PRAMANA — journal of physics

Vol. 81, No. 2
August 2013
pp. 309–317

Quantum capacitance of the armchair-edge graphene nanoribbon

LING-FENG MAO
School of Urban Rail Transportation & Institute of Intelligent Structure and System, Soochow University, Suzhou 215006, People's Republic of China
E-mail: lingfengmao@suda.edu.cn

MS received 16 August 2012; revised 17 March 2013; accepted 26 March 2013

Abstract. The quantum capacitance, an important parameter in the design of nanoscale devices, is derived for armchair-edge single-layer graphene nanoribbon with semiconducting property. The quantum capacitance oscillations are found and these capacitance oscillations originate from the lateral quantum confinement in graphene nanoribbon. Detailed studies of the capacitance oscillations demonstrate that the local channel electrostatic potential at the capacitance peak, the height and the number of the capacitance peak strongly depend on the width, especially a few nanometres, of the armchair-edge graphene nanoribbon. It implies that the capacitance oscillations observed in the experiments can be utilized to measure the width of graphene nanoribbon. The results also show that the capacitance oscillations are not seen when the width is larger than 30 nm.

Keywords. Graphene electronics; finite-size effects; capacitance; quantization.

PACS Nos 73.63.−b; 85.30.Tv

1. Introduction

Graphene, which is a hexagonal lattice of a single layer of carbon atoms, has a two-dimensional (2D) crystal structure. Graphene has recently emerged both as a unique system for fundamental studies of condensed matter and quantum physics [1] and a fascinating building block for future devices in post-silicon era [2–26]. Graphene ribbons with nanometre-sized width have been studied extensively [2–6]. Since graphene nanoribbons are just geometrically terminated single graphite layers, their electronic structures have been modelled by imposing appropriate boundary condition on Schrödinger's equation [7–11]. Graphene can be patterned in nanoribbons by using planar technologies such as electron beam lithography and etching [2]. An energy gap might be opened when graphene is patterned into a nanoribbon, and the carriers are confined in a quasi-one-dimensional (Q1D) system. It is predicted that graphene ribbons with armchair shaped edges can be either metallic or semiconducting depending on their width [7–11], and that

DOI: 10.1007/s12043-013-0556-x; ***e*Publication: 22 June 2013**

graphene nanoribbons with zig-zag shaped edges are metallic with peculiar edge states on both sides of the ribbon regardless of its width [7–14].

Luryi used the concept of 'quantum capacitance' to develop an equivalent circuit model for devices that incorporate a highly conducting 2D electron gas [27]. This concept has also been used in modelling one-dimensional (1D) systems [28–30]. Recently, an analytical formulation of the quantum capacitance in bilayer graphene nanoribbon has been proposed and quantum size effects on the quantum capacitance have been studied [31]. In this paper, we study the finite-size effects on the quantum capacitance of armchair-edge single-layer graphene ribbon and how the finite-size effects affect its oscillations.

2. Theory

The total charge density in a single-layer graphene sheet with a local channel electrostatic potential $V_{\rm ch}$, which equals the electron charge density charge minus the hole charge density, can be written as [29,30]

$$Q = q\int_0^\infty g\,(E)\left[f\left(E+\frac{E_{\rm G}}{2}+qV_{\rm ch}\right)-\left(E+\frac{E_{\rm G}}{2}+qV_{\rm ch}\right)\right]{\rm d}E, \qquad (1)$$

where q is the electronic charge, E is the energy, $g(E)$ is the density of states, $f(E)$ is the Fermi–Dirac distribution function and $E_{\rm G}$ is the band gap.

The semiconducting property of armchair grapheme nanoribbons (GNRs) occurs when $n = 3m$ or $3m+1$, where m is an integer ([8], and references therein). Here, we define n as the number of the dimmer (two carbon sites) lines for the armchair ribbon. It means that the armchair-edge ribbon contains n dimmer lines of carbon. The width of the GNR is proportional to n which is given by the expression

$$W = (n-1)\,\frac{\sqrt{3}}{2}a, \qquad (2)$$

where $a = 1.42$ Å is the bond length between carbon atoms. The low energy expansion of the first conduction or valance band for armchair single-layer GNRs is

$$E = \pm\frac{3}{2}at\sqrt{k_x^2+\left(\frac{2}{\sqrt{3}a}\left(\frac{p\pi}{n+1}-\frac{2}{3}\pi\right)\right)^2} \qquad (3)$$

where the hopping integral of perfect GNRs $t = 2.7$ eV and p is the subband index.

