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Amphoteric doping of single-wall carbon-nanotube thin films as probed by optical absorption spectroscopy

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We have separately probed the doping behavior of semiconducting (S) and metallic (M) single-wall carbon-nanotube (SWNT) films, by optical absorption and dc resistance (R) measurements. Either electron acceptors (Br_2, I_2) or donors (K, Cs) were used as dopants with controlled stoichiometry. Disappearance of absorption bands at 0.68, 1.2, and 1.8 eV, and concomitant decrease of R by doping have been attributed to electron depletion from or filling to specific bands in S- or M-SWNT's, demonstrating their amphoteric doping behavior. Changes in the electronic properties are discussed in terms of the charge-transfer mechanism in the framework of the rigid-band model. [S0163-1829(99)02743-5]

I. INTRODUCTION

Owing to their unique structural and electronic properties, single-wall carbon nanotubes (SWNT's) constitute a new class of materials that could contribute to the development of novel nanoscale electronic devices.[1–6] Since the control of valence electrons is crucial in any of such device applications, their doping behavior is one of their most important solid-state properties that must be elucidated

Indeed, the doping of SWNT was originally studied through dc resistance and thermoelectric power measurements as well as Raman spectroscopy.[7–10] While these works pioneered the possibility of controlling SWNT's valence electrons, the information thus obtained was essentially the averaged one and the change in any specific electronic states could not be directly identified. Because all the SWNT samples investigated so far have inevitably been mixtures of the semiconducting and metallic phase, it has been virtually impossible to separate the doping behavior of the former from that of the latter. In this context, there is still a paucity of information on the nature (semiconducting or metallic) and electronic states of SWNT's that undergo charge transfer.

In the present contribution, we have clarified these issues by the measurements of the change in optical absorption spectra of SWNT thin films induced by both *p*-type (I_2, Br_2) and *n*-type (K, Cs) doping. It should be stressed that, different from conductivity and Raman measurements, optical absorption can detect changes in some specific electronic states.[11] Disappearance of several absorption peaks by doping has been attributed to electron depletion from or filling to specific bands in the semiconducting or metallic phase, demonstrating their amphoteric doping behavior. Emergence of new peaks is interpreted as arising from doping-induced optical transition involving high- or low-lying electronic states. Furthermore, the simultaneous measurements of the change in absorption and in dc resistance for controlled stoichiometry demonstrated their close correspondence, yielding the unambiguous interpretation about the doping effects. Changes in the electronic properties of SWNT films are presented and discussed in terms of the charge-transfer mechanism in the framework of the rigid-band model.

II. EXPERIMENTS

SWNT samples were synthesized by the electric arc discharge method using Ni/Y catalyst.[11] The raw material consists mainly of carbon nanotubes, with a significant quantity of carbon particles and traces of the catalysts. From the A_{1g} breathing mode in Raman scattering, the transmission electron microscope and scanning tunnel microscopy (STM) measurements, the diameter of individual nanotubes were found to be distributed from 1.2 to 1.6 nm with various chirality.

SWNT's films were prepared by dispersing the raw material in ethanol and then by spraying on top of predeposited Au electrodes (for 4-probe dc resistance measurements) on quartz plate (for optical measurements) using an airbrush. The obtained films showed reasonably good optical quality and low resistivity (in the range 4×10^{-2}–4×10^{-3} Ω cm).

To carry out *in situ* doping while simultaneously recording optical absorption and dc resistance, we used a two-zone quartz vacuum vessel equipped with electrical connections. SWNT samples and doping sources were positioned far apart from each other to prevent direct coating. Doping was carried out with Br_2 (300 K), I_2 (320 K), K (500 K), and Cs (470 K) in gas phase at indicated temperatures, whereas all the optical and electrical measurements were performed at 300 K *in situ*.

