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Effect of ion irradiation on the properties of carbon nanotube buckypapers

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Optical, electrical and structural properties of argon (Ar) ion-irradiated buckypapers of multi-walled carbon nanotube (MWCNT) at various doses prepared by a vacuum filtration method were investigated. It was found that the direct current (DC) conductivity and absorption spectra in the visible range were decreased with an increasing Ar ion irradiation dose. A subsequent heating of nanotube buckypapers at 800 K in a vacuum at each irradiation dose improved the conductivity of buckypapers, whereas optical absorption was unchanged. Moreover, the graphite structure of MWCNTs was transformed to amorphous structure with an increasing Ar ion irradiation dose. The decrease of optical absorption and electrical conductivity of MWCNT buckypaper at room temperature can be ascribed to the increase of defects in the irradiated MWCNTs.

Keywords: multi-walled carbon nanotubes; ion beam irradiation; amorphisation; optical properties; electrical conductivity

1. Introduction

Remarkable electrical, optical and mechanical properties of individual carbon nanotubes (CNTs) indicate that CNTs can be used in various nano devices and nano materials [1]. Nevertheless, it is still difficult for the macroscopic CNT samples to preserve as many of the unique properties of individual CNTs as possible. The fabrication of CNT fibres [2–4] and sheets [5–8] opens a viable path for the utilisation of the outstanding characteristics of CNTs. CNT sheets, i.e. buckypapers have been proposed for different applications in electronics, optoelectronics, sensors and mechanical materials [6–12].

Moreover, the present ion beam irradiation technique is useful for defect production in CNTs, which help to alter their structural, optical, magnetic and electrical properties in a highly controlled manner [13,14]. Irradiation-induced changes of buckypaper play a significant role in the case of nanocomposites. As far as CNT buckypapers are concerned, their electrical and optical studies irradiated by ion beams are lacking. The majority of studies have focused on irradiation-induced changes in the electrical conductivity of single-walled carbon nanotubes (SWCNT) films [15–17]. Therefore, a lot more needs to be done to understand the effects of ion irradiation on the properties

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of MWCNT buckypapers. These studies will be extremely useful in assessing the viability of using MWCNT buckypaper-based nanocomposites. Experimentally, the effects of vacancies, topological defects and random disorder on the nanotubes have been investigated. Surprisingly, less experimental results have been published concerning the transport regime of localisation and, to our knowledge, no experimental evidence on the influence of controllably induced defects on the variation of the optical absorption of MWCNT buckypaper has been reported yet. In order to study this issue, we irradiate MWCNT buckypaper with Ar ions and measure the optical, electrical and structural characteristics of the CNT buckypaper. For this purpose, we have used characterisation techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), four-point probe technique and UV-Vis spectrophotometry. We observed irradiation-induced reduction in the DC conductivity and the optical absorption in the whole visible spectral range. The results are attributed to irradiation-induced defect production.

2. Experimental details

A vacuum filtration method was used to prepare CNT buckypapers. Commercially available purified MWCNTs with a purity of 99% (Applied Nanotechnologies, Inc.) were dissolved in a 1% solution of sodium dodecyl sulfate (SDS) surfactant. Mixed cellulose filter membranes with a pore size of 400 nm were used in vacuum filtration. After that, the filtration membrane with attached nanotube buckypaper was placed directly into an acetone bath, where the cellulose filter quickly dissolves. The nanotube buckypaper left drifting in the bath is picked up on a glass substrate and transferred to a clean acetone bath, where it was left for 20–30 min to remove the dissolved cellulose filter diffused into the porous membrane in the first bath. The processes are repeated through several baths to ensure effective complete removal of the cellulose filter and transferred it onto a quartz glass substrate or dried it to make a free-standing sample. Lastly, the prepared CNT membranes or buckypapers [18] on quartz glass were annealed at 800 K in a vacuum chamber pumped to $\sim 10^{-4}$ Pa in order to remove any absorbate contamination in the CNT buckypapers (e.g. H_2O molecules, C–H molecules, etc.).