The volume of 1D k-space between energy E and $E+\delta E$ can be obtained as

$$\begin{aligned}\Delta V_{\rm 1D}(E) &= \Delta k_x = \Delta E\frac{\partial k_x}{\partial E} = \frac{\Delta E}{(\partial E/\partial k_x)}\\ &= \Delta E\frac{E}{(3/2)\,at\sqrt{E^2-3t^2\left((p\pi/(n+1))-(2/3)\pi\right)^2}}.\end{aligned} \qquad (4)$$

Since two electrons of opposite spin require a volume of 2π in phase-space and two valleys in the first Brillouin zone, the density of states for the nth subband of such a graphene nanoribbon can be obtained as

$$g_n^{1D}(E) = \frac{4E}{3\pi at\sqrt{E^2 - E_p^2}}\Theta(E - E_p), \tag{5}$$

where $E_p = t\sqrt{3}\left|\frac{p\pi}{n+1} - \frac{2}{3}\pi\right|$ and $\Theta(x)$=1 for $x \geq 0$ and zero otherwise.

Thus, electron density in the nth subband of such a graphene nanoribbon is

$$Q_n^{1D}(E) = \int_{E_p}^{\infty} \frac{4E}{3\pi at\sqrt{E^2 - E_p^2}} \frac{1}{1 + \exp\left((E - E_F)/k_B T\right)} \mathrm{d}E. \tag{6}$$

Hence the total density of states per unit length is the quasi-1D expression for an armchair single-layer graphene nanoribbon

$$g_{Q1D}(E) = \sum_{p=1}^{+\infty} \frac{4E}{3\pi at\sqrt{E^2 - E_p^2}}\Theta(E - E_p). \tag{7}$$

Thus, the number of electrons per unit length in an armchair single-layer graphene nanoribbon

$$Q_a = q\sum_p \int_{E_p}^{\infty} \frac{4E}{3\pi at\sqrt{E^2 - E_p^2}} \times \left(\frac{\Theta(E - E_p)}{1 + \exp\left(\frac{E - E_F + qV_{ch}}{k_B T}\right)} - \frac{\Theta(E - E_p)}{1 + \exp\left(\frac{E - E_F - qV_{ch}}{k_B T}\right)}\right) \mathrm{d}E. \tag{8}$$

Therefore, the quantum capacitance for an armchair single-layer graphene nanoribbon can be obtained as [17],

$$C_{Qa} = \frac{\partial Q_a}{\partial V_{ch}}. \tag{9}$$

As a comparison, the quantum capacitance of the single-layer graphene nanoribbon neglecting the edge shape will be given in the fowling part. The density of states of the single-layer graphene nanoribbon without considering the actual ribbon shape (regardless of the effect of symmetry of the ribbons on the energy dispersion relation) was given as [18],

$$g_n^{Q1D}(E) = \frac{4}{\pi\hbar v_0} \frac{E}{\sqrt{E^2 - (E_n)^2}}\Theta(E - E_n), \tag{10}$$

where v_0 is the velocity and $\hbar$ is the reduced Planck's constant. The velocity v_0 is independent of energy and the predicted value is $v_0 = 3a_0\gamma_0/2\hbar \approx 10^6\,\mathrm{m\,s^{-1}}$. Here γ_0 is

the interatomic overlap energy, $a_0 = 1.42$ Å is the interatomic spacing and $E_n = nv_0\hbar(\pi/W)$. Thus, the number of electrons per unit length in a graphene nanoribbon without considering the actual ribbon shape and its quantum capacitance can be written as

$$Q_n = q\sum_n \int_{E_n}^{\infty} \frac{4E}{\pi\hbar v_0} \frac{\Theta(E-E_n)}{\sqrt{E^2-(E_n)^2}} \times \left(\frac{1}{1+\exp\left(\frac{E+\frac{E_G}{2}+qV_{ch}}{k_BT}\right)} - \frac{1}{1+\exp\left(\frac{E+\frac{E_G}{2}-qV_{ch}}{k_BT}\right)} \right) dE \tag{11}$$