The stoichiometry (CM_x) of the doped samples, essential in the forthcoming discussions, was determined *in situ* at each doping step (where C stands for carbon atom, M for dopant atom, and x their ratio). It was deduced by measuring the increase in the mass of SWNT film accompanying doping using a quartz crystal microbalance. To calculate $x=(m_M/m_C)(M_C/M_M)$, we implicitly assume that the samples are only consisting of carbon SWNT's, admittedly the main source of uncertainty of the estimated compositions

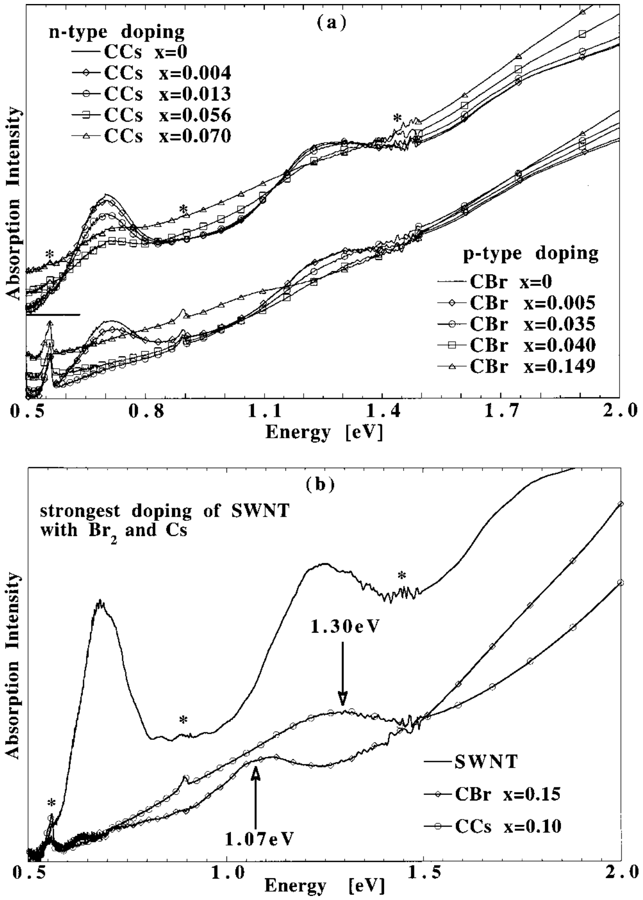

FIG. 1. (a) shows the evolution of the optical absorption spectra of SWNT films for various stoichiometry CM_x ($M=$Br, Cs). The entire set of spectra for CCs_x is offset for clarity with a short line indicating the 0 level. (b) shows the absorption spectra for strongly doped samples. * indicates features coming from the quartz and the noise from the spectrometer.

[where m_C and M_C (m_M and M_M) stand for the mass and molecular weight of the SWNT's (dopant), respectively].

III. PRISTINE SWNT FILMS

As shown in Fig. 1 (for $x=0$), the optical absorption spectrum of a pristine SWNT film is essentially the same as that already reported and analyzed by Kataura *et al.*[11] They established that the main features at 0.68, 1.2, and 1.8 eV superimposed on the broad absorption band centered at around 5 eV (not shown) derive from the bulk properties of SWNT. Furthermore, by comparing with calculated peak positions based on the zone folding method,[12] these features were assigned to optical transitions between Van Hove singularities of the density of states (DOS) of SWNT. Specifically, the features at 0.68 and 1.2 eV were unambiguously attributed to electronic transitions between pairs of singularities in semiconducting SWNT's ($v_s^1 \rightarrow c_s^1$ and $v_s^2 \rightarrow c_s^2$, respectively), whereas the feature at around 1.8 eV came predominantly from the first pair of singularity ($v_m^1 \rightarrow c_m^1$) in metallic SWNT's. At energies higher than 2 eV, the absorption features are less resolved and consequently their assignment to specific electronic transitions are unsecured. The above-mentioned assignments are consistent with STM studies of individual SWNT's,[13] as well as with high-resolution momentum-dependent electron-energy-loss spectroscopy (EELS) experiments of bulk SWNT's.[14]

IV. DOPED SWNT FILMS

Now that the origin of each absorption bands is established, we can directly and systematically study how the electronic states of semiconducting and metallic SWNT's are affected by doping with typical electron donors (K, Cs) or electron acceptors (I_2, Br_2) for various stoichiometry.

