phys. stat. sol. (c) 5, No. 8, 2595–2599 (2008) / DOI 10.1002/pssc.200779127

physica status solidi c
www.pss-c.com
current topics in solid state physics

Linear optical response of (6,0) boron nitride nanotubes adsorbed with molecular hydrogen

N. Arzate[1,*], R. A. Vázquez-Nava[1], and J. E. Mejía[2]

[1] Centro de Investigaciones en Óptica, León Gto., México
[2] Centro Universitario de los Lagos, Universidad de Guadalajara, México

Received 26 August 2007, revised 19 November 2007, accepted 3 December 2007
Published online 21 May 2008

PACS 68.43.Bc, 68.43.Fg, 71.15.Mb, 78.20.Bh, 78.67.Ch

* Corresponding author: e-mail narzate@cio.mx

We performed a study of the molecular adsorption of hydrogen on BN nanotubes. We present *ab initio* calculations for the linear optical response of single wall zigzag BN(6,0) nanotubes as a function of the hydrogen adsorption on the exterior surface of the nanotube. The calculation of the linear optical response is performed by using density functional theory with the use of plane waves and pseudopotentials. We consider four different nanotube-structures adsorbed with different coverage of molecular hydrogen. We find optimized atomic coordinates for such structures and calculate binding energies for the molecule of hydrogen on the nanotube. After having the linear response of the considered structures, we have calculated their energy loss function spectra.

1 Introduction The adsorption of atomic or molecular adsorbates on nanotubes can relevantly influence their physical properties, and thus enhance the potentiality to technological applications. For instance, the adsorption of atomic hydrogen[1,2] as well as molecular hydrogen [3–7] on nanotubes has currently been studied mainly for hydrogen-storage applications on fuel cells. On carbon nanotubes molecular hydrogen can bind on the outer surface by either physisorption or by chemisorption [5]. The former case mainly depends on electrostatic and weak Van der Waals interactions, hence it has weak binding energies [3,4] and therefore small changes on the electron density. In the physisorption process, the hydrogen is weakly bound due to a strong bonding between hydrogen atoms and closed electronic shell. Some studies of molecular hydrogen have been focused mainly on the different adsorption sites on carbon nanotubes and their corresponding binding energies. By a radial deformation of the nanotubes or by co-adsorption of other atoms such binding energies can be changed [4]. Similar studies have been done on boron nitride (BN) nanotubes whose existence were proposed by Rubio *et al.* [8] and synthesis were confirmed by Chopra *et al.* [9]. Unlike the structurally similar carbon nanotubes, the BN nanotubes are polar and noncentrosymmetric. They have a wide band gap and they posses large ionicity on the B-N bond.

Thus their physical properties show to be different from that of carbon nanotubes. On the one hand, It has been shown that atomic hydrogen can be adsorbed chemically on the exterior surface on BN nanotubes up to 50% of coverage [1]. On the other hand, studies of molecular hydrogen adsorbed on BN nanotubes show that deviations from the sp^2 bonding tend to increase the binding energy of the hydrogen molecule [7]. Activated forms of BN nanotubes have also been studied where the binding energy and the specific surface area is increased by creating pore structures of various sizes and various atomic edges [6].

In the present paper we performed a study of the molecular adsorption of hydrogen on BN nanotubes. We present *ab initio* calculations for the linear optical response of single wall BN nanotubes as a function of the hydrogen adsorption on the exterior surface of the nanotube. We choose

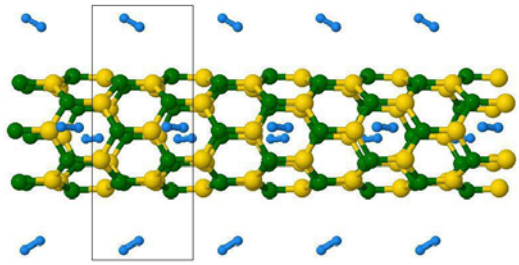

Figure 1 Scheme for the BN(6,0) nanotube with adsorption of molecular hydrogen. The rectangle specifies the unit cell of the nanotube.

the zigzag BN(6,0) nanotube for the study, since it has been reported that the BN nanotubes forms preferentially with zigzag orientation, and it has small diameter (of 4.74 Å) which, in turn, has a small unit cell with 24 atoms. This allows us to keep the calculation feasible since *ab initio* calculations of optical properties of nanotubes demand heavy computing resources.