The prepared samples were irradiated by Ar beam with different doses at room temperature in a 100 kV electromagnetic isotope separator (EMIS). The vacuum of the specimen chamber was kept at $\sim 10^{-4}$ Pa. These buckypapers were characterised by SEM, TEM, UV–Visible spectrophotometer and a four-point probe technique.

3. Results and discussion

Figure 1(a) is a photograph of free-standing buckypaper, which has a certain strength, and it is flexible enough to facilitate handling the experiments. Figure 1(b) displays scanning electron micrographs revealing the morphology of the top surface of as-grown MWCNT membrane or buckypaper [18] indicating that the network consists of continuous individual MWCNTs self-assembled by a van der Waals force. Figure 1(c) illustrates the SEM image of the cross-section of the buckypaper, where the thickness of the buckypaper is 2.8 μm. High-resolution TEM (HRTEM) reveals (Figure 1d) that the as-grown CNTs are well-ordered graphitic sheets in [0 0 2] orientation (average plane spacing ~0.34 nm)

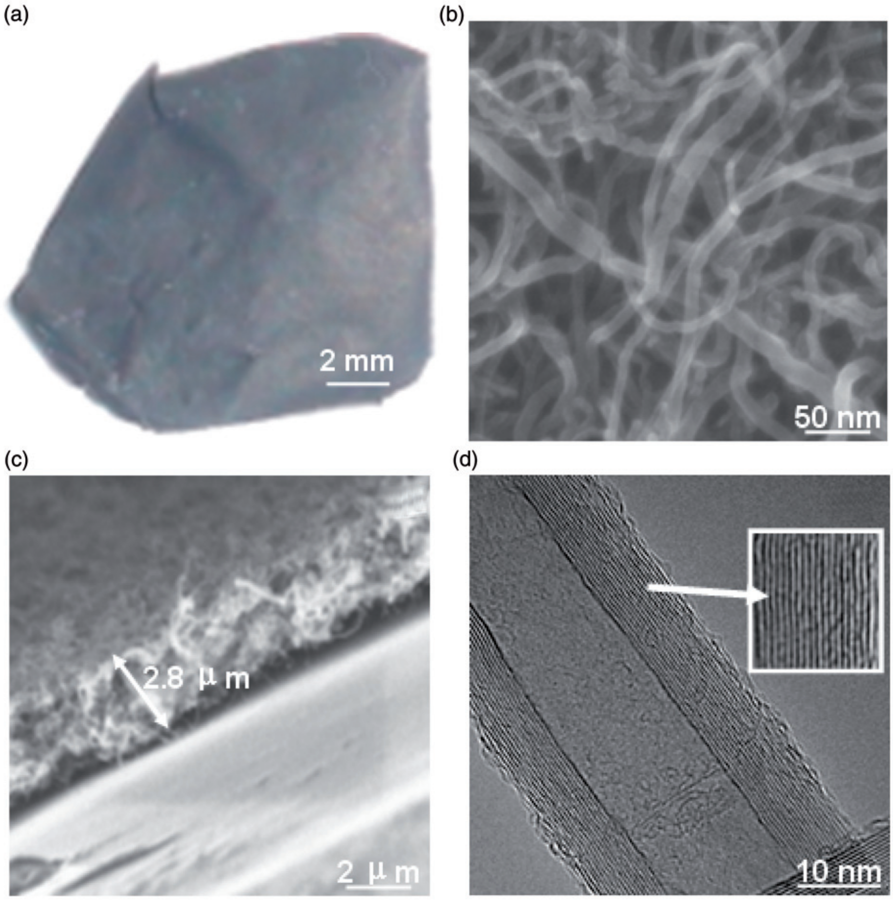

Figure 1. (a) MWCNT buckypaper; (b) SEM image of buckypaper; (c) Cross-section view of buckypaper and (d) HRTEM image of as-grown MWCNT, the inset is corresponding magnified image.

with some disordered graphitic lattice in the outer walls and the inset is its corresponding magnified image. After this first characterisation, the sample was irradiated with an Ar ion beam at the energy of 70 keV. After each ion dose, the same MWCNT buckypaper was again electrically, optically and structurally characterised. In addition, the same MWCNT buckypaper was also annealed at 800 K in a vacuum at each irradiation dose and was again electrically and optically characterised. We emphasise that the ion-irradiated buckypaper annealed at 800 K exhibits a better minimum annealing temperature which can change the properties of buckypaper, especially electrical conductivity.

