Formation and electronic properties of BC$_3$ single-wall nanotubes upon boron substitution of carbon nanotubes

G. G. Fuentes, E. Borowiak-Palen, M. Knupfer, T. Pichler, and J. Fink

Leibniz-Institute für Festkörper- und Werkstoffforschung Dresden, P.O. Box 270016, D-01171 Dresden, Germany

L. Wirtz and A. Rubio

Department of Material Physics, University of the Basque Country, Centro Mixto CSIC-UPV, and Donostia International Physics Center, Po. Manuel de Lardizábal 4, 20018 San Sebastián, Spain

(Received 17 November 2003; revised manuscript received 3 February 2004; published 10 June 2004)

We report a detailed experimental and theoretical study on the electronic and optical properties of highly boron-substituted (up to 15 at.%) single-wall carbon nanotubes. Core-level electron energy-loss spectroscopy reveals that the boron incorporates into the lattice structure of the tubes, transferring $\sim 1/2$ hole per boron atom into the carbon derived unoccupied density of states. The charge transfer and the calculated Fermi-energy shift in the doped nanotubes evidence that a simple rigid-band model can be ruled out and that additional effects such as charge localization and doping induced band-structure changes play an important role at this high doping levels. In optical absorption a new peak appears at 0.4 eV which is independent of the doping level. Compared to the results from a series of ab initio calculations our results support the selective doping of semiconducting nanotubes and the formation of BC$_3$ nanotubes instead of a homogeneous random boron substitution.

DOI: 10.1103/PhysRevB.69.245403 PACS number(s): 78.30._j, 61.46._w, 63.20.Dj

I. INTRODUCTION

Tuning the electronic properties of single-wall carbon nanotubes (SWCNT) (Refs. 1 and 2) by substitution of carbon by heteroatoms represents one of the most promising routes to extend their application possibilities. It also opens a series of basic scientific questions regarding, e.g., charge transfer between B and C atoms, band-structure change, and charge-carrier localization. Recent studies were mainly focused on boron and nitrogen doping of multiwalled carbon nanotubes (MWCNT). They have already successfully achieved boron or nitrogen incorporation by different procedures. Recently, Golberg et al. reported the B and N substitution of SWCNT by a substitution reaction at high temperatures.

Despite the importance of these one-dimensional (1D) heteroanstructures, only very few experimental studies have been devoted to their electronic properties. The electronic structure of multiwalled boron doped nanotubes was studied on a local scale by scanning tunneling spectroscopy (STS). Spectroscopic studies of the electronic properties of single-wall heteronanotubes are still missing to our knowledge.

In theory, the role of the B or N atoms in the electronic structure of modified $sp^2$-hybridized carbon networks has been treated using different approaches. Mele and Ritsko used a tight-binding approach to calculate the core exciton spectrum of graphite and showed that the changes induced by low B substitution (0.5 at.%) can be explained by a rigid-band shift model, i.e., assuming that the Fermi level is shifted downwards due to the missing $\pi$ electrons from the boron atoms while the valence-band structure remains otherwise undisturbed. Yi and Bernholc calculated ab initio for a (10,0) nanotube with 1.25 at.% B substitution the formation of a shallow acceptor state at 0.16 eV above the Fermi level. Band-structure calculations of hypothetical tubule forms of hexagonal BC$_3$ predicted that these tubes form as likely as carbon and BN nanotubes and have a minimum energy gap of about 0.2 eV. Carroll et al. proposed that B substitution of CNT’s leads to the formation of BC$_3$ nanodomains inserted in the 1D nanotube structure, giving rise to an acceptor state 0.4 eV below the Fermi level due to the realignment of this superstructure with the graphitic one. Lammert et al. showed that under doping with boron and nitrogen, the microscopic doping inhomogeneity of carbon nanotubes is larger than in normal semiconductors leading to charge fluctuations that can be used to design nanoscale devices (diode behavior).

In this paper we report on a spectroscopic study of highly B-doped SWCNT (B-SWCNT) using high-resolution non-spatially resolved electron energy-loss spectroscopy and optical spectroscopy. The spectroscopic response is then interpreted with the help of ab initio band-structure calculations using density-functional theory in the local-density approximation (DFT-LDA). Our results evidence the preferential doping of semiconducting SWCNT and the formation of BC$_3$ single-wall nanotubes in boron substituted SWCNT samples.