Figure 1 shows the BN(6,0) nanotube with adsorption of molecular hydrogen. The rectangle specifies the unit cell of the nanotube. Into the unit cell there are four molecules of hydrogen (H_2). Here we consider the cases of adsorption of n hydrogen molecules on the exterior nanotube surface per unit cell. We will denote such cases as: nm, where n can take the values 1,2,3 and 4.

2 Method of calculation

2.1 *Ab initio* calculations We have used an *ab initio* method in order to determine the BN-nanotube structures. The method is based on the framework of Kohn-Sham density functional theory (DFT) within the local density approximation (LDA). The calculations have been obtained thanks the use of the ABINIT code [10–12], that is based on pseudopotentials and plane waves. The ionic-core potential was replaced by a relativistic separable dual-space Gaussian pseudopotential of Hartwigsen, Goedecker and Hutter [13]. The plane-wave energy cutoff used was of 30 Ha. A supercell geometry was formed in such a way that there would be nanotubes aligned in a square array with a distance between nanotubes of at least 11 Å. Spin-orbit interaction is not considered in the calculation. In order to reduce the computational effort we do not include neither local-field [14, 15] effects (LFE) nor excitonic effects [16]. The inclusion of the former effects only modify the absorption spectrum for light polarized perpendicular to the nanotube axis. Thus we only focus on the case where the incident light is polarized along the nanotube axis, and study the qualitative effects on the linear optical response of nanotubes as a function of the adsorption of molecular hydrogen.

In order to construct the nanotube system, a BN layer was simulated by a slab supercell approach with an inter-layer distance of 8 Å. After having obtained the optimal lattice constant, $a = 2.485$ Å, of the BN layer, the nanotubes were formed by rolling up the layer. In the calculation of such lattice constant, an energy cutoff of 100 Ha and a $\mathbf{k}$ point grid of $100 \times 100 \times 2$ were used. Then, the underlying nanotube-structure was obtained through a full relaxation of the atomic positions. The equilibrium structures were obtained by using a uniform $\mathbf{k}$ point grid, of $1 \times 1 \times 20$, along the nanotube axis and, when the forces acting on the atoms were less than 0.003 eV/ Å. The self consistent electronic band structure calculations were then carried out for the theoretically determined BN nanotube structures.

2.2 Binding energy Having obtained the optimized structures, we calculate the binding energy of the hydrogen molecule through the relation

$$E_b = E_{tot}[BNNT - H_2] - E_{tot}[BNNT] - n\, E_{tot}[H_2] \quad (1)$$

where $E_{tot}[BNNT - H_2]$ is the total energy of the BN nanotube with n hydrogen molecules adsorbed on its surface, $E_{tot}[BNNT]$ is the total energy of the clean BN nanotube, and $E_{tot}[H_2]$ is the total energy of the isolated hydrogen molecule.

2.3 Linear response On the evaluation of the linear response, we calculate the imaginary part of the dielectric function. The calculations were done within the independent particle approximation. We use the linear analytical tetrahedron method to perform the Brilloin zone integrations [17]. The linear response is normalized to a unit cell volume Γ, which is not well-defined for nanotubes. Instead of using the volume of the supercell, which is arbitrary, we used the effective unit cell volume of the nanotube employed in reference [18]: $\Gamma = \pi[(D/2 + d/2)^2 - (D/2 - d/2)^2]T$, where d is the nanotube wall thickness that is set to the interlayer distance of hexagonal BN, $d_{h-BN} = 3.281$ Å. D and T are the diameter and the lenght of the translational vector of the nanotube respectively. We note that the use of a different unit cell volume would affect the magnitude of the response coefficient but not the positions of the different peaks of the spectrum. The energy eigenvalues and matrix elements were calculated at 20 $\mathbf{k}$ points in the irreducible Brilloin zone that were unifomly distributed along the nanotube axis. In the calculations we used 152 conduction bands.

3 Results and discussion

We have obtained optimized structures for BN(6,0) nanotubes with n adsorbed molecules of hydrogen per unit cell. The respective binding energies and binding distances of the hydrogen molecule are tabulated in Table 1. The binding distance is the distance between the nanotube and the center of mass of the hydrogen molecule. The hydrogen molecule adsorbs on top

Table 1 Binding energy (E_b) and binding distance (D_b) of the hydrogen molecule for the cases of study: zigzag BN(6,0) nanotubes adsorbed with n molecules of hydrogen (nm) per unit cell.