Figure 1 shows the progressive changes of the optical absorption spectra when doped with Br_2 and Cs, respectively. A remarkable observation is the sizable decrease of the intensity of the absorption bands at 0.68 eV without a significant change of the features at 1.2 and 1.8 eV, at the initial stage of the doping (typically for $x<0.005$) irrespective of the nature of the dopants. Subsequent doping (typically for $x<0.04$) leads to a dramatic depletion of both bands at 0.68 and 1.2 eV without a substantial alteration of the band at 1.8 eV. In this range of stoichiometry ($0<x<0.04$), we have observed neither a shift of the absorption bands nor an appreciable increase of the absorption background, again for all dopants. In this context, Fig. 2 specifically displays the variation of the normalized intensity of several absorption peaks ($I_x/I_{x=0}$) at 0.68, 1.2, and 1.8 eV versus stoichiometry CM_x ($M=$Br, Cs). A reasonable statement is that ($I_x/I_{x=0}$) only at 0.68 and 1.2 eV show a considerable decrease with increasing x. Since this simplistic analysis ignores that the absorption features are broad and to some extent overlapping with increasing energy, we refrain from further quantitative analysis. We note that essentially the same changes were observed for I_2 and K doped SWNT's.

At high doping level (typically for $x>0.04$), only achieved with Cs and Br_2, all the above-mentioned features almost completely vanish (Fig. 1). In this range of stoichiometry we stress that the absorption feature at 1.8 eV is completely smoothed out. Moreover, two important changes were detected at this doping level: the gradual increase of the absorption background and the emergence of new bands at approximately 1.07 and 1.30 eV as clearly evidenced for stoichiometry at $CBr_{0.15}$ and $CCs_{0.10}$, respectively (Fig. 1). Their origins will be discussed separately.

The optical absorption band at 5 eV (assigned to π plasmon) gained intensity and broadened without significantly shifting with increasing the dopant concentration, irrespective of the nature of the dopants (not shown and not analyzed in this paper).

These results are in good agreement with a recent report on purified and chemically modified SWNT in CS_2 solution doped with I_2 or Br_2 (Ref. 15) and EELS experiments on K-doped SWNT.[16] With all these well corresponding results, it can be concluded that the observed changes in the optical absorption spectra upon doping reflect the inherent property of SWNT's.

A remarkable observation here is that SWNT films doped with either electron donors (K, Cs) or electron-acceptors (I_2, Br_2) show very similar changes in optical absorption spectra. This is the direct experimental demonstration of the amphoteric behavior of both the semiconducting and metallic

