Optical absorption of ion irradiated multi-walled carbon nanotube sheets in the visible to terahertz ranges

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Abstract Optical absorption of Ar and H ion beam irradiated multi-walled carbon nanotube (MWCNT) sheets at various doses in the visible and terahertz spectral ranges was investigated. It was found that the optical absorption of MWCNT sheets in the visible range was decreased with increasing ion irradiation dose. Similar behavior was observed in terahertz range, where the optical absorption of MWCNT sheets in the range of 0 to 1.5 THz was also decreased with increasing ion irradiation dose. The optical absorption decreases in irradiated MWCNT sheets can be ascribed to the increase of defects in the irradiated MWCNTs.

Key words Carbon nanotubes, Ion irradiation, Optical absorption

1 Introduction

Carbon nanotubes (CNTs) exhibit extraordinary mechanical, thermal and electrical properties, and are considered as a key component of the emerging nanotechnology. At present, the CNTs have presented tremendous potential application in nano science field[1–4].

It has been reported that ion irradiation is a useful tool for adjusting defects and structures in CNTs in a controlled manner[5,6]. The structural changes can obviously alter the properties of CNTs. For instance, the effect of defects on the conducting properties of individual metallic single-walled CNTs (SWCNTs) was shown by the controlled reduction of the electronic localization length by Ar ion irradiation[6]. Also, irradiation-induced CNT films have shown great change in properties[5–7]. For example, electrical conductivity of irradiated CNT films at room temperature (RT) decreases with increasing irradiation dose[6]. However, electrical conductivity of the irradiated CNT sheets at a 800 K could be enhanced[8]. This study should be useful in assessing the viability of CNTs in optoelectronic and photonic applications. Optical properties of irradiated CNT films are important issues, and some transparent CNT thin films have been applied in optoelectronics[9,10].

Nevertheless, to the authors' knowledge, optical absorption of irradiated CNTs films has not been reported yet. In order to study this issue we irradiated MWCNT sheets with Ar and H ion beams and measured the optical characteristics of the MWCNT sheets. The reduction in the optical absorption of the irradiated MWCNT sheets was observed in the whole visible and terahertz spectral ranges. The results are attributed to irradiation induced defect production, which is helpful for an application of CNT films on transparent conducting materials.

2 Experimental

To prepare MWCNT sheets, a vacuum filtration method was adopted. Purified nanotubes (in purity of 99%, from Applied Nanotechnologies, Inc.) were

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dissolved in 1% solution of sodium dodecyl sulfate (SDS) surfactant. The solution was bath-sonicated for 4 h, and was placed for 24 h for settling down the un-dissolved MWCNT bundles. Mixed cellulose filters with pore size of 400 nm were used in vacuum filtration. After filtration, the CNT sheets were peeled from the filter membranes and transferred on to the target substrates of quartz glass or silicon. Residual surfactant adsorbed on the CNT sheets was washed away with purified water and acetone. The prepared samples were irradiated by Ar or H ion beams with different doses at RT in a 100-kV electromagnetic isotope separator (EMIS). The samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Optical properties of the samples were measured by UV-vis spectrophotometer and THz–TDS (terahertz time-domain spectroscopy).

3 Results and discussion

Fig.1 is a typical low magnification SEM picture of an un-irradiated MWCNT sheet. The thickness of the MWCNT sheet is ~3 micrometer, which was measured by a cross-sectional SEM image of the sheet. Using the UV-vis absorption spectrophotometer, optical properties of the MWCNT sheets on quartz substrate in visible range were investigated. The absorption spectra of the MWCNT sheets irradiated by Ar or H ion beams in the wavelength range of 300–900 nm are shown in Figs.2a and 2b, respectively. The results reveal that with increasing doses of Ar or H ion beam onto the MWCNT sheets, the optical absorption decreases as compared to un-irradiated MWCNT sheets having high optical absorption. Figs.2c and 2d show the variation of optical absorption at the wavelength of 400 nm as a function of Ar and H ion irradiation dose, respectively. It shows that the optical absorption decreases with increasing Ar or H ion dose.

