Energy Band Gap Study of Semiconducting Single Walled Carbon Nanotube Bundle

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***Abstract* — The electronic properties of multiple semiconducting single walled carbon nanotubes (s-SWCNTs) considering various distribution inside a bundle are studied. The model derived from the proposed analytical potential function of the electron density for an individual s-SWCNT is general and can be easily applied to multiple nanotubes. This work demonstrates that regardless the number of carbon nanotubes, the strong coupling occurring between the closest neighbours reduces the energy band gap of the bundle by 10%. As expected, the coupling is strongly dependent on the distance separating the s-SWCNTs. In addition, based on the developed model, it is proposed to enhance this coupling effect by applying an electric field across the bundle to significantly reduce the energy band gap of the bundle by 20%.**

Keywords –coupling effect, energy band gap, potential function, semiconducting single-wall carbon nanotube.

I. Introduction

Carbon Nanotubes (CNTs) consists of a rolled mono-atomic sheet of carbon also known as graphene. Nanotube physical properties including high thermal and electrical conductivities, great tensile strength, and elastic modulus have certainly attracted researchers in the last two decades [1]. For instance, the chiral angle pair of indices (*n,m*) which defines how the graphene sheet is wrapped and the diameter of a single-walled carbon nanotube (SWCNTs) also determine the semiconducting or conducting nature of the nanotube [1].

Although those physical properties have extensively been studied over the years based on the structural carbon atoms assembly, experimental data still lack to reach such theoretical values. Consequently, to enhance the performance of future carbon based devices, it is essential to improve simulated model closer to experiments. Thus, two different approaches can be considered to develop new models. First, experiments are performed to extract the electrical properties of carbon nanotube that are directly implemented in simulation software. For instance, Decrossas et al. built a measurement setup to extract the frequency dependence of the complex permittivity of carbon nanotube in a powder form to engineer novel composite material for high frequency applications [2],[3]. An accurate model predicting the behaviour of the complex nano-powder mixture including both semiconducting and metallic nanotubes entangled together was developed. Second, more efficient model based on experimental observations considering fabrication technique, nanotube defects, parasitic effects are developed by imposing new constraints. This is the approach utilized in this work. In fact, with the emergence of new technologies and growth techniques, semiconducting carbon nanotube highly uniform can now be produced allowing models to predict the behaviour of a device more accurately justifying this approach. The developed model at high frequency considers either metallic or semiconducting nanotubes depending on the applications. For instance, Sarto *et al.* predicted the coupling effect occurring between conducting nanotubes in a bundle based on a hybrid transmission line quantum mechanical model for signal integrity purposes [4]. In this work instead, semiconducting SWCNTs are studied due to their unique property: the energy band gap is inversely proportional to their diameter leading to potential future terahertz devices [5].

However, fabrication techniques and experimental observations show that highly dense aligned s-SWCNTs are organized in bundles [6] in a device. Hence, the presented model predicts the energy band gap of a bundle of aligned s-SWCNTs arranged in semi-random order as shown in Fig. 1 considering different radii and distances separating nanotube. A typical diameter of s-SWCNT is in the order of 1.4-2.1nm, and the minimum distance between s-SWCNTs is the graphite interlayer distance 0.34 nm [7]. First, a novel proposed analytical potential function of the s-SWCNT is introduced and generalized to the bundle. Then, the potential function is implemented in the Schrödinger equation to determine the ground state wave function and the energy band gap variations. Finally, the energy band tuning is demonstrated after applying an external electric field across the bundle.

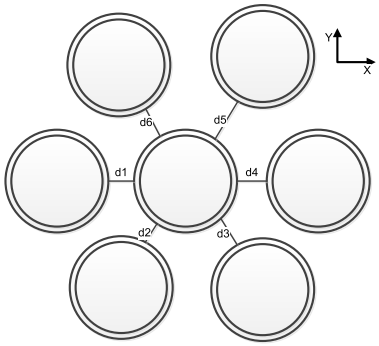


Fig. 1. Geometrical configuration of the semi-conducting single wall carbon nanotube bundle where parallel nanotubes are randomly distant from a centred one (d1, d2, …, d6). (not to scale).

II. Analytical Potential Function

The analytical potential function describes the electron carrier concentration localized around the tube wall due to the tube's cylindrical geometry. Having a well-defined potential function facilitates the study of the electrical and optical properties of a single nanotube as well as the interaction occurring in a bundle. The potential function expression of s-SWCNT was first proposed in [5] as:

$$V_{eff}(r) = \frac{B \times c^2 r^2}{\left(r^2 - R_t^2\right)^2 + c^2 r^2} \tag{1}$$

where R_t is the nanotube radius, $c = \frac{R_t}{11.446}$ represents the effective SWCNT's wall thickness [8], and $B = 8.25\,\text{eV}$ is the potential well depth is calculated from the general energy dispersion of SWCNT [9] . From (1), the potential function of a single s-SWCNT plotted in Fig. 2 clearly shows that the free carrier electrons are localized on the surface wall of the nanotube.