When energetic Ar ions collide with the MWCNT buckypaper-induced defects in nanotubes due to displacement collisions and collision cascade effect, it generated large quantities of defects (vacancies and interstitials) on the tube walls and between the walls [18,19]. The concentration of higher defects results in the increment of degree of disorder. It is clear from the TEM image (Figure 2) that the density of defects created by Ar ion

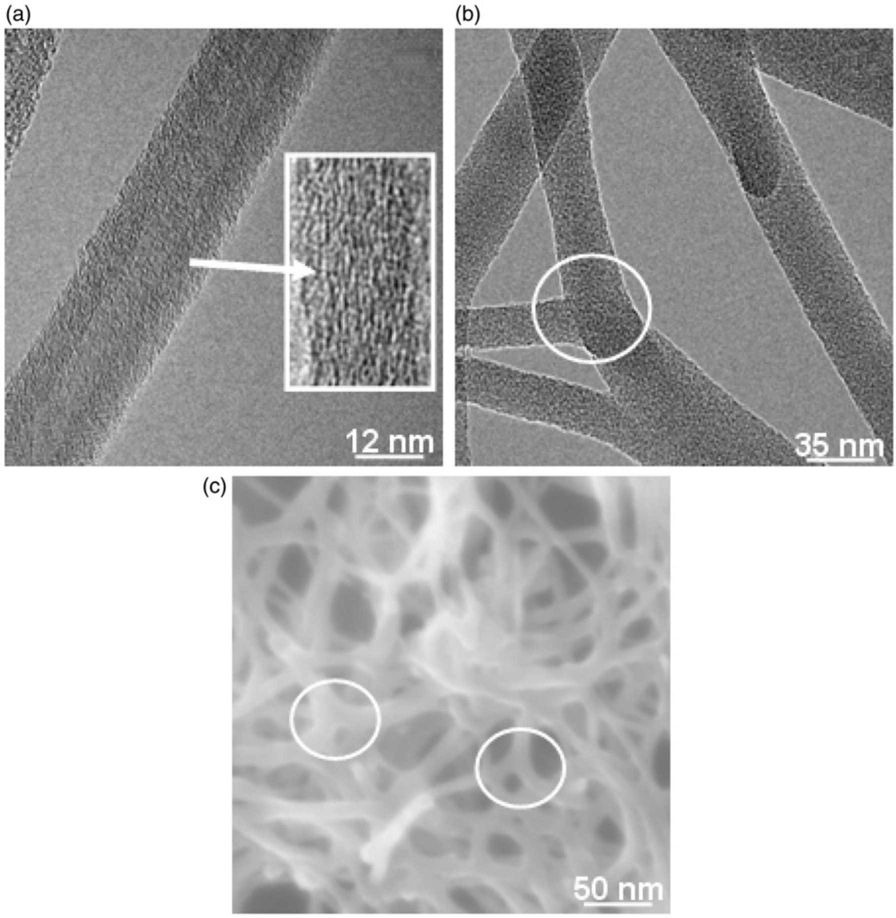

Figure 2. (a) HRTEM image of MWCNT irradiated at the dose of 5×10^{15} ions/cm^2, the inset is corresponding magnified image; (b) HRTEM image of MWCNT irradiated at the dose of 1×10^{17} ions/cm^2, the inset is corresponding SAD image and (c) Morphology of MWCNT buckypaper irradiated at the dose of 1×10^{17} ions/cm^2.