The terahertz range optical properties of MWCNT sheets on quartz substrate irradiated by Ar or H ion beams are shown in Fig.3. The results were obtained by using THz–TDS, a useful method for characterization of material optical properties in the far-infrared range. Fig.3a shows the reference (without samples) and output (with samples) electromagnetic pulses measured by the THz–TDS, whereas Fig.3b shows the frequency-domain spectra of the reference and samples (from 0 to 1.5 THz), obtained by numerical Fourier transform. Frequency-domain spectra of the samples range from 0 to 1.5 THz. Figs.3a and 3b illustrate that the THz signal intensity of the un-irradiated MWCNT sheets was reduced to nearly half of the reference. The THz signal passed only through the quartz substrate. After irradiating the samples with Ar or H ion beams, however, it can be found that the THz signal intensity of Ar or H ion irradiated MWCNT sheets increased with the irradiation dose as shown in Figs.3a and 3b.

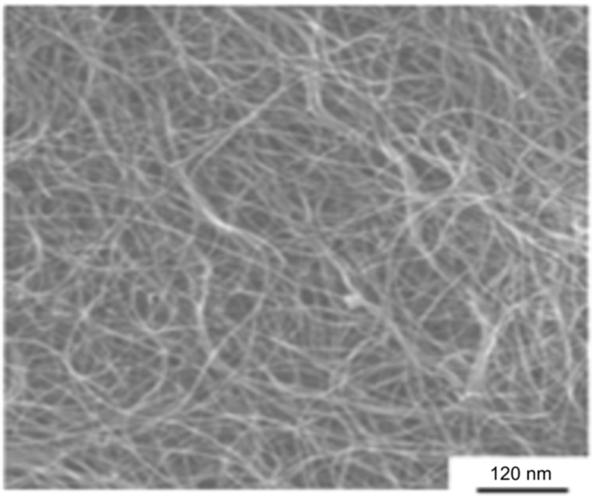

Fig.1 Morphology of un-irradiated MWCNT sheet.

In fact, the output THz signals include the sample's power absorption coefficient and index of refraction. Here, power absorption coefficient is a CNT sheet property to absorb an optical energy through a unit length. Using the relationship of Refs.[11] and [12], the power absorption coefficient can be determined by the measured input and output THz signals. Fig.3c shows the corresponding absorption spectrum for un-irradiated and irradiated samples at various doses. The absorption coefficients of all samples are slightly increased with the increasing frequency. The whole absorption coefficient in frequency range from 0 to 1.5 THz is decreased with the increasing ion irradiation dose.