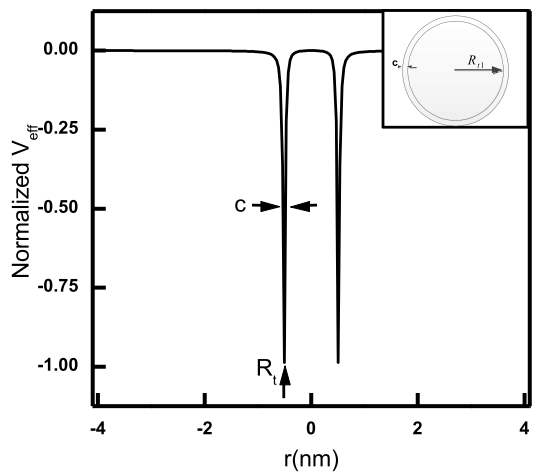


Fig. 2. Normalized potential function across a single s-SWCNT as shown in the inset. R_t is the nanotube radius and c the wall thickness.

The random configuration can be considered as a superposition of several individual s-SWCNTs. Hence, the overall potential is derived as the sum of the individual potentials of each tube.

$$V_{eff-total} = V_{eff1} + V_{eff2} + \ldots + V_{effn} \tag{2}$$

where n is the number of nanotubes.

The potential function including the contribution of each individual s-SWCNT is then inserted in the differential Schrödinger's equation:

$$\left(\frac{-\hbar}{2m^*}\nabla^2 + V_{eff-total}\right)\Psi(r,\phi,z) = E\Psi(r,\phi,z) \tag{3}$$

where $\hbar$ is the Planck's constant, m^* is the effective mass obtained from [1], ∇^2 is the Laplacian and Ψ is the wave function in cylindrical coordinates.

Schrödinger's equation is then solved using *Multiphysics ComSol Simulator* [10]. An ordinary differential equation (ODE) is defined in the radial direction where the azimuthal dependence is sinusoidal and the longitudinal axis is the propagating direction by considering the high aspect ratio (defined by the length and radius) of s-SWCNT. The potential function is then inserted as the analytical expression in Eq. (1) for individual s-SWCNT or the resultant from Eq. (2) in case of a bundle.

III. Simulations and Discussions

Let's first considers three adjacent tubes as shown in Fig.3. All tubes have a diameter of 1.4nm and are separated by 3.4Å.

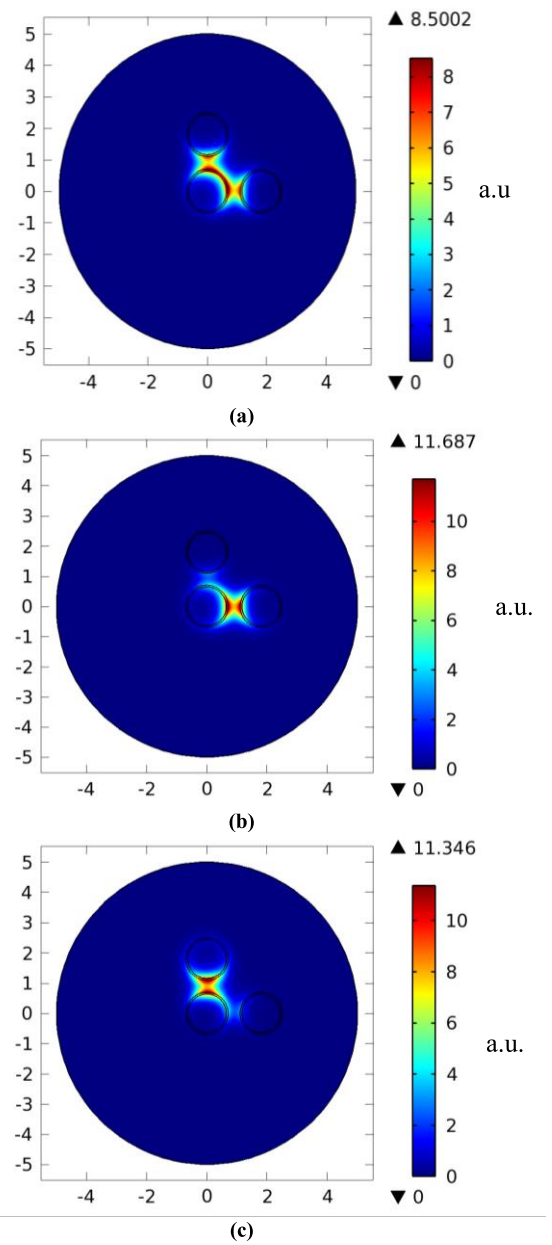


Fig. 3 Coupling effect occuring between three adjacent s-SWCNT orthogonally localized; (a) uniformly distributed without the presence of an external electric field (b) maximized along the x-axis where the external electric field is applied (c) maximized in the y-axis direction of the applied external electric field .