bombardment is increased with an increasing ion irradiation dose. These defects modify the optical, structural and electronic properties of the buckypaper. HRTEM image of Figure 2(a) indicates that few defects were created at the dose of 5×10^{15} ions/cm^2 and the corresponding magnified image shows that it is composed of disordered graphite. It is clear in Figure 2(b) that at the dose of 1×10^{17} ions/cm^2 the graphite structure of MWCNTs was strongly damaged resulting to destroy the layer structure after irradiation with Ar ion beam. Selective area electron diffraction pattern (SAED) shown in Figure 2(b), which shows typical amorphous halo rings, gives obvious evidence that the lattice structure of CNTs becomes unordered and formed an amorphous structure. SEM of the buckypaper (Figure 2c) irradiated by Ar ion at the dose of 1×10^{17} ions/cm^2 reveals that the buckypaper looks like an amorphous structure. Experiments and theoretical simulations have demonstrated that the ion beam irradiation can create various junctions between the

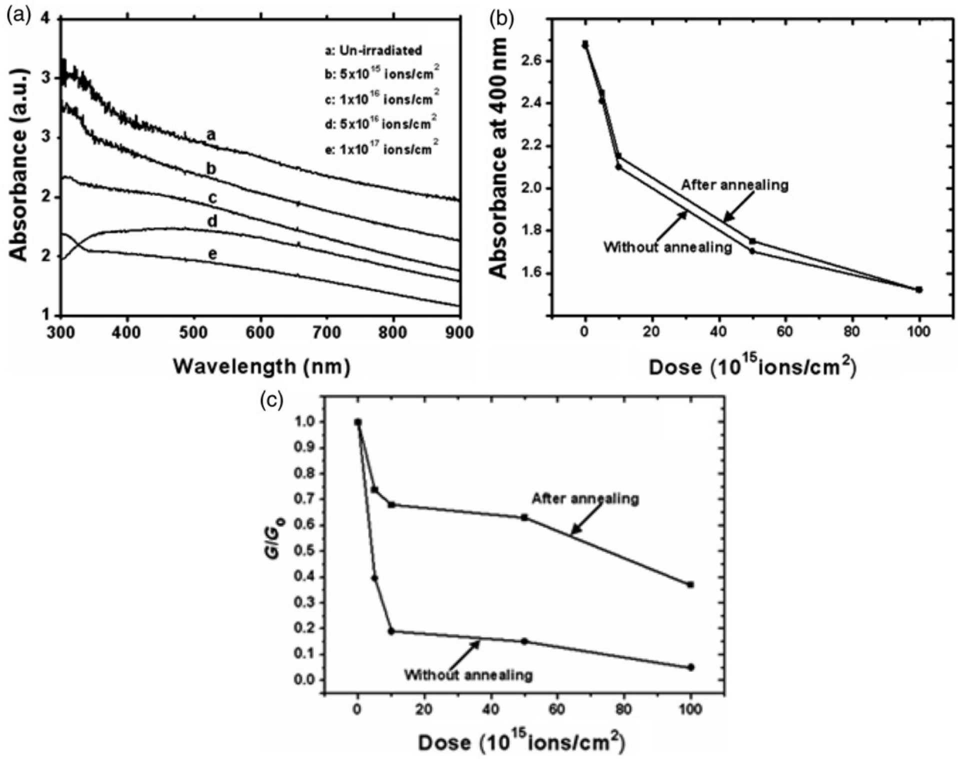

Figure 3. This figure shows (a) UV-Vis absorption spectra of Ar-irradiated MWCNT buckypaper at various doses; (b) variation in the optical absorption at 400 nm at various doses and (c) electrical conductivity as a function of irradiation doses.

crossed and the paralleled CNTs [20–22]. Amorphous junctions can be clearly seen in Figure 2(b) and (c), indicated by circles.

