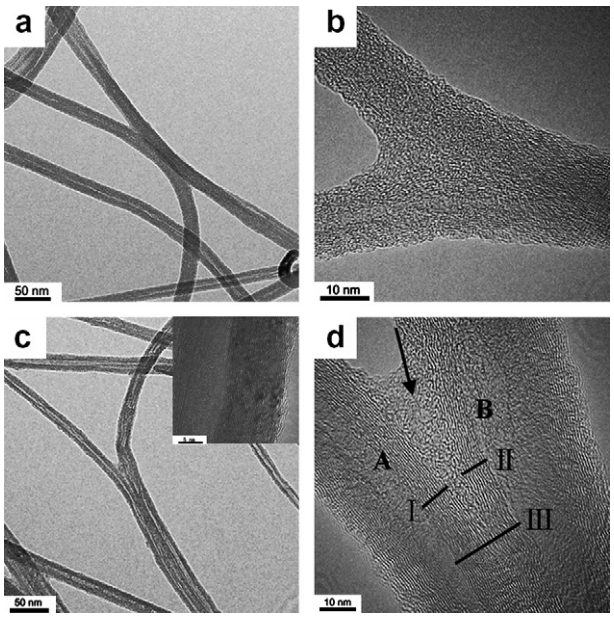

Fig. 1 – TEM and HRTEM images of the MWCNTs irradiated at the dose of 5×10^{16} ions/cm^2 at different temperatures: (a and b) 550 K, (c and d) 600 K. The inset of (c) is the HRTEM of the as-grown MWCNT. In (d), the widths of the wall A, the wall B and the junction are indicated by the lines I, II, III. And the amorphous carbon is denoted by the arrow.

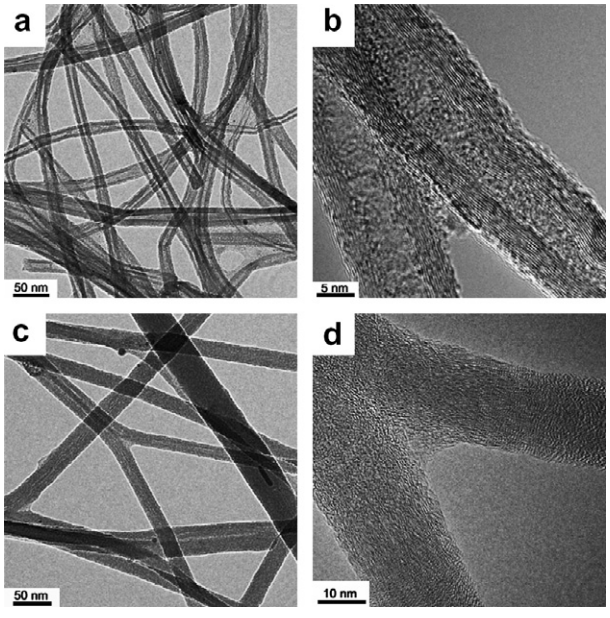

Fig. 2 – TEM and HRTEM images of the irradiated MWCNTs with different doses at the temperature of 600 K: (a and b) 1×10^{16} ions/cm^2, (c and d) 5×10^{17} ions/cm^2.

MWCNTs and the formed junction only have amorphous structure (see Fig. 2d). Therefore, the irradiation dose has great effect on the welding and the structure of the MWCNTs. At the low dose irradiation, the sputtered carbon atoms and disordered graphite lattices are not enough to result in the interconnection of the two adjacent MWCNTs. At the high dose irradiation, the MWCNTs may be damaged too much to remedy even at the elevated temperature.

In conclusion, the welding of the MWCNTs has been realized at elevated temperature by Si ion beam irradiation. And the formation of the MWCNT junctions is ascribed to the fact that the two adjacent MWCNTs share a common grapheme, which is a self-assembly process of structural transformation by irradiated induced defect production and recombination at the elevated temperature. Moreover, both the irradiation dose and temperature greatly effect the welding of the MWCNTs. At the irradiation dose of 5×10^{16} Si ions/cm^2, the formed MWCNT junctions have well-ordered structure at the temperature range of 600–850 K. The ion irradiation technology combined with heating provides an optional approach for the construction of MWCNT junctions for interconnection in the future nanodevices.