In this case, the coupling effect between the two adjacent tubes and the centred SWCNT appears to be uniform as presented in Fig. 3(a).

Then an external electrical field of 10 V/m is applied in the x direction, the coupling distribution varies with the field direction as shown in Fig.3 (b). It is observed that when applying electric field the coupling is maximized along the tubes in the direction of the electrical field as presented in Fig.3(c) where the electric field is applied in the y-direction.

In the second case, the three nanotubes are now parallel to each other along the x-axis and is referred as configuration A shown in Fig. 4. Similarly to the previous case, all tube diameters are 1.4nm and the distance separating them is fixed to 3.4Å. Again in the absence of an external electric field, the coupling is uniformly distributed, Fig. 4(a). The second case depicted in Fig. 4(b) shows the coupling distribution with the presence of an external electric field along the x-axis from left to right. It should be noted that the applied electric field greatly enhances the coupling between the two tubes on the left along the field direction.

The third case shows a centered s-SWCNT surrounded by six peripheral s-SWCNTs and is referred as configuration B configuration B. Again all tubes 1.4nm wide and equidistant by 3.4Å.

Without external electric field, the coupling effect occurring along the s-SWCNT is equally distributed between the nanotube at the centre and its adjacent ones. It should be noted that less coupling occurs among the out of centre ones as shown in Fig. 5 (a). Then an external electric field is applied along x-direction from left to right to redistribute the localized coupling among the carbon nanotubes bundle as shown in Fig.5 (b).

In order to clearly understand the effect of the coupling between the adjacent tubes on the electrical and optical properties, the difference of the energy band gap due to the contribution of the coupling effect is calculated:

$$\Delta E = E_g(coupled) - E_g(\text{one s-SWCNT}) \tag{4}$$

To calculate the energy band gap for the proposed configuration accounting the influence of the electric field, Schrödinger's equation is modified according to [11]:

$$\left(\frac{-\hbar}{2m*}\nabla^2 + V_{eff-total} - eFr\cos\phi\right)\Psi(r,\phi,z) = E\Psi(r,\phi,z) \tag{5}$$

where e is the electron charge, F is the electric field applied along the x-axis expressed in cylindrical coordinates.

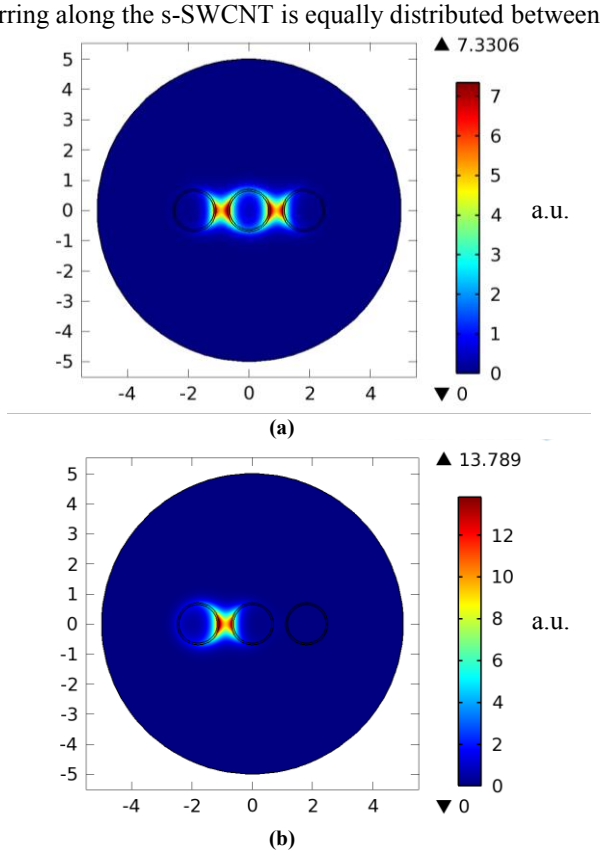


Fig. 4 Configuration A: Coupling effect distribution between three parallel s-SWCNT; (a) in the absence of an external electric field, (b) with the presence of an external electric field applied along x-axis from left to right.

