Energetics and electronic structure of semiconducting nanotubes adsorbed on SiO$_2$ Surfaces

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Abstract

First-principle calculations are performed to explore the energetics and electronic structures of semiconducting nanotubes adsorbed on the (0001) surfaces of α-quartz (SiO$_2$). We find that the absorption energy of nanotube on SiO$_2$ is ~ 0.4 eV/nm, strongly depends on the adsorption site and the inter-unit spacing of the nanotube and the SiO$_2$. The electronic structure of this hybrid structure is semiconducting so that the electronic states near the energy gap are caused by those of the nanotubes. A detailed analysis of the electron states of the nanotubes reveals that the energy gaps between valence and conduction bands are slightly modulated by adsorption.

1 Introduction

In recent years, carbon nanotubes [1] have stimulated much attention due to their characteristic geometric properties, i.e. size, structure, and dimensionality, as well as their various electronic properties ranging from metallic to semiconducting characters depending on their geometry [2,3]. These unique properties open up the possibility e.g. for electronic [4–7] and biomedical [8] applications of nanotubes in wide areas of current technology. Carbon nanotubes are a key constituent unit in these devices in building hybrid structures

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with conventional materials. Thus their stability and electronic properties are one of the key issues in technologies of next generation.

Hybrid structures formed between nanotubes and metals or their interfaces are important in determining the electronic properties of nanotubes in field-effect transistors (FETs) [4–7]. The properties of FETs are reported to depend on the electrode metal species; e.g. FETs exhibit n- and p-type behavior for Ca and Pd electrodes, respectively [6]. These properties depend mainly on the work function difference of the metal species. In addition, the metal species are also known to affects the detailed electronic structure of the nanotubes adsorbed on these metals due to the hybridization and charge transfer between the nanotubes and the metal atoms [9].

Insulators such as silicon-dioxide (SiO_2) and sapphire (Al_2O_3) are also considered as key materials as widely used in the preparation of hybrid structures with nanotubes in various nanotube-based devices. These insulators are also important stages for the growth processes of nanotubes. A recent experiment has shown that semiconducting nanotubes adsorbed on SiO_2 substrates do not yield a photoluminescence spectrum [10]. This result indicates that SiO_2 substrates substantially affect the electronic properties of the nanotubes that are adsorbed upon them. On the other hand, from a structural viewpoint, the highly orientated growth of nanotubes has been found to take place on particular surfaces of SiO_2 [11–14] and Al_2O_3 [15]. In the case of sapphire surfaces, the nanotubes are highly aligned on the R and A surfaces, but randomly dispersed on the C surfaces. These results indicate that the nanotubes substantially interact with the insulating substrate. However, it is still unclear what is the mechanism for such aligned growth of these nanotubes on the surfaces of SiO_2 and Al_2O_3. Thus an analysis of the energetics and electronic properties of the nanotubes adsorbed on such insulating substrates may unravel the fundamentals of these experimental evidences, which have not been addressed to date.

The purpose of the present Letter is to explore the energetics and electronic properties of the interfaces formed between semiconducting nanotubes and α-quartz (SiO_2). Here, we take a semiconducting (10,0) nanotube adsorbed on the (0001) surface of α-quartz to clarify the salient characteristics of the energetics and electronic properties of the interfaces formed between nanotubes and insulators. Since no charge density is observed between the nanotubes and the SiO_2 surface, it is considered that the nanotubes are physically adsorbed on the SiO_2 via weak interactions. On the other hand, the energetics of the interfaces depend significantly on the sites where the nanotubes are adsorbed. The calculated adsorption energy of nanotubes on α-quartz is found to be ~ 400 meV/nm. The electronic structure of this hybrid structure is semiconducting so that the electron states near the energy gap are caused by those of the nanotubes. A detailed analysis of the electron states of the nanotubes

has revealed that the energy gap between the first van Hove singularities of the valence and conduction bands (E_{11}) and the gap between the second van Hove singularities of the valence and conduction bands (E_{22}) become slightly modulated by adsorption.