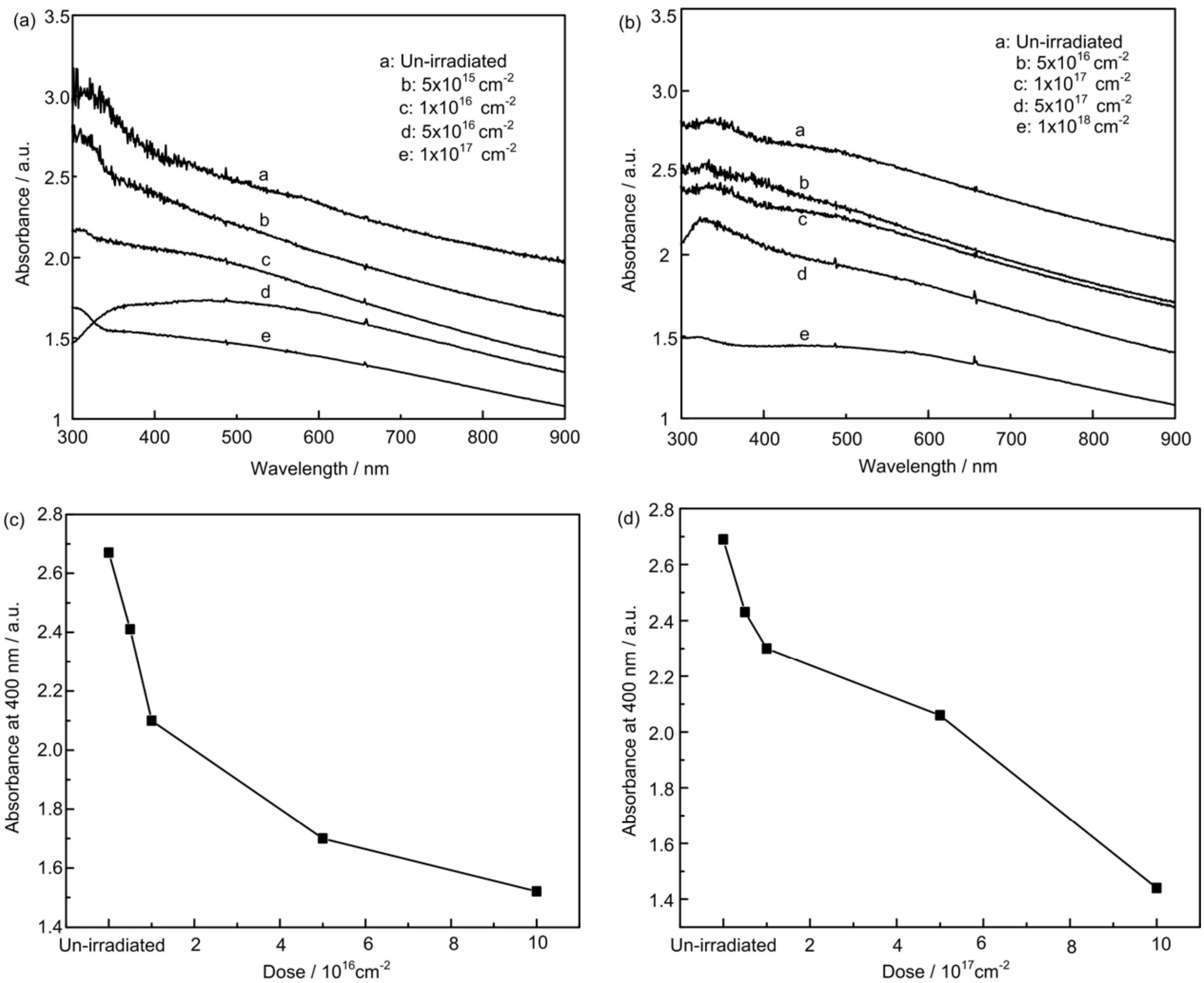

Fig.2 UV-vis absorption spectra of MWCNT sheets irradiated by (a) Ar and (b) H ions at various doses, and optical absorption at the wavelength of 400 nm with the MWCNT sheets irradiated by (c) Ar and (d) H ions.

This reduction apparently decreases in the optical absorption of the irradiated MWCNT sheets in the whole visible and the terahertz spectral ranges 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 Fig.4 that the amorphous structures caused by Ar or H ion bombardment increased with the irradiation dose. From the TEM results of MWCNTs irradiated to different doses (Fig.4), the amorphous structure in the MWCNTs can be observed. The amorphous structures were found in some zones at the dose of 5×10^{15} Ar/cm^2 and 5×10^{16} H/cm^2 (Figs.4a and 4c). Moreover, at the dose of 1×10^{17} Ar/cm^2 and 1×10^{18} H/cm^2, the MWCNTs are strongly damaged and almost become amorphous, as shown in Figs.4b and d. Compared with the graphite structures of MWNCTs, the light absorption of the amorphous structures of the irradiated MWCNTs might become small. Broitman *et al*[13] reported that the optical band of carbon film composed of graphite and amorphous structure was changed due to the presence of disorder graphite structure. Therefore, one possible reason is that the amorphous carbon structures have some energy gaps and the light absorption decreases to some extent. We will deeply investigate the light absorption of the irradiated MWCNTs.