$$C_{Qn} = \frac{\partial Q_n}{\partial V_{ch}}. \tag{12}$$

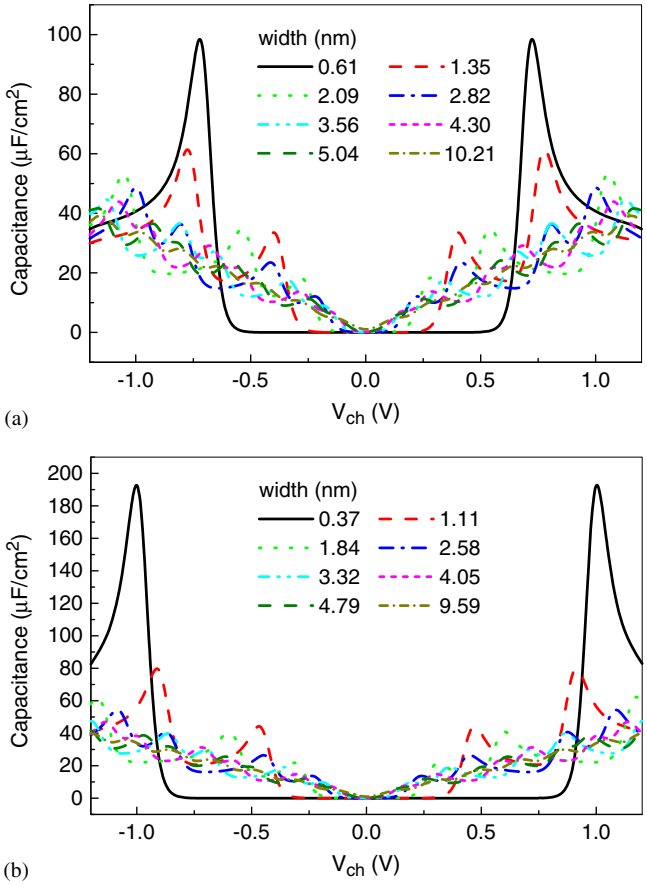

Figure 1. Quantum capacitance as a function of the local channel electrostatic potential for armchair-edge graphene nanoribbon with (**a**) $n = 3m$ and (**b**) $n = 3m+1$ when its width is a few nanometres.

3. Results and discussion

In the following calculations, the temperature is set as 300 K. Figure 1 shows how the quantum capacitance changes with the local channel electrostatic potential when the width of the armchair-edge graphene nanoribbon is a few nanometres for $n = 3m$ and $3m+1$, respectively. One can clearly see from this figure that the quantum capacitance oscillations can be found for the armchair-edge graphene nanoribbon with semiconducting property ($n = 3m$ and $3m+1$). The peak height of the capacitance oscillations largely decreases when the width of the ribbon increases, whereas the peak number of the capacitance oscillations increases when the width of the ribbon increases. The increase in