2 Calculation methods and models

All calculations in the present work were performed based on the density functional theory (DFT) [16,17]. The local density approximation (LDA) was used to treat the exchange-correlation energy of the interacting electrons [18,19]. Norm-conserving pseudopotentials with separable forms were adopted to describe the electron-ion interactions [20,21]. The valence wave functions were expanded in terms of the plane-wave basis set with a cutoff energy of 60 Ry, which gave sufficient convergence of the relative energies for nanotube-related materials as well as SiO_2. The conjugate-gradient minimization scheme was utilized for the electronic-structure calculation [22].

The (0001) surfaces of α-quartz were chosen as representatives of oxide-insulator surfaces to clarify the salient characteristics of the semiconducting nanotubes adsorbed on the insulator surfaces. The SiO_2 surface was simulated by using the repeating slab model with 10 Å thickness. Both sides of the SiO_2 surface were covered with oxygen atoms to simulate the oxygen-rich condition in the experiment and to keep the stoichiometry of the slab as SiO_2. Each slab was then separated by 20 Å-vacuum regions to analyze the electronic structures and energetics of the carbon nanotubes adsorbed on the surface. The atomic structure of the SiO_2 slab was fully optimized and all the oxygen bonds were saturated resulting in an insulating electronic structure. Each nanotube was separated in the lateral direction by 6.92 Å from its adjacent nanotubes in their initial geometry to simulate the characteristics of the individual nanotubes on SiO_2. Commensurability conditions were imposed between the one-dimensional periodicity of the nanotubes and the lateral periodicity of the SiO_2 surface. Consequently, a unit cell along the tube axis parallel to the SiO_2 surfaces contained double periodicity of the zigzag nanotubes and was elongated in this direction by 1 %. All atoms were fully optimized under these lattice parameters. Integration over the two-dimensional Brillouin zone was carried out using four ($= 2 \times 2$) $\boldsymbol{k}$ points.
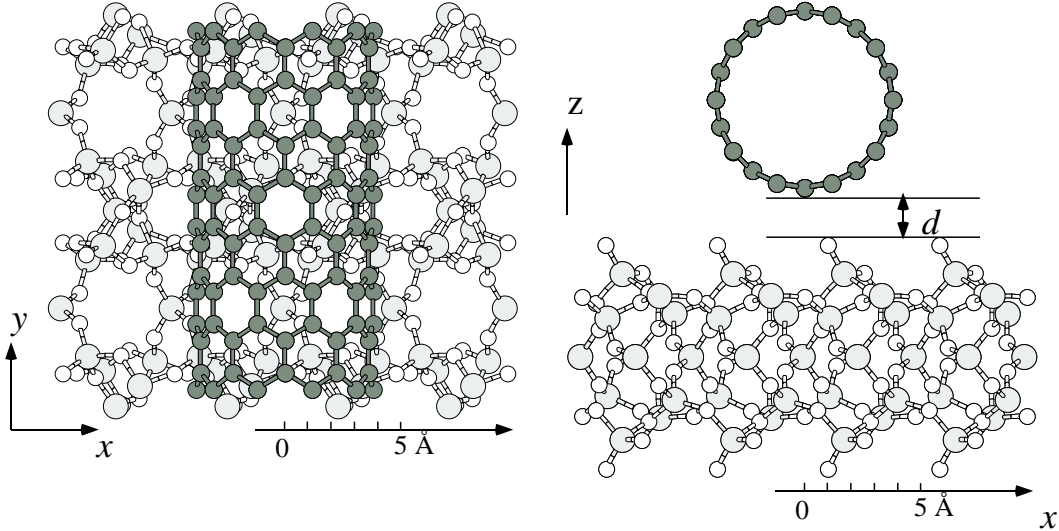
Fig. 1. Top (left panel) and side (right panel) views of the optimized structure of a semiconducting (10,0) nanotube adsorbed on a SiO_2 surface. Dark-shaded, pale-shaded and open circles denote carbon, silicon, and oxygen atoms, respectively.

3   Results and discussion

3.1   Energetics

Figure 1 shows the optimized structure of a (10,0) nanotube adsorbed on a SiO_2 (0001) surface. No significant structural deformation of the nanotube is observed to take place, and thereby maintaining the cylindrical shape of the nanotube is maintained. The structural properties of the nanotube on the SiO_2 surface indicate that the nanotube is not bound via covalent bonds but via weak interactions between the nanotube and the surface of the SiO_2 slab.