BN(6,0) - nH$_2$	E_b (meV)	D_b (Å)
1m	-39	2.36
2m	-82	2.37
3m	-125	2.36
4m	-168	2.37

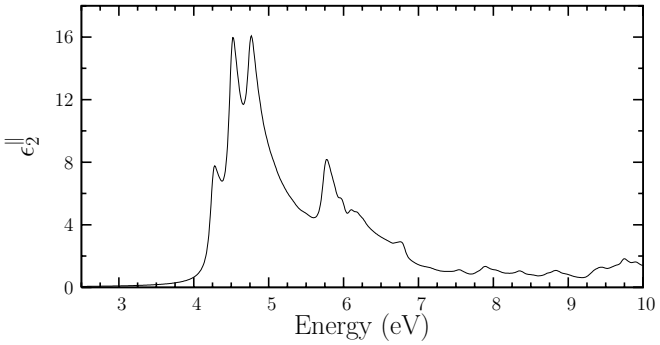

Figure 2 Imaginary part of the dielectric function of the clean zigzag BN(6,0) nanotube with the electric field polarized parallel to the nanotube axis.

of an hexagon of the nanotube forming an angle of 30^o degrees with respect to the axis of the nanotube just in the way shown in Fig. 1. For the case of adsorption of 2 molecules of hydrogen, there can be two possibilities of having the hydrogen molecules: each one in opposite sides of the nanotube and one beside the other. The corresponding data of the former case is the one tabulated in Table 1. The binding energy of the latter case differs in 1% from the former case and their binding distance are equal. We can see from Table 1 that the binding energy decreases significantly as the molecular hydrogen adsorption increases. This kind of behavior has also been reported on the atomic adsorption of hydrogen on the zigzag BN(10,0) nanotube [1]. The binding energy is negative meaning that the adsorption is exothermic. In reference [7] an study of the adsorption of molecular hydrogen is performed on a BN(10,0) nanotube. The authors consider the adsorption of just 1 molecule of hydrogen per two unit cells of the BN nanotube. They fix the center of mass of the molecule and get relaxed structures. Then they presented binding energy curves as a function of the binding distance. They found a minimum of the binding energy, for the case where the hydrogen molecule is on top the hexagon center, at a binding distance of 3 Å. Comparing the cases of just one row of molecules of hydrogen along the nanotube, the binding distance (the binding energy) is less (greater) in the adsorption of hydrogen on BN(6,0) nanotubes than that on BN(10,0) nanotubes.

Recent calculations have shown that the inclusion of local-field effects (LFE) are crucial to fully interpret the

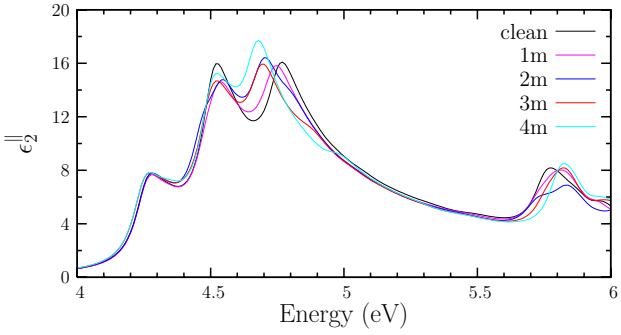

Figure 3 Imaginary part of the dielectric function of the zigzag BN(6,0) nanotube as a function of the number n of adsorbed hydrogen molecules (nm) per unit cell. The electric field is polarized parallel to the nanotube axis.

experimental absorption spectra of nanotubes [14, 15], and nanowires [19, 20]. In these kind of systems it is important to take into account the induced microscopic components in the response to the external field. As a result a so-called depolarization effect takes place for perpendicular polarization of the field to the nanostructure surface. This effect suppress the absorption of the light at lower energies. In the present paper, we thus focus only on the optical response with the field polarized along the nanotube axis. The optical absorption for such a case is unaltered with the inclusion of LFE on the calculation. In Fig. 2 we plot the imaginary part of the dielectric function of the clean zigzag BN(6,0) nanotube for light polarized parallel to the nanotube axis. The spectrum shows structures at 4.28, 4.52, 4.77 and 5.77 eV. Similar spectra are reported in references [15] and [18], where the calculations were done in the framework of time-dependent density-functional theory and by using the full-potential projected augmented wave method respectively. On reference [15], the spectrum of the BN(6,0) nanotube for the parallel polarization of the electric field shows the structures near 4.28, 4.52 eV as a small shoulders. Here those shoulders appear enhanced. In particular, the structure at 4.52 eV appears as a peak.