II. EXPERIMENTAL RESULTS

SWCNT with a mean diameter of 1.23 nm were produced by the laser ablation technique. Boron doping with an averaged substitution level of $\sim 15$ at.% was achieved by a substitution reaction in an NH$_3$ atmosphere. Transmission electron microscopy (TEM) characterization after the substitution reaction revealed the presence of high-purity nanotube bundles with a homogeneous diameter distribution. Transmission electron microscopy electron energy-loss spectro-
interaction between the excited electron and the core-hole in B-SWCNT, one can expect that the $\pi'$ resonances related to the density-of-states (DOS) singularities of the different types of SWCNT are washed out, resulting in the broad $\pi'$ resonances. Nevertheless, the edges can be used to study some details in the electronic structure. The $1s$ spectrum of B-SWCNT shows an intense peak at 192 eV assigned to the $1s \rightarrow \pi'$ resonance and a less intense double peak at 199 eV due to the $1s \rightarrow \sigma'$ resonance. The small shoulder at 194 eV can be assigned to residual $B_2O_3$ from the precursor material. The $1s$ spectrum of B-SWCNT shows the excitonic $1s \rightarrow \pi'$ absorption at 285.3 eV, as in the case of the SWCNT reference, and the corresponding $1s \rightarrow \sigma'$ absorption at 292 eV. The spectral shape of the $1s \rightarrow \pi'$ and the $1s \rightarrow \sigma'$ resonances of the B-SWCNT resemble quite well those of the pure material, indicating that the boron substitution does not alter the chemical environment of the carbon atoms of the tube significantly.

The comparison of the $1s$ spectrum of the B-SWCNT with that of the BN nanotubes indicates that the chemical environment of boron is rather similar to that expected for an $sp^2$-hybridized environment, as it is also characteristic of h-BN, which constitutes clear experimental confirmation that the boron atoms are incorporated into the hexagonal lattice structure of the nanotube, in good agreement with the theoretical predictions. The area below the $\pi'$ resonance gives a measure of the charge transfer and bonding environment. We observe that the $1s \rightarrow \pi'$ peak is about 13% lower in the B-SWCNT than in the MWBNNT, which shows that there is a different charge distribution within the B-C bonds which results in a higher electron density at the boron site. Turning back to the $1s$ excitation spectra, the inset of Fig. 1 provides evidence for the appearance of additional unoccupied states of carbon character in the electronic structure of the B-SWCNT, as clearly shown by the low-energy shoulder observed at the $1s$ excitation threshold and indicated by the arrow. The energy position of this feature can be roughly estimated around 0.7 eV below the corresponding $1s \rightarrow \pi'$ threshold of the pure SWCNT. In analogy to $p$-type doping in graphite intercalation compounds, the presence of this doping-induced feature reflects that the Fermi level of the B-SWCNT shifts to lower energies with respect to that of the SWCNT. Although the corresponding total shift of the Fermi level from a comparison of both spectra alone can be complicated by additional effects such as different excitation effects or the mixture of semiconducting and metallic tubes, the observed shift by 0.7 eV of the $1s$ excitation onset establishes a good estimate for the Fermi-level shift assuming a rigid-band shift without strong changes of the SWCNT band structure as it is observed, for instance, for FeCl$_3$ intercalated SWCNT. Hence, the shift in the onset of spectral weight and the increase of the response of the $\pi'$ resonance confirms that there exists a charge transfer from the boron atom to the C-derived bands. However, the analysis of Fig. 1 indicates that the shoulder is only about 6% of the total area, suggesting a charge transfer to carbon derived states of $\sim 1/2$ holes per boron atom which is lower than the estimation by Mele et al. for B-doped graphite (0.8 holes per B). This difference in the charge transfer also means a different charge
are less affected by the substitution reaction than the
reduced to about 20% of its intensity. The fact that the metallic
delocalization around the B site and therefore is a hint for a
due to the boron substitution. In other words, the boron doping
of SWCNT cannot be solely explained within the framework of a
simple rigid-band model and additional changes in the
the valence band into a new unoccupied acceptor
bands are formed. This corresponds to the formation of an
acceptor level (occupied state within the band gap) in
self-consistent calculations with a pseudorandom ordering of
acceptor bands.27 In particular, self-consistent
dissymmetries arise due to the mixing of p and s orbitals. Doping of the tubes leads to a lowering of the Fermi
level into the valence band of the undoped tubes [Figs.
3(b), 3(d)]. Clearly, the stronger the doping, the stronger is
also the shift of the Fermi level. For a substitution level of 25%, the level shift reaches 2.2 eV. The rigid-band shift
model (shift of the Fermi level without altering the band
structure) clearly breaks down for strong concentrations:
Above the highest occupied state of the undoped tube new
bands are formed. This corresponds to the formation of an
acceptor level (unoccupied state within the band gap) in
semiconductors with very low dopant concentration. How-
ever, in the present case, due to the strong concentration of
boron atoms, the acceptor levels hybridize with the carbon
levels and form strongly dispersive “acceptor bands,” i.e.,
new bands that are unoccupied due to the lower number of
valence electrons of the boron atoms. Correspondingly, in the
DOS, new unoccupied vHS appear giving rise to additional
possibilities for electronic excitations.