Figures 2 (a) shows the binding energies of the semiconducting (10,0) nanotube on the SiO_2 surface as a function of the distance between the wall of the nanotube and the topmost surface O atom. The optimum spacing d is found to be $\sim$ 2.5 Å, and the calculated adsorption energy per unit length of nanotube under this spacing is 0.42 eV/nm. Since this spacing is significantly wider than the interatomic spacing between the C and O atoms in CO or CO_2 molecules, the nanotubes are indeed considered to be physically adsorbed to the SiO_2 substrate without the formation of covalent bonds with the substrate. Indeed, the electrons are not distributed between the nanotube and the topmost O atoms, corroborating the fact that the nanotube is loosely bound on the substrate.

We have also explored how the energetics depends on the lateral position of the nanotube adsorbed on the SiO_2 (0001) surface. As shown in Fig. 2(b),
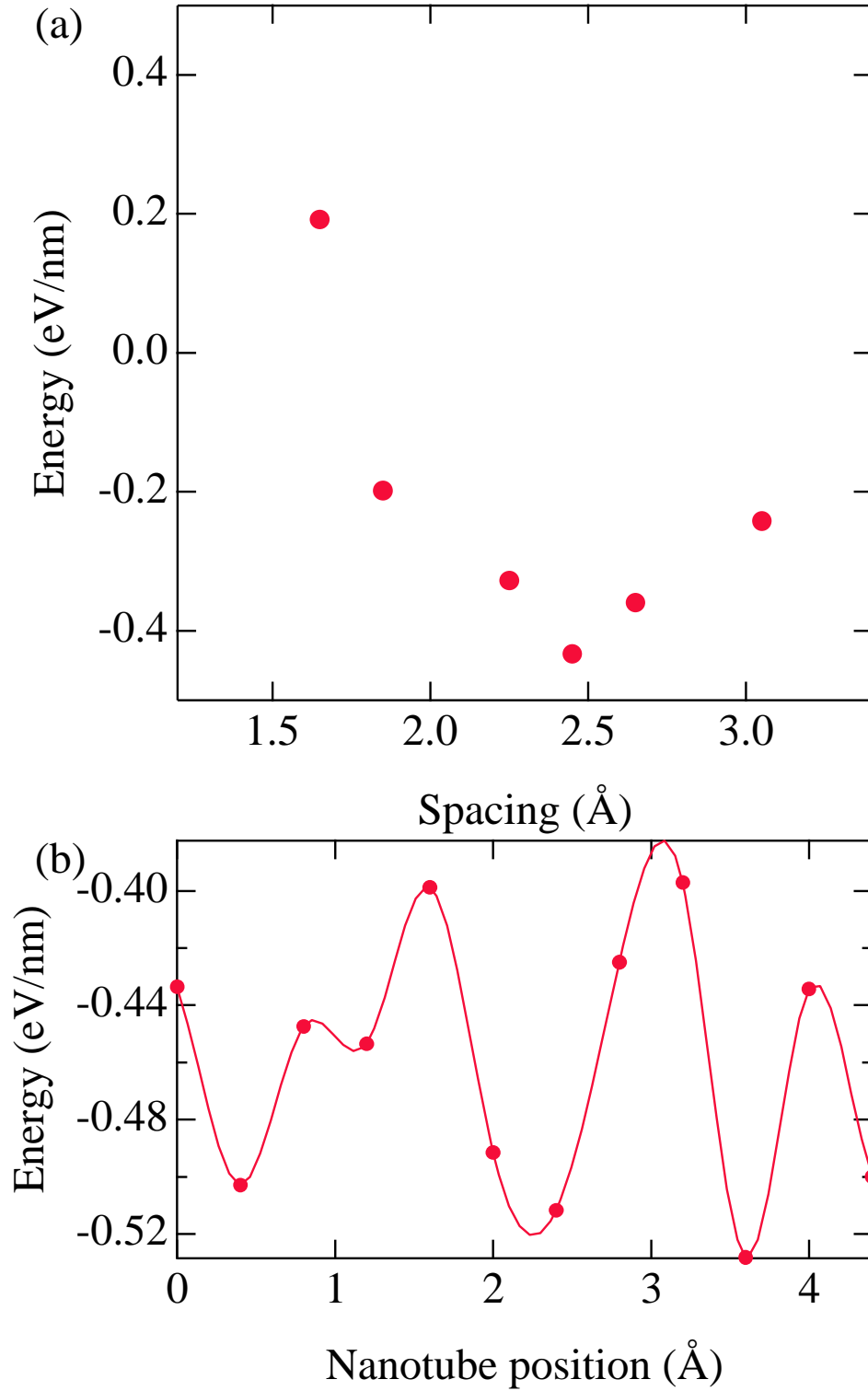
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Fig. 2. (Color online) (a) Calculated adsorption energy of the nanotube on the SiO_2 surface as a function of the spacing between the nanotube wall and the positions of the topmost