CHIN. PHYS. LETT. Vol. 35, No. 11 (2018) 117801

First Principle Study on Optical Properties of Tri-Group Doped (6,6) SiC Nanotubes *

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(Received 27 July 2018)

The optical properties of tri-group (B, Al, Ga, In) doped (6,6) SiC nanotubes (SiCNTs) are studied from first principles. The results show that the main absorption and dispersion of SiCNTs caused by the intrinsic transition appear in the ultraviolet-visible region (below 500 nm), and the tri-group doping increases the minimum dielectric constant value resulting in enhanced transmittance. In addition, the tri-group doping can introduce a weak absorption and dispersion region in the near-mid-infrared region, and the response peak blue shifts as the diameter of the doping atom increases. Comparative studies of reflectance, absorptivity, and transmittance show that the key factors affecting the transmittance of SiCNTs are reflectance (or refractive index) rather than absorption coefficient.

PACS: 78.66.Li, 78.67.Ch, 74.62.Dh, 63.20.dk DOI: 10.1088/0256-307X/35/11/117801

Since the discovery of carbon nanotubes (CNTs) in 1991,[1,2] these types of quasi-one-dimensional structures (such as silicon carbide nanotubes, boron nitride nanotubes) have caused tremendous research,[3–6] and they have fascinating physical properties. Silicon carbide (SiC) materials have stable electronic properties and high thermal conductivity, they are considered to be suitable candidate materials for the manufacture of electrons and sensors in harsh environments with high power and high temperatures.[7–9] The quantum size effect in SiC nanomaterials makes SiC materials more unique and has great potential applications in the electronics and optoelectronics industries.[10–12] Therefore, it is very important to study SiC nanotubes. It is well known that doping is a common method for the study of SiC nanotubes.[13,14] In the existing literature on doped single-walled SiC nanotubes, the dopants are mostly ⅢA and VA elements.[15–21] Some of these studies on SiC nanotubes focus on the electrical properties, magnetic properties and functionalization,[21–24] however there are few in-depth studies on the optical properties of doped SiC nanotubes, systematic research on the SiC nanotubes doped with the same main group element is even less frequent.[25–28] Therefore, it is important to systematically study the influence of the tri-group doping on the optical properties of armchair SiCNTs. The results are expected to provide meaningful information for further research on SiCNT optoelectronic devices.

In the present study, the optical properties of the third group element (B, Al, Ga, In) doped (6,6) SiCNTs are studied by first-principles methods. All structures are optimized using the density functional theory (DFT) based on the CASTEP software. Among them, the plane wave cut-off energy is set to 310 eV and the exchange correlation effects are described by generalized gradient approximation (GGA). All atomic geometric optimizations are performed in the first Brillouin zone using k-points generated by a uniform $1 \times 1 \times 6$ grid parameters. All of the SiC nanotubes are twice as large as the smallest unit of SiCNTs constructed at 30 Å × 30 Å × c, and each SiCNT contains 48 atoms. To set the doping model, X-SiCNTs (X=B, Al, Ga, In) are constructed by substituting the same silicon atom (Si) in SiCNTs, respectively. Figures 1(a) and 1(b) are the dielectric constant spectra of undoped SiCNTs and doped SiCNTs, and Figs. 1(c)–1(g) are their electronic densities of states distribution.