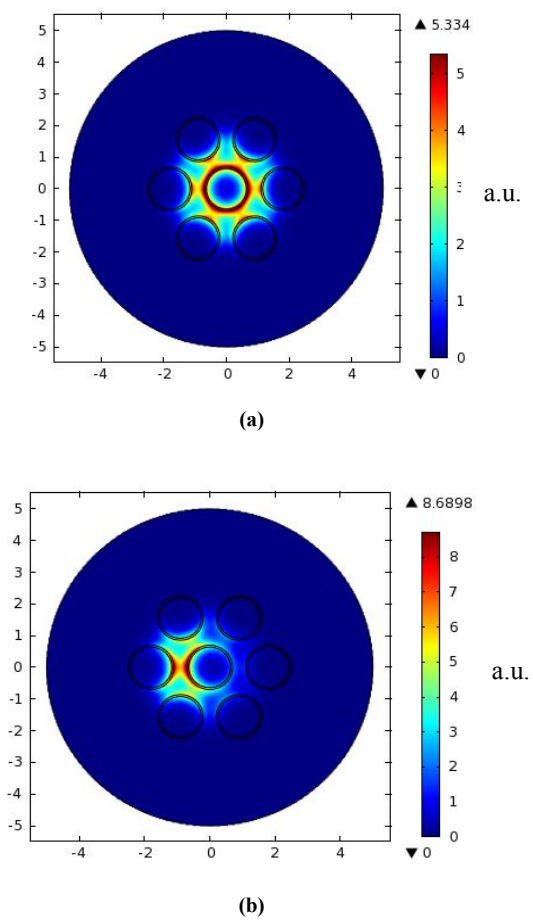
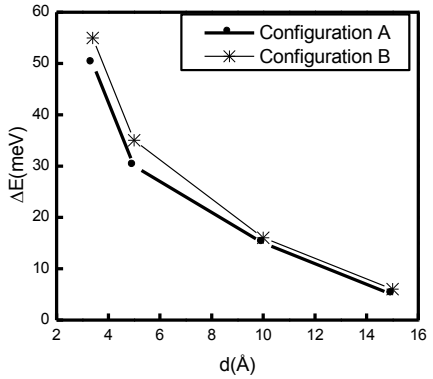
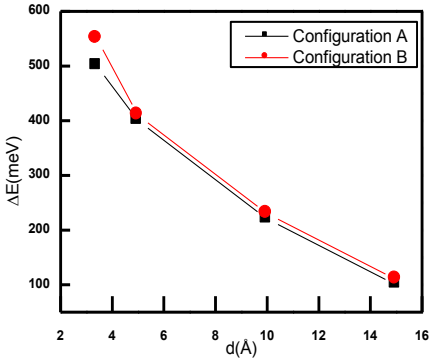


Fig. 5 Configuration B: Coupling effect distribution between seven adjacent s-SWCNT; (a) in the absence of an external electric field, (b) with the presence of an external electric field applied along x-axis from left to right.

Fig. 6 (a) shows the energy band gap variation versus the distance separating the semi-conducting single-walled carbon nanotubes considering configuration A and B. When the carbon nanotube are close to each other, the contribution of the coupling effect becomes non negligible. As expected the coupling effect is highly dependent of the distance separating the nanotube. The energy band gap is reduced from 50meV to 5meV when the distance between the nanotubes in configuration A and B increases from 3.4Å to 15Å. It should be mentioned that no noticeable effect occurs based on the different configurations. In fact, the coupling effect is equally distributed between the numbers of SWCNTs in the absence of an external electrical field. Fig. 6 (b) presents the energy band gap distinction in the existence of an external applied electric field for both configurations. Applying the electric field clearly enhances the coupling between the s-SWCNTs and; hence, the energy band gap change is 20% more than the case where there no electric field.



(a)



(b)

Fig. 6 the change in the energy band gap for both configurations A and B (a) with no electric field applied, (b) with an electric field applied along x-axis.

IV. Conclusion

A comprehensive study of the coupling effect between semi-conducting single-walled carbon nanotube is demonstrated considering different configurations. In the absence of an external electric field, the coupling between the nanotubes is equally distributed among the SWCNT in the bundle. Then by applying an external electric field, our data show that not only the coupling is now localized between the first nanotubes encounter by the electric field along its direction, but also the energy band gap of the bundle is greatly enhance. This is an important property for terahertz or far infrared optical applications where the development of devices in this spectrum is limited by the current semiconductor material properties. Finally, the potential to tune or reduce the energy band gap of semiconducting single-walled carbon nanotube can improve solar cell efficiency by enlarging the absorption spectrum compared to the current technology.

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