O atoms in the SiO_2 slab. (b) Adsorption energy of the nanotube on the SiO_2 surface as a function of the lateral position of nanotubes along the x direction in Fig. 1. The line is a guide for eyes. Dispersion of the adsorption energy around the minimum originates from the flexibility of surface reconstruction of SiO_2 resulting in a number of local minima.
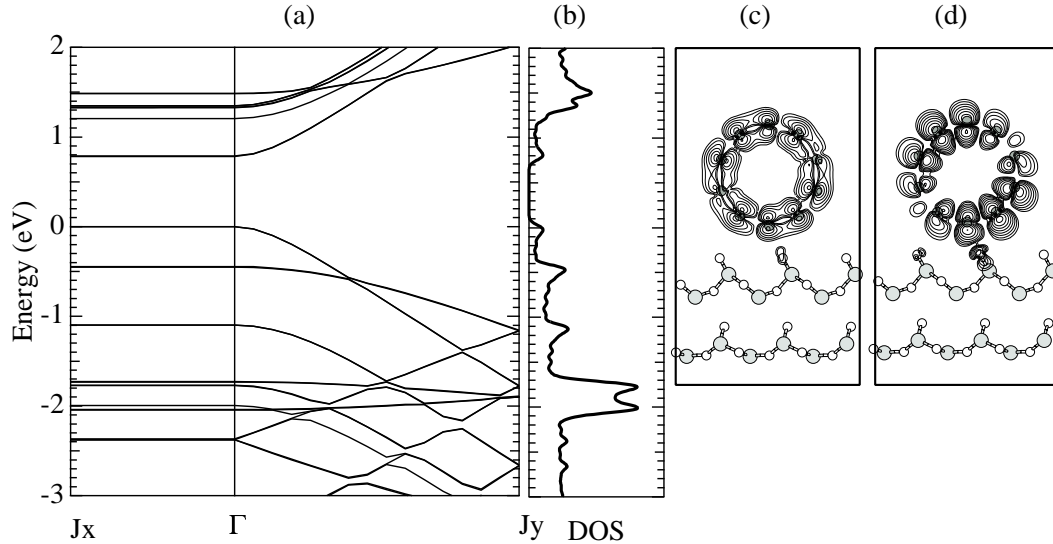
Fig. 3. (a) Electronic energy band of the (10,0) nanotube adsorbed on the SiO_2 surface along the high symmetry lines. The direction of the nanotube corresponds to the Γ-J_y line. (b) Total density of states (DOS) of the nanotube on the SiO_2 surface. Contour plots of the squared wave function. (c) The top of the valence band, and (d) the bottom of the conduction band. Energies are measured from the top of the valence band. Each contour represents twice (or half) the density of the adjacent contour lines. Dark shaded, pale shaded and open circles denote carbon, silicon, and oxygen atoms, respectively.

the calculated amount of adsorption energy, $0.4 \sim 0.5$ eV/nm, seems to be substantially dependent on the adsorption site of the nanotube; we have found several potential energy valleys.