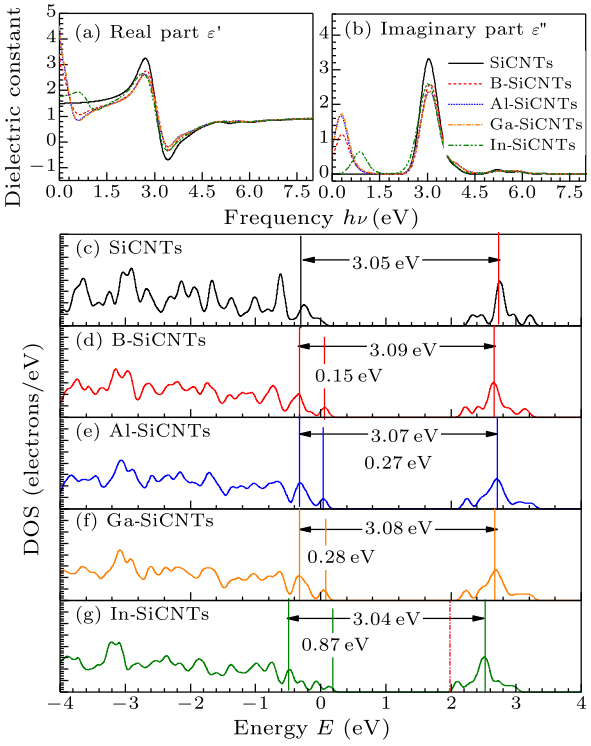

Fig. 1. The dielectric constant spectra [(a), (b)] of SiCNTs and X-SiCNTs (X=B, Al, Ga, In), and (c)–(g) Their electronic densities of states.

*Supported by the National Natural Science Foundation of China under Grant Nos 11574261 and 51132002, and the Natural Science Foundation of Hebei Province under Grant No A2015203261.

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It can be seen from Fig. 1 that there is only one obvious dielectric response region for undoped SiCNTs, and two dielectric response regions for doped SiCNTs. According to solid dielectric theory, the dielectric constant of semiconductor SiCNTs can be expressed as

$$\varepsilon(\omega) = 1 + \frac{\omega_{\rm p}^2}{(\omega_0^2 - \omega^2) - i\omega/\tau}, \tag{1}$$

where $\omega_{\rm p} = (4\pi Ne^2/m)^{1/2}$ is the plasma frequency, and τ is the relaxation time of the oscillation. From Figs. 1(b) and 1(c), the central frequency ω_0 corresponds to an energy of about 3.05 eV (ultraviolet-visible region). It is apparent that the dielectric response is derived from the electronic transition between the valence band and the conduction band of SiCNTs. For doped SiCNTs, the dielectric constant can be expressed as

$$\varepsilon(\omega) = 1 + \frac{\omega_{1p}^2}{(\omega_{10}^2 - \omega^2) - i\omega/\tau_1} + \frac{\omega_{2p}^2}{(\omega_{20}^2 - \omega^2) - \iota\omega/\tau_2}, \tag{2}$$

where the central frequencies of the two response peaks are $\omega_{10} = (3.04 - -3.09)$ eV and $\omega_{20} = (0.15 - -0.88)$ eV, which are derived from the valence band-conducting band and the valence band-impurity level of the doped SiCNTs, respectively (Figs. 1(d)–1(g)). Comparing the dielectric constant and electronic density of SiCNTs, we can find that the doping of the three groups of atoms leads to a weakening of the dielectric response in the ultraviolet-visible region. At the same time, a new dielectric response is generated in the infrared region, and as the doping atom diameter increases, this dielectric response undergoes a blue shift. This blue shift phenomenon occurs because the band gap of doped SiCNTs is smaller than that of undoped SiCNTs.[28]

Figure 2 shows the refractive index and dispersion coefficient from the deep ultraviolet to the mid-infrared range, where the dispersion coefficient of SiCNTs is obtained by

$$D(\lambda) = -\frac{\lambda}{c}\frac{d^2 n(\lambda)}{d\lambda^2}, \tag{3}$$

where λ is the wavelength, c is the propagation speed of the electromagnetic wave in the vacuum, and n is the refractive index of SiCNTs.

Figure 2(a) shows that in the near-ultraviolet-visible range, the refractive indices of SiCNTs and X-SiCNTs have large fluctuations (from 0.3 to 2.0). According to the relationship between dielectric constant and refractive index, this refractive index fluctuation is derived from the intrinsic transition of SiCNTs.[28] This refractive index fluctuation causes SiCNTs to have large dispersion in the spectral region below 500 nm, and the dispersion coefficient of In-doped SiCNTs is slightly smaller, as shown in Fig. 2(c). Figure 2(b) shows that in the near-mid-infrared range, X-SiCNTs exhibit a smaller peaks derived from the transition of electrons between the impurity level and the valence band. Compared with B, Al, and Ga doping, In doping has the least effect on the refractive index of SiCNTs. However, In doping produces greater dispersion than B, Al, and Ga, although the dispersion in the infrared region is much lower than in the ultraviolet region, as shown in Fig. 2(d).