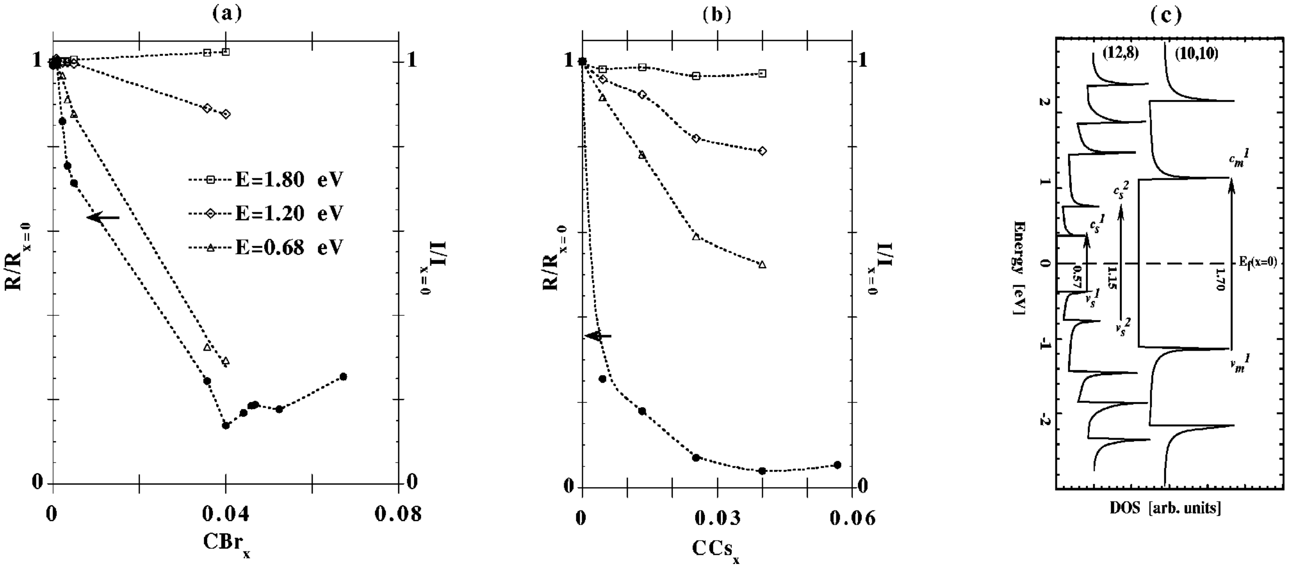

FIG. 2. (a) and (b) Normalized intensity of the absorption peaks ($I_x/I_{x=0}$) at 0.68, 1.2, and 1.8 eV and the normalized dc electrical resistivity ($R_x/R_{x=0}$) for various stoichiometry CM_x ($M=$Br, Cs) at 300 K. The dashed lines are guides to the eye. (c) DOS calculated in a tight-binding model for (10,10) metallic and (12,8) semiconducting SWNT's. The energies (eV) correspond to allowed electronic transitions between Van Hove singularities of the DOS. E_f is the Fermi level at $x=0$.

SWNT's. We stress that this was made possible by using optical absorption spectroscopy, which can separately probe their intrinsic properties.

To illustrate the above and also the forthcoming discussions, we assume an ''ideal sample'' consisting only of one type of semiconducting and one type of metallic SWNT's with chirality index (12,8) and (10,10), respectively. These were deliberately chosen because their calculated DOS [Fig. 2(c)] accounts for most of the electronic transitions observed in the optical absorption spectra, except for their broadening. Because the position of singularity peak depends on the tube diameter and chirality, which have considerable distribution, and also because in solid state intertube interaction causes additional band dispersion,[17,18] the experimentally observed absorption bands are inevitably broad.

A straightforward interpretation of the experimental results can be derived by invoking a charge-transfer mechanism within the framework of the rigid-band model, by analogy to carbon graphite intercalation compounds.[19] By choosing the nature of the dopant (K, Cs, I_2, Br_2) and by controlling the stoichiometry, we have been able to tune the electron transfer so that the Fermi level (E_F) coincides with specific bands (or distribution of bands) of DOS of semiconducting and metallic SWNT's. In the case of a strong electron donor such as Cs, the charge transfer occurs to specific electronic states of the semiconducting and metallic SWNT's in the following sequence: first to c_s^1 and then to c_s^2 of the same semiconducting SWNT and finally to c_m^1 of the metallic SWNT [Fig. 2(c)]. Accordingly, the absorption bands also deplete with the same sequence: first 0.68, then 1.2, and finally 1.8 eV. In the case of a weak electron donor such as K, the charge transfer occurs and affects predominantly the electronic states of semiconducting SWNT, consistent with the depletion of the band at 0.68 and then at 1.2 eV, within the doping level achieved in the present work. A similar explanation can be applied to I_2 and Br_2 doping, where electrons are depleted from the highest occupied energy level.

V. DOPING-INDUCED ABSORPTION

We have observed the emergence of doping-induced optical transitions at around 1.07 and 1.3 eV for Br_2 and Cs doping, respectively, but their origins are still open to speculation. We propose a tentative interpretation for Br_2 doping. The fact that the feature at 1.07 eV emerges at relatively high doping concentration indicates an involvement of a change in the first valence band of metallic SWNT (v_m^1). This is supported by the observation that the absorption feature at 1.8 eV (attributed to the $v_m^1 \rightarrow c_m^1$ transition) disappears at high doping level. A change in the semiconducting band, if involved, would emerge at much lower doping level [Fig. 2(c)]. The depletion of v_m^1 should enable new optical transitions from deep-lying valence bands to v_m^1, explaining the experimental results. A similar explanation can be applied to Cs doping (filling of c_m^1). The discrepancy of the band position (1.07 and 1.30 eV for $CBr_{0.15}$ and $CCs_{0.10}$, respectively) might be an indication of the asymmetry of the electronic structure of SWNT's, if the rigid-band model is valid.

The increase of the absorption background upon doping does not originate from the metallic coating (this effect occurs for both Cs and Br_2 doping) or the degradation of the optical quality of the SWNT sample (this effect is reversible) but does reflect important contribution from low-energy electronic transitions and also from free-carriers absorption (or Drude behavior). Further work in the IR range is necessary to elucidate its origin, but it is beyond the scope of the present paper.