This result indicates that the surface atomic arrangement of the SiO_2 surface intrinsically triggers self-aligned horizontal growth of the nanotubes on particular surfaces of α-quartz. For instance, in the present calculation, the nanotube is expected to be aligned along the y direction at the nanotube position of $x = 3.5$Å. We note that our calculations have only examined the energetics for particular adsorption geometries of nanotubes without consideration of the rotational freedom and other possible adsorption directions due to the computational limitation. Further calculations on a huge lateral unit cell will provide clearer evidence for the selective adsorption on the surfaces of α-quartz.

3.2 Electronic structures of the optimized geometry

Figure 3 shows the electronic structure of the (10,0) nanotube adsorbed on the SiO_2 surface. The hybrid structure formed between the nanotube and the SiO_2 substrate is semiconducting, since the nanotube is a semiconductor and

the SiO_2 substrate, in which all bonds associated with the O and Si atoms are saturated, is a wide gap insulator. The characteristics of the electronic structure of the nanotube emerge around the energy gap, such as the first, second, and third van Hove singularities. Thus the electronic states around the energy gap possess the π character of the nanotube, whereas those of the SiO_2 substrate are located below -3 eV and above 4 eV due to its wide energy gap.

It is important to investigate detailed modulation of the electronic structure of the nanotube. Small but substantial modulation of the electronic states were found near the energy gap of the nanotubes. The gap between the first van Hove singularities, E_{11} gap, and the second van Hove singularities, E_{22}, are slightly modulated. The E_{11} gap of the nanotube adsorbed on SiO_2 is narrower by 50 meV than that of the isolated nanotubes, while the E_{22} is wider by 180 meV. These modulations are expected to be observable in experiments under appropriate conditions. In a recent experiment, it has in fact been reported that the E_{22} gap of the nanotubes adsorbed on SiO_2 increases by ~ 100 meV from that of pristine nanotubes [23]. These modulations are ascribed to the strain effect on the π states of the nanotubes [24]. This effective strain is caused by the small hybridization between the π states of the nanotube and the p state of the O atoms situated on the surface of the SiO_2 substrate, as shown in Figs. 3(c) and 3(d). The hybridization expands the distribution of the π wave function of the nanotubes compared with that of the isolated nanotube. This expansion increases the overlap of the π wave function between the adjacent C atoms and effectively results in the reduction of the diameter of the nanotubes, as in the case of peapods [25,26]. A similar narrowing of the E_{11} gap has been observed in the nanotubes adsorbed on Al (001) surfaces [9]. In this case, the substantial hybridization between the π states of the nanotubes and the p states of the Al take place resulting in an extension of the π electron distribution.

3.3   *Electronic structures of the initial geometry*

How are the electronic structures are modulated under the condition where unsaturated bonds exist in the SiO_2 slab? A solution to this question will provide a theoretical insight into explain the absence of the photoluminescence spectra of nanotubes adsorbed on SiO_2 substrates. In experiments, imperfections introduced into the SiO_2 substrate are essential as they can cause deep energy levels in the energy gap thereby acting as nonradiative recombinations. Such levels may affect the electronic structures of the nanotube-SiO_2 hybrid systems. To simulate such situations, we have considered a structural model in which the nanotube is put on a SiO_2 slab having a structure that is not relaxed possessing a number of unsaturated bonds. Although such unsaturated
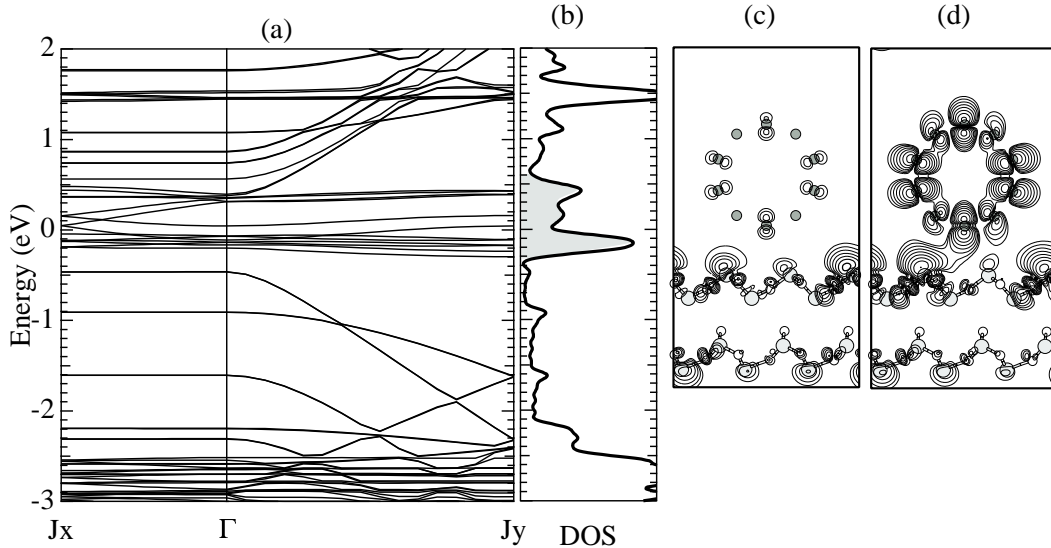
Fig. 4. (a) Electronic energy band of the (10,0) nanotube adsorbed on the SiO_2 surface. (b) Total density of states of the nanotube on the SiO_2 surface. The atomic geometries of SiO_2 are fixed in the calculation with respect to the initial atomic geometry resulting from numerous unsaturated bonds. These energies are measured from the Fermi level energy. The shaded area denotes the density of states, which corresponds to the electronic states originating from the unsaturated bonds of SiO_2. Contour plots of the squared wave function. (c) The highest branch of the gap states and (d) the bottom of the anti-bonding π band of the nanotube. Energies are measured from the top of the valence band. Each contour represents twice (or half) the density of the adjacent contour lines. Dark shaded, pale shaded and open circles denote carbon, silicon, and oxygen atoms, respectively.