In Fig. 3 we plot the imaginary part of the dielectric function of the zigzag BN(6,0) nanotube for electric fields polarized parallel to the nanotube axis and as a function of the number n of hydrogen molecules per unit cell. We can see from Fig. 3 that as the coverage of molecular hydrogen on the surface of the nanotube is increased, the structure found at around 4.52 eV of the spectrum for the linear response is slightly decreased but keeps at the same frequency. Meanwhile the structures found at around 4.77 (5.77) eV shifts downwards (upwards) by 0.09 (0.06) eV and slightly increases its magnitude, when the adsorption coverage is of 4 hydrogen molecules per unit cell.

We have also calculated the spectrum for the electron energy loss function (EELS) that is related through the momentum-dependent dielectric function as: Im$[1/\varepsilon(\omega, q)]$,

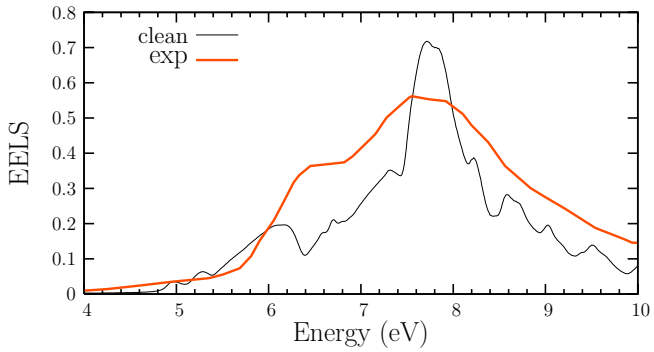

Figure 4 EELS spectra of the clean zigzag BN(6,0) nanotube with the electric field polarized parallel to the nanotube axis.

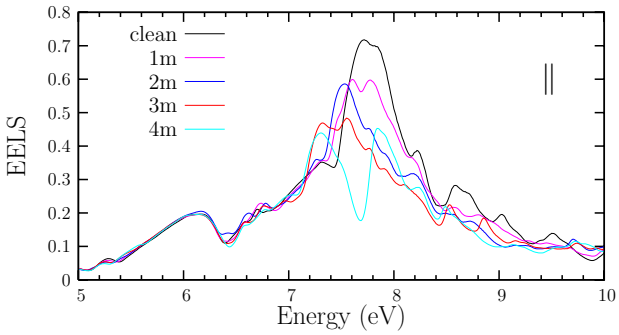

Figure 5 EELS spectra of the zigzag BN(6,0) nanotube as a function of the number n of adsorbed hydrogen molecules (nm) per unit cell. The electric field is polarized parallel to the nanotube axis.

being q the momentum transfer. Here we show spectra for EELS with momentum transfer $q \to 0$. Figure 4 shows the EELS spectrum of the clean zigzag BN(6,0) nanotube for electric fields polarized parallel to the nanotube axis. The experimental data [21] are also plotted. They were obtained by performing measurements on multiwalled BN nanotubes for momentum transfer $q = 0.1$ Å^{-1} [21]. The spectrum shows a structure at around 7.57 eV, which is related to a collective π plasmon oscillation. The position of such a structure on the calculated spectrum depends on the radius and chirality of the nanotubes. We have shifted upwards the calculated spectra by 0.65 eV in order to have coincidence of the peak-structure found on the calculated spectrum with that of the experiment. Such difference in energy between the calculated spectrum and the experimental data is related to the well known underestimation of the band gap of DFT-LDA calculations. Despite of the fact that the experimental data was gotten on multiwalled nanotubes, we find that the calculated spectrum shows qualitatively good agreement with the experimental data.