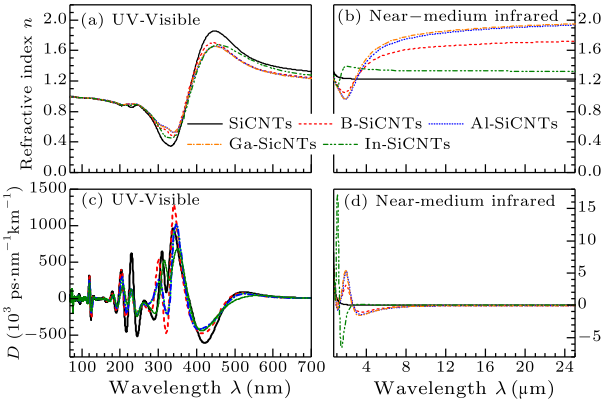

Fig. 2. The refractive indexes of SiCNTs and X-SiCNTs (X=B, Al, Ga, In) (a) in the deep ultraviolet range and (b) in the mid-infrared range, and the dispersion coefficients of SiCNTs and X-SiCNTs (X=B, Al, Ga, In) (c) in the deep ultraviolet range and (d) in the mid-infrared range.

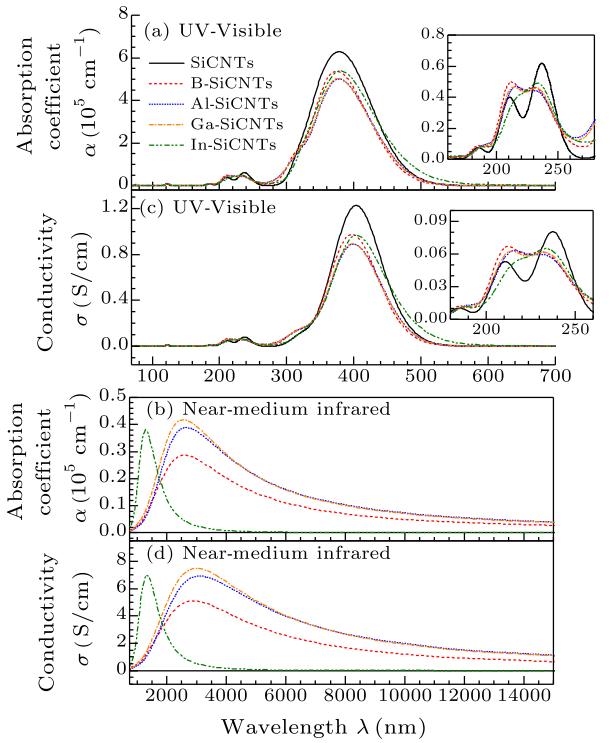

Fig. 3. The absorption coefficients of SiCNTs and X-SiCNTs (X=B, Al, Ga, In) (a) in the deep ultraviolet range and (b) in the mid-infrared range, and the photoconductivities of SiCNTs and X-SiCNTs (X=B, Al, Ga, In) (c) in the deep ultraviolet range and (d) in the mid-infrared range.

Figure 3 shows the absorption coefficients and conductivity spectra of undoped SiCNTs and doped SiCNTs from the deep ultraviolet to the mid-infrared range. It can be seen from Fig. 3 that undoped and doped SiCNTs have peaks in the far ultraviolet range, and the first strong peak appears at a position near the wavelength of 210 nm (energy is 5.3 eV). The peak

values of doped SiCNTs are smaller than the undoped peaks, and the peaks of doped SiCNTs blue shift. The second strong peak appears near the wavelength of 240 nm (energy is 5.9 eV). However, the peak value of the doped structure is larger than the undoped peak, and the position of the peak of the doped structure red shifts. In the visible range (Fig. 3(a)), each SiCNT exhibits a single strong absorption peak, which is caused by intrinsic excitation. Moreover, the peak of this absorption peak of SiCNTs is larger than the peak of X-SiCNTs (X=B, Al, Ga, In), and the peaks of the doped structure are similar, and the positions of the absorption peaks of the doped structure blue shift.