bonds of the O atoms located at the topmost of the slab may result in the formation of covalent bonds with the nanotube [27], we calculated the electronic structure under the fixed geometries in which the nanotube is separated by 2.5 Å from the topmost O atoms of the SiO_2 slab.

Figure 4 shows the electronic structures of nanotubes adsorbed on a SiO_2 slab possessing unsaturated oxygen and silicon bonds. As shown in the figure, several flat dispersion bands are evident in the energy gap between the first van Hove singularities of the nanotubes. Some of these states are mainly distributed on the oxygen and silicon atoms in the SiO_2 slab with unsaturated bonds. On the other hand, it was found that the remaining states located near the bottom of the conduction band of the nanotube show their hybridized nature with the π states of the nanotubes [Fig. 4(c)]. The substantial overlap of the wave functions between the nanotube and the SiO_2 [Figs. 4(c) and 4(d)] causes the electron transfer between them. Thus these states may act as nonradiative recombinations for electrons in the E_{11} gap, and they may also play a crucial role in preventing the luminescence. In a recent experiment, photoluminescence spectra were observed only for nanotubes suspended from electrodes but for nanotubes adsorbed on SiO_2 substrates [10]. The results of

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the present calculations agree well with these experimental results.

4 Summary

Our calculations based on DFT have clarified that the nanotubes are weakly bound on the SiO_2 surfaces without the formation of covalent bonds between the C atoms and O/Si atoms. The calculated adsorption energy is found to be 0.4 eV/nm under the fully optimized geometry where the wall of the nanotube is separated by 2.5 Å from the topmost O atoms. Furthermore, a substantial site dependence of adsorption of the nanotube is found to take place. Since the nanotubes are weakly bound on the SiO_2 surfaces, no substantial modulation of their electronic structure takes place. The nanotubes on the SiO_2 slab, in which all bonds associated with the Si and O atoms are saturated, are still semiconductors. However, a detailed analysis of the electronic structure has revealed that the energy gaps between the first and second van Hove singularities, E_{11} and E_{22}, respectively, are slightly modulated. The E_{11} gap of the nanotubes adsorbed on the SiO_2 surfaces is narrower by 50 meV than that of the isolated nanotubes, while the E_{22} is wider by 180 meV. The modulation is ascribed to a small but substantial hybridization between the π states of the nanotubes and the p state of the surface O atoms. Our calculation provides a theoretical insight on the interfaces between nanotubes and a SiO_2 substrate, which is essential not only for nanotube-based electronic devices but also for the growth processes of the nanotubes.

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