In Fig. 5 we have plotted spectra for EELS of the zigzag BN(6,0) nanotube for electric fields polarized parallel to the nanotube axis and as a function of the number n of hydrogen molecules per unit cell. From Fig. 5 we can see that the structure at around 7.7 eV in the spectrum of clean BN nanotubes and corresponding to parallel polarized electric fields, shifts downwards and its intensity reduces as the adsorption coverage of molecular hydrogen is increased. Such structure becomes a double peak for a coverage of 4 molecules per unit cell.

4 Conclusions We have performed an study of the adsorption of molecular hydrogen on single walled zigzag BN(6,0) nanotubes. Molecular hydrogen can bind on the outer surface of BN nanotubes with weak binding energies. The greater the coverage of molecular hydrogen on the surface of the nanotube, the lower their binding energy. Their values range from -39 meV for the nanotube with 1 adsorbed hydrogen molecule per unit cell to -168 meV for the nanotube with 4 adsorbed molecules of hydrogen per unit cell. The binding distance showed to be either 2.36 or 2.37 Å. Both the linear optical response and the energy loss function spectrum of BN(6,0) nanotubes is influenced as the adsorption of molecules of hydrogen on the nanotube increases. Thus the present study takes insight on the behavior of the linear optical response of BN nanotubes as a function of molecular hydrogen.

Acknowledgements This work has been partly supported by CONACYT, México, grants: SEP-2004-C01-48142 and SEP-2003-C02-42576. The authors gratefully acknowledge useful and stimulating discussions with Fred Nastos and John E. Sipe.

References

[1] S. S. Han, S. H. Lee, J. K. Kang, and H. M. Lee, Phys. Rev. B **72**, 113402 (2005).
[2] X. Wu, J. Yang, J. G. Hou, and Q. Zhu, Phys. Rev. B **69**, 153411 (2004).
[3] D. Henwood and J. D. Carey, Phys. Rev. B **75**, 245413 (2007).
[4] D. Henwood and J. D. Carey, Phys. Rev. B **75**, 245413 (2007).
[5] G. Chen, X. Gong, and C. Chan, Phys. Rev. B **72**, 045444 (2005).
[6] S. Jhi, Phys. Rev. B **74**, 155424 (2006).
[7] S. Jhi and Y. Kwon, Phys. Rev. B **69**, 245407 (2004).
[8] A. Rubio, J. Corkill, and M. Cohen, Phys. Rev. B **49**, 5081 (1994).
[9] N. Chopra, K. C. R.J. Luyken, V. Crespi, M. Cohen, S. Louie, and A. Zettl, Science **269**, 966 (1995).
[10] The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.abinit.org).
[11] X. Gonze, J. M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G. M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J. Y. Raty, and D. Allan, Comput. Mater. Sci. **25**, 478 (2002).
[12] X. Gonze, G. M. Rignanese, M. Verstraete, J. Beuken, Y. Poillon, R. Caracas, F. Jollet, M.Torrent, G. Zerah, M. Mikami, P. Ghosez, M. Veithen, J. Y. Raty, V. Olevano,

F. Bruneval, L. Reining, R. Godby, G. Onida, D. Hammann, and D. Allan, Zeit. Kristallogr. **220**, 558 (2005).
[13] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).
[14] A. Marinopoulos, L. Reining, A. Rubio, and N. Vast, Phys. Rev. Lett. **91**, 046402 (2003).
[15] A. Marinopoulos, L. Wirtz, A. Marini, V. Olevano, A. Rubio, and L. Reining, Appl. Phys. A **78**, 1157 (2004).
[16] L. Wirtz, A. Marini, and A. Rubio, Phys. Rev. Lett. **96**, 126104 (2006).
[17] D. Moss, J. Sipe, and H. van Driel, Phys. Rev. B **36**, 1153 (1987).
[18] G. Guo and J. Lin, Phys. Rev. B **71**, 165402 (2005).
[19] F. Bruneval, S. Botti, and L. Reining, Phys. Rev. Lett. **94**, 219701 (2005).
[20] M. Bruno, M. Palummo, A. Marini, R. Del Sole, and S. Ossicini, Phys. Rev. Lett. **98**, 036807 (2007).
[21] G. Fuentes, E. Borowiak-Palen, T. Pichler, X. Liu, A. Graff, G. Behr, R. Kalenczuk, M. Knupfer, and J. Fink, Phys. Rev. B **37**, 035429 (2003).