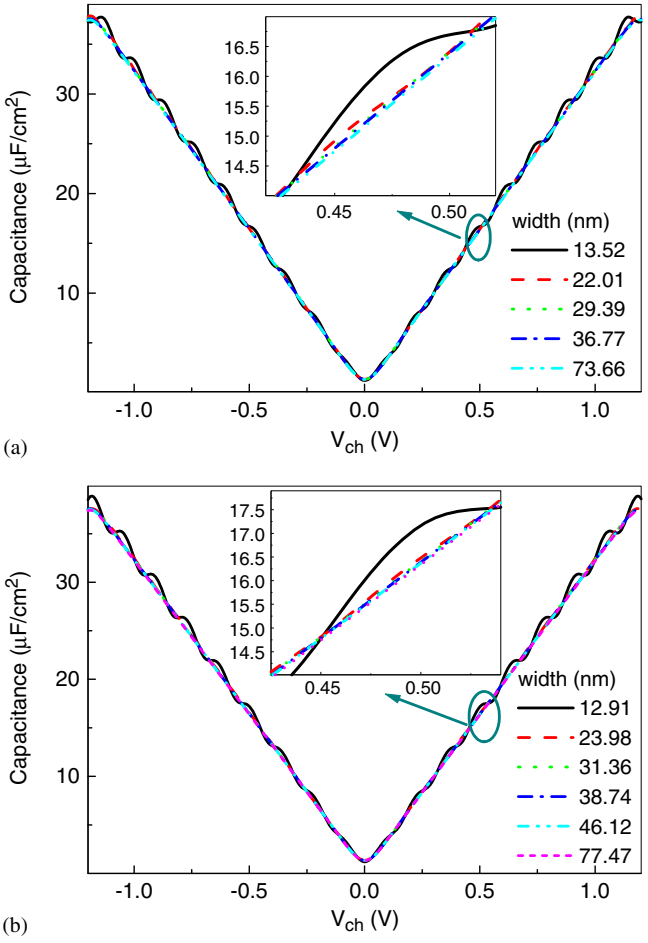

Figure 2. Quantum capacitance as a function of the local channel electrostatic potential for armchair-edge graphene nanoribbon with (**a**) $n = 3m$ and (**b**) $n = 3m+1$ when the width is lager than 10 nm. For comarison, the curve of the quantum capacitance vs. the local channel electrostatic potential is also given as an inset in this figure.

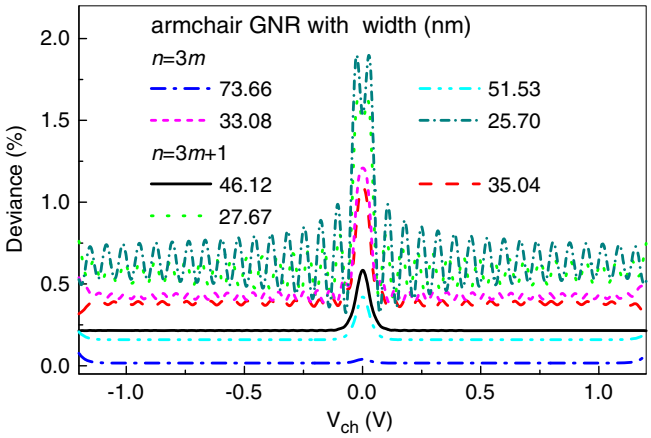

Figure 3. The relative deviance in the calculated quantum capacitance when the width of the nanoribbon changes from 27 nm to 74 nm compared to that when the width is 77.47 nm.

the peak number results from wider armchair-edge graphene nanoribbon leading to more quantized levels in a given energy range. It also can be noted that the local channel electrostatic potential where the capacitance peak occurs is strongly dependent on the width of the armchair-edge graphene nanoribbon.

Figure 2 shows how the quantum capacitance changes with the local channel electrostatic potential when the width of the armchair-edge graphene nanoribbon is larger than 10 nm for $n = 3m$ and $3m+1$, respectively. The inset of this figure shows the curve of quantum capacitance vs. the local channel electrostatic potential. One can clearly see from this figure that there are no obvious quantum capacitance oscillations when the width of the nanoribbon is larger than 30 nm. It can also be seen that the quantum capacitance seems to be constant with the width of nanoribbon when the oscillation in the quantum capacitance is not obvious. Figure 2 also shows that quantum capacitance is constant when the width of the nanoribbon is large.

Figure 3 demonstrates how the quantum capacitance changes with the width of the wider armchair-edge graphene nanoribbon. This figure depicts the relative deviance in quantum capacitance when the width of the nanoribbon changes from 27 nm to 74 nm compared to that when the width of the nanoribbon is 77.47 nm. The relative deviance in oscillations originates from the oscillations in the quantum oscillations. This figure also illustrates that peak height decreases largely with the increasing width for wider armchair-edge single-layer graphene nanoribbon.

Figure 4 shows the relation between the local channel electrostatic potential where the first capacitance peak occurs and the width of the nanoribbon. For comparison, the band gap of armchair-edge graphene nanoribbon as a function of the width of the nanoribbon is also given in this figure. Such a relation approximately obeys an exponential relation similar to the relation between the band gap and the width of the nanoribbon. When the width of the nanoribbon is less than 10 nm, the local channel electrostatic potential where the first capacitance peak occurs is very strongly dependent on the width of the nanoribbon.