In the infrared range (Fig. 3(b)), SiCNTs have no peaks, while X-SiCNTs (X=B, Al, Ga, In) show a new single peak. This newly emerging peak is formed by the transition of impurity energy levels to valence bands. As can be seen from Fig. 1(b), the distances of X-SiCNTs (X=B, Al, Ga, In) from the impurity energy level to the top of the valence band (ionization energy) are 0.15 eV, 0.27 eV, 0.28 eV, 0.87 eV, respectively. Because the In doping has a larger ionization energy than B, Al, Ga, a significant blue shift phenomenon occurs. The smaller ionization energy of B, Al, Ga doping causes the blue shift phenomenon to be inconspicuous (Fig. 3(b)). Since this peak appears in the infrared band, a photosensitive semiconductor device in the infrared band can be prepared using a doped structure. The change law of the photoconductivity in the whole band is the same as the absorption coefficient, except that there is a small difference in the position of the peak (Figs. 3(c) and 3(d)).

Figure 4 shows the reflectances and transmittances of undoped and doped SiCNTs in different wavelength bands, where the reflectivity $R = (E_r/E_0)^2$, the loss rate $A = 1 - (E_l/E_0)^2 \exp(-2\alpha l)$, transmission $T = 1 - A - R$, E_0 and E_r are the electric field amplitudes of the incident wave and the reflected wave, respectively, E_l is the electric field amplitude of the electromagnetic wave when the distance l is propagated. In the optimized SiCNTs model, l is 0.618 nm.

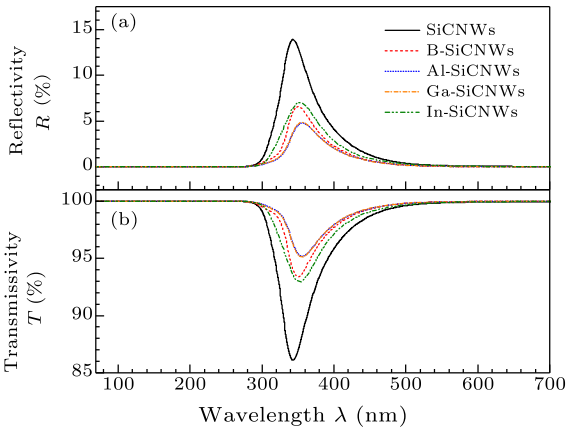

Fig. 4. (a) The reflectivities of SiCNTs and X-SiCNTs (X=B, Al, Ga, In) in different wavelength bands. (b) The transmittances of SiCNTs and X-SiCNTs (X=B, Al, Ga, In) in different wavelength bands.

It can be seen from Fig. 4 that the reflectance and transmittance of SiCNTs and doped SiCNTs reach a maximum around 350 nm. This symmetry indicates that the attenuation of the transmittance of SiCNTs is not derived from the absorption loss of the material, but from the reflection loss. According to $R = (n-1)^2/(n+1)^2$ and Fig. 2(a), when the refractive index of SiCNTs is the smallest, the reflection loss is the largest and the light transmittance is the lowest. For doped SiCNTs, doping increases the refractive index minimum, reduces reflection loss and improves light transmittance. Among the three elements, the change in reflectance and transmittance caused by Ga doping is the largest, that is, the transmittance is most obvious.

In summary, we have studied the optical frequency dielectric response, refractive index and dispersion, absorption coefficient, conductivity, reflection and transmittance of (6,6) SiCNTs and tri-group doped SiCNTs by first principles. The results show that SiCNTs have a dielectric response in the near-ultraviolet light, while the doped SiCNTs introduce a dielectric response in the near-infrared region in addition to the near-ultraviolet response. Comparative studies have found that SiCNTs have better light transmission except in the near ultraviolet (350 nm) region. At around 350 nm, there is a significant attenuation in the transmission of SiCNTs. The doping of the tri-group elements can increase the minimum dielectric constant, thus reduces the reflection coefficient and results in an increase in transmittance of SiCNTs.

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