VI. CORRELATION WITH RESISTANCE CHANGE

Next, we further inquire into the consequences of the charge-transfer properties and the changes in electronic states, by performing dc electrical resistance measurements concurrently with those of optical absorption, as a function of doping concentration. The normalized dc resistance

$R_x/R_{x=0}$ (Fig. 2) invariably decreases with increasing the doping concentration (for $x<0.04$) irrespective of the nature of dopants, consistent with an increase of the carrier density. The behavior of $R_x/R_{x=0}$ parallels that of the optical absorption ($I_x/I_{x=0}$) at 0.68 and 1.2 eV, but not that at 1.8 eV. We have established a striking correlation between ($R_x/R_{x=0}$) and ($I_x/I_{x=0}$, for $x<0.04$) as demonstrated in Fig. 2, yielding unambiguous interpretation about the charge transfer. These results altogether suggest that the changes in $R_x/R_{x=0}$ (transport properties) upon doping are largely governed by the changes in the electronic properties of semiconducting SWNT's.

The way $R_x/R_{x=0}$ change with the doping concentration is qualitatively different for the weak and the strong dopants. While $R_x/R_{x=0}$ decreases monotonically and saturates in the case of K and I_2, it goes through a minimum and significantly increases in the case of Cs and Br_2 doping. Further analysis of our results shows that this minimum coincides qualitatively with the disappearance of the absorption band at 1.8 eV, the rise of the new features (at 1.07 and 1.30 eV) and of the absorption background, as clearly demonstrated in the case of Br_2 and Cs doping. This minimum occurs for stoichiometry corresponding approximately to $CCs_{0.040}$ and $CBr_{0.044}$. It is worth noting that, in this range of stoichiometry, a phase transformation was theoretically predicted in the case of K doped SWNT crystal.[20] These results conjointly suggest that the complex behavior of $R_x/R_{x=0}$ is related to the changes of both the electronic and the crystal structure of SWNT's. Grigorian *et al.* noticed similar behavior for SWNT mat doped with K and Cs based on resistivity measurements.[10]

VII. REVERSIBILITY OF DOPING

Finally, we briefly discuss the reversibility of intercalation/deintercalation cycles for I_2 and Br_2 doping. For I_2, the vanished absorption bands at 0.68 and 1.2 eV almost perfectly restored after deintercalation by annealing under vacuum. This suggests that semiconducting SWNT's can undergo reversible charge transfer with no appreciable damage to its electronic structures. For highly Br_2 doped SWNT's, the vanished absorption bands are only partially restored with considerable broadening after annealing at temperatures as high as 573 K under vacuum. This indicates the irreversibility of the charge transfer, probably deriving from strong interaction between Br and SWNT's.

VIII. SUMMARY

In summary, we have separately probed the doping behavior of semiconducting (S) and metallic (M) single-wall carbon-nanotube (SWNT) films, by optical absorption and dc resistance (R) measurements. Either electron acceptors (Br_2, I_2) or donors (K, Cs) were used as dopants with controlled stoichiometry. Disappearance of the absorption bands at 0.68, 1.2 (assigned to semiconductor SWNT's) and 1.8 eV (assigned to metallic SWNT's), and the concomitant decrease of R by doping were attributed to electron depletion from or filling to the specific bands in S- or M-SWNT's, demonstrating their amphoteric doping behavior. S- and M-SWNT's undergo charge transfer in a specific sequence: first 0.68, then 1.2, and finally 1.8 eV, depending on the nature and concentration of the dopant. Changes in the electronic properties were discussed in terms of the charge-transfer mechanism in the framework of the rigid-band model.The present results provide important information for further understanding of SWNT's basic properties as well as for its applications to electronic devices.

Note added. During the preparation of this manuscript, we came to know about the work of Petit *et al.*[21] In the latter work Li^+ doping was carried out in tetrahydrofuran solution with several radical anions, and for Br_2 and I_2 doping in gas phase, in very good agreement with one part of our optical absorption results. However, the compositions were not estimated nor was the correlation with the electrical resistivity considered, essential for the discussion of the doping behavior of SWNT. Here, we have filled the gap by an exhaustive and systematic study.

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