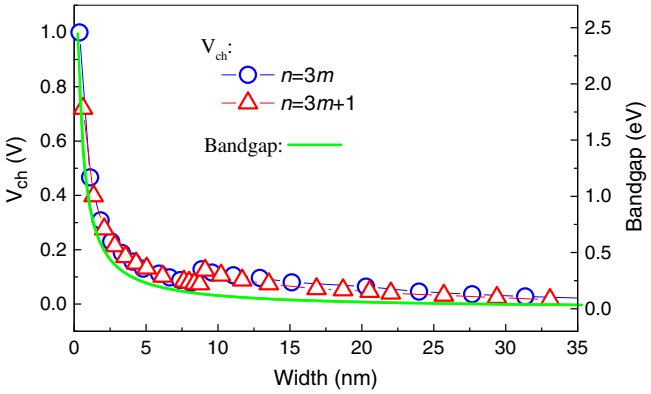

Figure 4. The local channel electrostatic potential at the first capacitance peak as a function of the width of the armchair-edge graphene nanoribbon. For comparison, its band gap is also given in this figure.

It is also noted that results for the armchair-edge single-layer graphene nanoribbon with (a) $n = 3m$ and (b) $n = 3m+1$ obey the same relation. This implies that we can use such a relation and the capacitance peak observed in the experiments to determine the width of the armchair-edge single-layer graphene nanoribbon when the width of the nanoribbon is less than 35 nm.

Figure 5 shows the relation between the height of the first capacitance peak and the width of the armchair-edge graphene nanoribbon. This relation approximately obeys an exponential-dependent relation also. It is also noted that the height of the first capacitance peak for the armchair-edge single-layer graphene nanoribbon with (a) $n = 3m$ and (b) $n = 3m+1$ obeys the same relation. This implies that this relation can be utilized to determine the width of the armchair-edge single-layer graphene nanoribbon when the width of the nanoribbon is less than 30 m in the experiments.

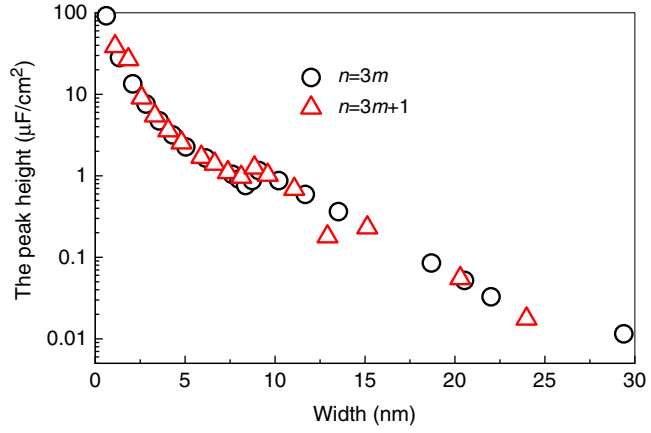

Figure 5. The first capacitance peak height as a function of the width of the armchair-edge graphene nanoribbon.

When we compare ref. [31] with this work, both study the quantum capacitance, but ref. [31] studies bilayer graphene nanoribbon, our work studies the single-layer graphene nanoribbon, and thus it has different band structures. Additionally, both works study the quantum capacitance, but this work focusses on the finite-size effects on height and position of peaks in the capacitance oscillations whereas the work in ref. [31] does not.

4. Conclusion

In conclusion, the finite-size effects on the capacitance vs. the local channel electrostatic potential curve of an armchair-edge graphene nanoribbon have been theoretically investigated. The results demonstrate that typical characteristic oscillations can be found in the curve of the capacitance vs. local channel electrostatic potential for a thinner armchair-edge single-layer graphene nanoribbon. The finite-size effect (the lateral quantum confinement) leads to the splitting of the band of graphene into subbands. Thus, the formation of subbbands in one-dimensional graphene nanostructure is the origin of oscillations in the curve of the capacitance vs. the local channel electrostatic potential. The number of capacitance peaks at a given range of local channel electrostatic potential increases when the width of the nanoribbon increases. The quantum capacitance oscillations for the armchair-edge single-layer graphene nanoribbon with semiconducting property are remarkable when its width is smaller than 10 nm. The oscillations in the quantum capacitance are not obvious and quantum capacitance depends weakly on the width of the nanoribbon when width of the nanoribbon is larger than 30 nm. The local channel electrostatic potential at the first capacitance peak decreases with the increasing width of the nanoribbon. Such a decrease is especially large when the width of the nanoribbon is a few nanometres. On the other hand, the height of the first capacitance peak exponentially decreases approximately with the increasing width of the nanoribbon. In short, both decreases can be utilized to measure the width of the armchair-edge single-layer graphene nanoribbon in experiments.