The optical properties of Ar ion-irradiated MWCNT buckypapers were investigated by UV-Vis spectrophotometer. The UV-Vis absorption spectra of MWCNT buckypaper deposited onto the quartz substrate were measured using the UV-Vis spectrophotometer, with identical quartz substrate in the reference beam to cancel the substrate effect. The optical absorption of the MWCNT buckypaper in the wavelength of 350–900 nm is shown in Figure 3. It is clear that un-irradiated MWCNT buckypaper has a higher optical absorption, and optical absorption consequently decreases with increasing Ar ion beam irradiation doses, as shown in Figure 3(a). Figure 3(b) shows the variation of optical absorption without annealed and annealed to 800 K in vacuum (better than 10^{-4} torr) at 400 nm as a function of various Ar ion doses. It shows that the optical absorption decreases with increasing Ar ion beam irradiation doses. Moreover, after annealing, the absorption, spectra remains almost the same as taken in room temperature in each ion dose. This optical absorption variation is attributed to the defects creation by energetic ion beam bombardment. This result suggests that the Ar ion beam creates defects that result in a low-crystalline structure of MWCNTs. It is supposed that the decreased crystallinity has caused the decrement of optical absorption.

The electrical conductivity of the buckypaper before and after annealing as a function of irradiation dose was measured in air by the four-probe method. In this method, the needle probe consists of four needles with an equal distance between the adjacent needles and was positioned on the top of the buckypaper. During the measurement, the four needles were brought down to make a contact with the buckypaper and a constant current was applied to the two outer needles. The voltage between the inner two needles was then measured using a voltmeter. The thickness of the buckypaper was much smaller than either of the probe spacing, therefore the correction factor was assumed to be unity. Using the equation mentioned in ref. [23], the conductivity was measured.

Figure 3(c) shows the ratio of electrical conductivity (G) irradiated at different doses to as-grown electrical conductivity (G_o) of un-annealed and annealed at 800 K sample as a function of irradiation dose. As-grown electrical conductivity (G_o) was considered to be unity and compared with the conductivity of irradiated samples. Therefore, it is concluded from Figure 3(c) that the conductivity decreases with increasing irradiation doses. The reduction of conductivity of SWCNTs thin film at room temperature with Ar and nitrogen (N) ion beam irradiation has been reported [15,24]. After annealing, the conductivity of the buckypaper was improved. Conductivity improvement after annealing ascribes that heating can give rise to a substantial drop in the defect number due to the migration of carbon atoms [13,15].

The reduction of optical absorption in the whole visible spectral ranges and electrical conductivity of the irradiated MWCNT buckypapers indicate that the defects creation in the MWCNTs might be caused by the ion beam irradiation. It is clearly seen from the TEM images in Figure 2 that the amorphous structures caused by Ar ion bombardment increased with the irradiation dose. From the TEM results of MWCNTs irradiated to different doses (Figure 2), the amorphous structure in the MWCNTs can be observed. The amorphous structures were found in some zones at the dose of 5×10^{15} ions/cm^2 (Figure 2a). Moreover, at the dose of 1×10^{17} ions/cm^2, the MWCNTs are strongly damaged and almost become amorphous, as shown in Figure 2(b). Compared with the graphite structures of MWCNTs, the light absorption of the amorphous structures of the irradiated MWCNTs might become small. Broitman et al. [25] reported that the optical band of carbon film composed of graphite and amorphous structure was changed due to the presence of a disordered graphite structure. Therefore, one possible reason is that the amorphous carbon structures have some energy gaps and light absorption decreases to some extent, and similarly the reduction of electrical conductivity. We will deeply investigate the light absorption of the irradiated MWCNTs in our future work.

4. Conclusion

We reported the effects of Ar ions on the optical, electrical and structural properties of the irradiated MWCNT buckypapers. The optical absorption of irradiated MWCNT buckypapers decreases with increasing Ar ion irradiation dose. Similarly, the electrical conductivity of irradiated MWCNT buckypapers also decreases with increasing Ar ion irradiation dose. The optical absorption and electrical conductivity decrease in irradiated MWCNT buckypapers can be ascribed to the increase of defects in the irradiated MWCNTs.

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