We expect that the additional peak at 0.4 eV in the ab-
sorption spectrum (Fig. 2) is due to electron excitation from
the occupied valence states into one of these acceptor bands.
Indeed, the joint DOS (divided by $E^2$) in Fig. 3 display peaks in the energy region between 0.2 and 0.6 eV. The exact po-
position of the additional peaks is, however, strongly dependent
on the doping concentration. Furthermore, calculations with
the same degree of substitution but with different arrange-
ment of the boron atoms show large differences in the for-
mation of acceptor bands.27 In particular, self-consistent
tight-binding calculations with a pseudorandom ordering of
boron atoms in a large supercell containing several hundred
atoms display a smearing out of the vHS pattern.27 In that
case, a quasicontinuous set of electronic transitions would
completely wash out the optical-absorption pattern. Hence,
these results do not at all fit to the experimental observations.
Due to the strong dependence of the band structure on the

![FIG. 2. Optical-absorption spectra of boron doped SWCNT (solid) and pristine SWCNT (dashed).](image)
degree of substitution and the particular arrangement of the boron atoms, we conclude that the observed optical-absorption spectra in Fig. 2 can be best explained with the assumption that only one particular kind of boron substituted tubes is formed in our experiment. Only a subset of tubes from the sample are doped (with a corresponding higher concentration) while the other tubes remain almost pure carbon tubes. This explains the stable peak positions in the spectra. The peaks at 0.7 and 1.4 eV are due to the transitions between first and second vHS in the pure semiconducting carbon tubes. This explains the stable peak positions in the spectra. The peaks at 0.7 and 1.4 eV are due to the transitions between first and second vHS in the pure semiconducting carbon tubes. In strongly B-doped samples they should disappear because of the Fermi-level lowering. However, the survival of a large fraction of pure carbon tubes explains the survival of these peaks and the decreasing intensity with increasing fraction of boron atoms in the sample. The unchanged intensity of the peak at 1.9 eV is consistent with the assumption that metallic tubes are less susceptible for Boron substitution.

We assume the formation of BC₃ tubes in our samples (25% substitution) which is consistent with the average degree of substitution (up to 15%) in our sample. The BC₃ structure has been shown to be relatively stable (with respect to other arrangements) both for the sheet and for single-wall tubes. The relative stability is likely connected with the fact that these tubes are semiconducting with a gap between the occupied π orbitals and the π orbitals which are unoccupied due to the electron deficiency.

In Figs. 4(a) and 4(b) we present the band structure and DOS of a BC₃(3,3) tube. The tube displays a band gap of 0.4 eV between occupied and unoccupied π orbitals in agreement with the tight-binding band structure of Ref. 10. The joint density of states [divided by $E^2$ in Fig. 4(c)] displays accordingly the first vertical transition at about 0.4 eV in very good agreement with the observed absorption peak. We note that calculations of the optical response [dashed line in Fig. 4(c)] of such a perfect BC₃ nanotube show that the first optically allowed transition is at about 1.8 eV (very

FIG. 3. Band structure, DOS and joint DOS divided by $E^2$ of a C(16,0) tube with (a) 0%, (b) 6.25%, (c) 12.5%, and (d) 25% boron doping. Zero energy denotes the Fermi energy. Filled states are indicated by gray shadowing. Also displayed are the corresponding unit cells (C atoms black, B atoms white).

FIG. 4. (a) Band structure of BC₃(3,3) nanotube (Fermi energy at 0 eV). (b) Density of states (filled states shadowed with gray). (c) Joint density of states divided by $E^2$ (solid line) and calculated optical absorption (dashed line) of a perfect infinite BC₃(3,3) tube with light polarization along the tube axis. (d) Sketch of the unit cell.
similar to hexagonal BC₃ sheets). The fact that we observe a peak at 0.4 eV can be explained by symmetry breaking due to defects which are created during the substitution process.