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Catalytic graphitization of furan resin carbon by yttrium

Graphitization is a transformation of disordered carbon materials into three-dimensional graphite under high heat treatment temperature (HTT). However, it has been found that some carbon materials, such as those derived from the thermosetting resin, are non-graphitizable even after heating to temperatures above 3000 °C [1]. Increasing pressure or adding catalysts can be used to accelerate the graphitization of a non-graphitizable carbon. These processes are respectively called stress graphitization and catalytic graphitization.

An extensive study has been made of the catalytic graphitization of carbon by various elements, such as Al, Cr, Mn, Fe, Co, Ni, Ca, Ti, V, Mo, W and B [2–7]. However, the catalytic effects of rare-earth elements on the graphitization of non-graphitizing carbon have been seldom studied. The extent of graphitization of the carbon usually increases with increasing catalyst content. In general, a significant enhancement of graphitization of the non-graphitizing carbon could be observed only when the catalyst content more than 10 wt.% [2–6]. However, a high catalyst content is harmful for their further application because of the undesirable characteristics of graphites containing a great deal of the residual catalyst material.

In the present work, we introduced a rare-earth catalyst, yttrium, which can significantly catalyze the graphitization of non-graphitizing furan resin carbon with a low catalyst content (4 wt.% yttrium). The effects of the yttrium content and the HTT on the catalytic graphitization were investigated.

Yttrium nitrate dissolved in ethanol was added to the furan resin and the mixture stirred for 0.5 h to disperse the yttrium nitrate throughout the resin, the resulting resin was then cured at 160–200 °C for 2 h, followed by carbonization under Ar atmosphere at about 600 °C for 1hr [8]. The resin carbon containing the yttrium was then heat treated at different temperatures in a graphite crucible for 2 h under Ar atmosphere. The extent of graphitization of the samples was examined by X-ray diffraction (XRD). Silicon was used as the internal standard. The 2θ value was obtained from the centroid of the (002) diffraction peaks and the mean crystallite size (Lc) and interlayer spacing (d_{002}) were calculated using the Scherrer equation and the Bragg equation, respectively [9,10].

Fig. 1 shows the XRD patterns of furan resin carbon without (curve A) and with (curve B) yttrium catalyst after heat-treatment at 2400 °C. It can be seen that curve B has a sharper and higher (002) peak at a slightly higher angle. The d_{002} value for the curve B (3.360 Å) is much smaller than that in the curve A (3.547 Å), and is close to the 3.354 Å for the hexagonal graphite. In addition, another characteristic peak of graphite, the (004) peak, is also observed in curve B. These imply that yttrium has a good catalytic activity for the graphitization of furan resin carbon. On the other hand, the characteristic peaks of yttria, indicated by ♦, are observed in curve B, indicating that yttrium exists as yttria after catalytic graphitization. Further studies for the catalytic mechanism of yttrium are underway.

The effects of the yttrium content and the HTT on the catalytic graphitization of furan resin carbon were also investigated by XRD and the corresponding results are shown in Fig. 2. In order to express the catalytic graphitization of furan resin carbon at different yttrium content and HTT, the values of d_{002} and Lc of the (002) layer plane were calculated from Fig. 2 and listed in Tables 1 and 2. The corresponding changes were also plotted in Fig. 3. It is noted that the value of d_{002} decreases and the value of Lc (002) increases with yttrium

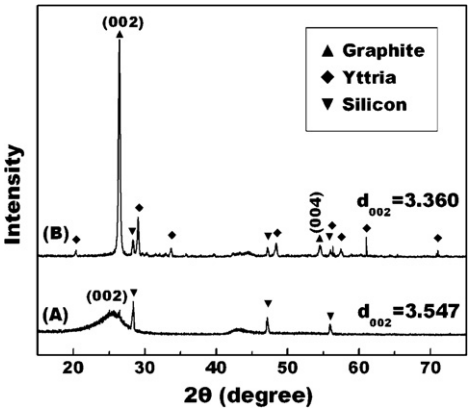

Fig. 1 – XRD patterns of furan resin carbon heat-treated at 2400 °C without (A) and with (B) 9 wt.% yttrium.