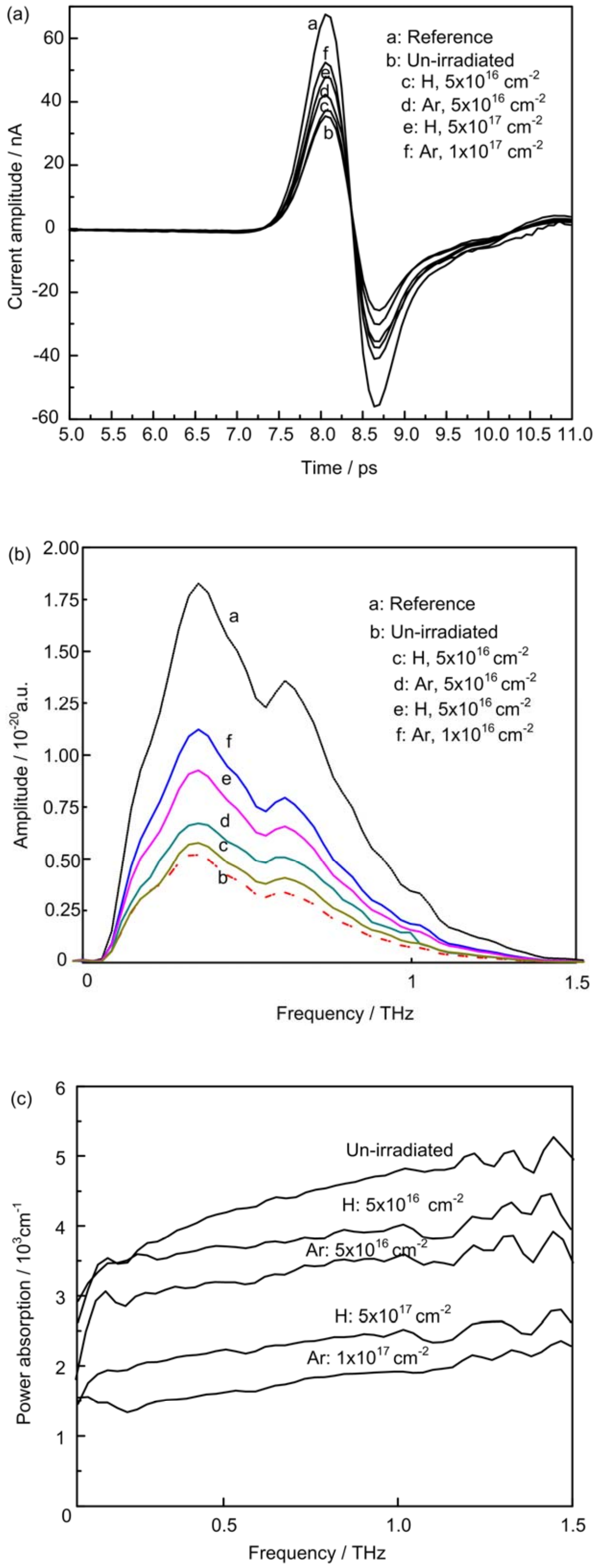

Fig.3 THz time-domain wave forms of the reference and ion irradiated MWCNTs (a), frequency-domain wave forms after Fourier transformation (b) and the power absorption of the un-irradiated carbon nanotubes and the ion irradiated MWCNTs (c).

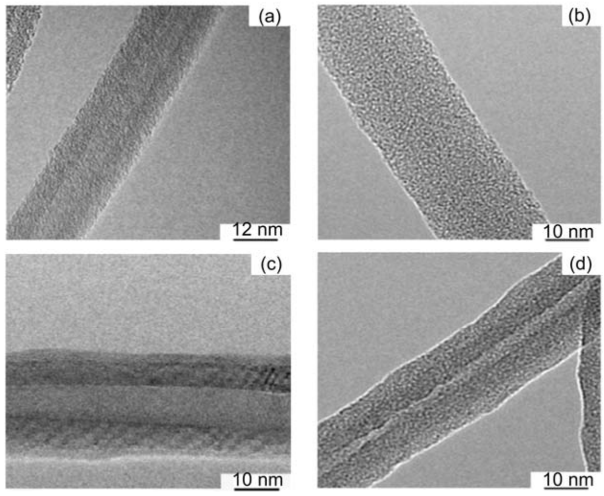

Fig.4 HRTEM images of MWCNT irradiated at various ions and doses, 5×10^{15} Ar/cm^2 (a), 1×10^{17} Ar/cm^2 (b), 5×10^{16} H/cm^2 (c) and 1×10^{18} H/cm^2 (d).

4 Conclusion

We reported the effects of Ar and H ions on the optical properties of the irradiated MWCNT sheets from the visible to terahrtz ranges. The optical absorption of the irradiated MWCNT sheets decreases as the Ar and H ion irradiation doses increase. The decreased optical absorption in the irradiated MWCNT sheets can be ascribed to the increase of defects in the irradiated MWCNTs.

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