Acknowledgements

The author acknowledges financial support from the National Natural Science Foundation of China under Grant 61076102 and Natural Science Foundation of Jiangsu Province under Grant BK2012614.

References

[1] A K Geim and K S Novoselov, *Nature Mater.* **6**, 18 (2007)
[2] C Berger, Z Song, X Li, X Wu, N Brown, C Naud, D Mayou, T Li, J Hass, A N Marchenkov, E H Conrad, P N First and W A de Heer, *Science* **312**, 1191 (2006)
[3] A Rycerz, J Tworzydlo and C W J Beenakker, *Nature Phys.* **3**, 172 (2007)
[4] M C Lemme, T J Echtermeyer, M Baus and H Kurz, *IEEE Electron Device Lett.* **28**, 282 (2007)
[5] B Huard, J A Sulpizio, N Stander, K Todd, B Yang and D Goldhaber-Gordon, *Phys. Rev. Lett.* **98**, 236803 (2007)

[6] K S Novoselov, A K Geim, S V Morozov, D Jiang, Y Zhang, S V Dubonos, I V Crigorieva and A A Firsov, *Science* **306**, 666 (2004)
[7] Y W Son, M L Cohen and S G Louie, *Phys. Rev. Lett.* **97**, 216803 (2006)
[8] H X Zheng, Z F Wang, Q W Shi and J Chen, *Phys. Rev. B* **75**, 165414 (2007)
[9] L Brey and H A Fertig, *Phys. Rev. B* **73**, 235411 (2006)
[10] M Ezawa, *Phys. Rev. B* **73**, 045432 (2006)
[11] D A Abanin, P A Lee and L Levitov, *Phys. Rev. Lett.* **96**, 176803 (2006)
[12] S Okada and A Oshiyama, *Phys. Rev. Lett.* **87**, 146803 (2001)
[13] H Lee, Y W Son, N Park, S Han and J Yu, *Phys. Rev. B* **72**, 174431 (2005)
[14] Y Miyamoto, K Nakada and M Fujita, *Phys. Rev. B* **59**, 9858 (1999)
[15] X Wang, Y Ouyang, X Li, H Wang, J Guo and H Dai, *Phys. Rev. Lett.* **10**, 206803 (2008)
[16] K S Novoselov, A K Geim, S V Morozov, D Jiang, Y Zhang, S V Dubonos, I V Gregorieva and A A Firsov, *Nature* **438**, 197 (2005)
[17] Y B Zhang, Y W Tan, H L Stormer and P Kim, *Nature* **438**, 201 (2005)
[18] H B Heersche, P Jarillo-Herrero, J B Oostinga, L M K Vandersypen and A F Morpurgo, *Nature* **446**, 56 (2007)
[19] V M Pereira and A H Castro Neto, *Phys. Rev. Lett.* **103**, 046801 (2009)
[20] L Jiao, L Zhang, X Wang, G Diankov and H Dai, *Nature* **458**, 877 (2009)
[21] G A Giovannetti, P Khomyako, G Brocks, V M Karpan, J van den Brink and P J Kelly, *Phys. Rev. Lett.* **101**, 026803 (2008)
[22] P Avouris, Z Chen and V Perebeinos, *Nat. Nanotechnol.* **2**, 60 (2007)
[23] L F Mao, X J Li, Z O Wang and J Y Wang, *IEEE Electron Device Lett.* **29**, 1047 (2008)
[24] L F Mao, *Nanotechnol.* **20**, 275203 (2009)
[25] L F Mao, X J Li, C Y Zhu, Z O Wang, Z H Lu, J F Yang, H W Zhu, Y S Liu and J Y Wang, *IEEE Electron Device Lett.* **31**, 491 (2010)
[26] L F Mao, *Carbon* **49**, 2709 (2011)
[27] S Luryi, *Appl. Phys. Lett.* **52**, 501 (1988)
[28] R Tarkiainen, M Ahlskog, J Penttila, L Roschier, P Hakonen, M Paalanen and E Sonin, *Phys. Rev. B* **64**, 195412 (2001)
[29] D John, L Castro and D Pulfrey, *J. Appl. Phys.* **96**, 5180 (2004)
[30] T Fang, A Konar, H Xing and D Jena, *Appl. Phys. Lett.* **91**, 092109 (2007)
[31] S Bhattacharya and S Mahapatra, *Physica E* **44**, 1127 (2012)