The formation of BC₃ SWNT during the substitution process also explains the higher local boron concentration observed on selected TEM spots and the remaining optical response of the pristine SWCNT. Furthermore, different concentrations of BC₃ tubes at different substitution levels also explain why the acceptor-induced absorption peak does not shift by changing the doping level between 5% and 15%. As a final consistency check we can estimate the upper limit for the substitution level from the decrease of the first absorption peaks of the semiconducting and metallic SWCNT, assuming that all of the remaining response is from not substituted nanotubes. Since BC₃ corresponds to 25% B substitution and from the decrease of the SWCNT intensity about 80% of the semiconducting SWCNT and within the experimental error none of the metallic tubes are doped we end up with an average doping level of about 13% in very good agreement with the value derived from the core-level excitation spectra which is confirmed by ab initio calculations of the electronic structure of a BC₃ SWNT. The electronic structure characteristic of the B-SWCNT is influenced by a strong hybridization of the B and C valence orbitals. Our results show that a simple rigid-band model as has been applied previously to intercalated SWCNT is not sufficient to explain the changes in the electronic properties of highly doped B-SWCNT and a new type of a highly defective BC₃ SWNT with new electronic properties is observed.

IV. CONCLUSION

We have studied the electronic properties of highly boron doped SWCNT by bulk sensitive spectroscopies and LDA band-structure calculations. Core-level excitation spectroscopy of the B1s and C1s edges revealed that the boron atoms substitute carbon atoms in the tube lattice keeping an sp²-like bond with their nearest C neighbor atoms. The effective charge transfer to the C derived conduction bands is about 0.5 holes per substituted B atom. Optical absorption indicates the formation of an acceptorlike band in the band structure of the semiconducting tubes. This is nicely confirmed by ab initio calculations of the electronic structure of a BC₃ SWNT. The electronic structure characteristic of the B-SWCNT is influenced by a strong hybridization of the B and C valence orbitals. Our results show that a simple rigid-band model as has been applied previously to intercalated SWCNT is not sufficient to explain the changes in the electronic properties of highly doped B-SWCNT and a new type of a highly defective BC₃ SWNT with new electronic properties is observed.

ACKNOWLEDGMENT

We acknowledge financial support from the EU: IST Project SATURN and Research Training Network COMEL-CAN (Grant No. HPRN-CT-2000-00167), and from the DFG (Project PI 440). G.G.F. thanks for financial support by the Marie Curie programm. L.W. and A.R. acknowledge additional support by Spanish MCyT (Grant Nos. MAT2001-0946 and MAT2002-04499) and by the University of the Basque Country (Grant No. 9/UPV/00206.215-13639/2001). The authors are grateful to K. Müller for the technical assistance and O. Jost for delivering of as-produced SWCNT raw material. We thank A. Marin for making available his code SELF.

24 The ab initio calculations have been performed with the code SELF.
The wave functions of the valence electrons are expanded in plane waves with an energy cutoff at 50 Ry. The core electrons are simulated by Troullier-Martins pseudopotentials. A supercell geometry is employed with a large intertube distance (10 a.u.) in order to minimize the overlap of wave functions of neighboring tubes. The density is calculated self-consistently using a sampling of eight \( k \) points for the (quasi-one-dimensional) first Brillouin zone of the tubes. A non-self-consistent calculation yields the energies of occupied and unoccupied states on a grid of 50 \( k \) points.

The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.abinit.org).

The calculation of the optical spectrum has been performed with the code SELF written by A. Marini. We use the random-phase approximation (RPA). The light is polarized along the tube axis. (The first absorption peak for vertically polarized light is at 2.1 eV.)

The intensity of the optically allowed \( E_{11} \) transition is a direct measure to the SWCNT abundance (see also Ref. 11). Since our sample consists of BC\(_3\) nanotubes and unsubstituted SWCNT this transition provides a measure of the remaining fraction of SWCNT in the transformed sample. We are aware of the fact that the optical response from the BC\(_3\) nanotubes in this energy range could complicate the analysis. However, since the absorption peaks below about 2 eV are only optically allowed by symmetry breaking the sheer number of optically allowed transitions only contributes to the broad background and not to the individual SWCNT derived absorption peaks.