



# Direct band gap GaP nanowires predicted through first principles

Charley B. E. Santos and T. M. Schmidt

Citation: Journal of Applied Physics **108**, 103715 (2010); doi: 10.1063/1.3511340 View online: http://dx.doi.org/10.1063/1.3511340 View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/108/10?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Strong surface passivation of GaAs nanowires with ultrathin InP and GaP capping layers Appl. Phys. Lett. **105**, 033114 (2014); 10.1063/1.4891535

Electronic and structural properties of InAs/InP core/shell nanowires: A first principles study J. Appl. Phys. **111**, 054315 (2012); 10.1063/1.3692440

Optical properties of functionalized GaN nanowires J. Appl. Phys. **109**, 053523 (2011); 10.1063/1.3552919

Band gap engineering of GaN nanowires by surface functionalization Appl. Phys. Lett. **94**, 073116 (2009); 10.1063/1.3086316

Hydrogen and oxygen on InP nanowire surfaces Appl. Phys. Lett. **89**, 123117 (2006); 10.1063/1.2345599



[This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to ] IP: 128.235.251.160 On: Fri, 19 Dec 2014 12:47:08

# Direct band gap GaP nanowires predicted through first principles

Charley B. E. Santos and T. M. Schmidt<sup>a)</sup>

Instituto de Física, Universidade Federal de Uberlândia, C.P. 593, 38400-902 Uberlândia, Minas Gerais, Brazil

(Received 9 August 2010; accepted 2 October 2010; published online 29 November 2010)

GaP nanowire, a potential material for new devices where optical and electronic applications can be merged, suffers some limitations because it presents indirect band gap. Using first principles calculations we demonstrate that, due to confinement effects, the band gap not only is enlarged when in a nanowire form, but can be transformed to a direct band gap semiconductor nanowire, just by reducing the nanowire diameter to few nanometers. This transition to a direct band gap is obtained for [111] oriented GaP nanowires but not for [110] oriented nanowires. The effects of surface states which can alter the band gap have been studied with hydrogen saturation and an oxide cap layer on the surface of the GaP nanowire. The results show that, while the hydrogen is a perfect passivator, the GaP/Ga<sub>2</sub>O<sub>3</sub> heterojunction presents a small conduction band offset but keeps direct band gap [111] oriented GaP nanowires. © 2010 American Institute of Physics. [doi:10.1063/1.3511340]

## I. INTRODUCTION

III-V semiconductor nanowires have been intensively studied due to their potential applications in optoelectronic devices and photonic circuits.<sup>1-3</sup> Gallium phosphide presents so many different nanoscale forms<sup>4-7</sup> and, among the different applications, is of particular interesting for miniature optical devices.<sup>8</sup> As reported recently<sup>9</sup> nanowires of gallium phosphide with few nanometers of diameters can be obtained with very simple techniques, making them useful as building blocks to fabricate nanodevices. However, gallium phosphide presents an indirect band gap of 2.26 eV, which makes it not so useful for optical applications. The generation of light can only occurs by means of excitons with isoelectronic dopants under uniaxial stress,<sup>10</sup> hydrostatic pressure<sup>11</sup> or shock compression.<sup>12</sup> There is not evidence that nanostructured III-V compounds change the minimum of the conduction band as compared to the bulk ones, but an enlargement of the band gap is observed, due to confinement effects.<sup>2,13</sup> Nevertheless extended defects like twinning superlattices have been predicted to transform indirect band gap zinc blended semiconductors to direct ones.<sup>14</sup> Recently it has been shown that twinning superlattices can be controlled in InP nanowires by controlling the nanowire morphology.<sup>15</sup> And if it could be extended to a indirect band gap semiconductor one would transform it in direct band gap material. However a transition from bulk indirect band gap to a nanoscale direct one, only due to nanoeffects, have not been observed in III-V nanostructures so far.

An important issue to obtain electronic properties in nanoscale semiconductors is the, usually hard to determine experimentally, surface structure of the nanomaterial. In order to avoid the surface effects, it has been shown that an oxide cap layer, usually  $Ga_2O_3$  coating,<sup>8,16,17</sup> let the inner GaP nanowire with very crystalline structure. Actually GaP or  $Ga_2O_3$  nanostructures can be transformed one to another. GaP nanowires can be synthesized from  $Ga_2O_3$ ,<sup>18</sup> as well

Ga<sub>2</sub>O<sub>3</sub> nanocrystals can be obtained from GaP nanocrystals.<sup>19</sup> Outer Ga<sub>2</sub>O<sub>3</sub> layers can work as a protection cap layer for the GaP nanowires, allowing the use of GaP/Ga<sub>2</sub>O<sub>3</sub> structure for nanodevices at high temperatures. What is no so clear till now is the atomic arrangement at the interface between both structures, how is the consequence on the electronic structure due to an oxide on the surface of a GaP nanowire, and how the confinement effects alter the electronic properties of thin nanowires. Theoretical simulations usually use hydrogens as a passivation mechanism to avoid surface dangling bonds,<sup>13</sup> while experimentally hydrogen passivation is not feasible, but surface treatment with increases significantly the photoluminescence acids intensity.<sup>20</sup>

In this work, using first principles calculations, it is demonstrated that the indirect bulk GaP band gap can be transformed to a direct band gap semiconductor, just by reducing the nanowire diameter to few nanometers. It was also studied the effects of surface saturation with hydrogens or an oxide cap layer. The results show that the hydrogen is a perfect passivator, and the core-shell GaP/Ga<sub>2</sub>O<sub>3</sub> heterojunction presents a small conduction band offset, but both keep direct band gap [111] oriented nanowires.

### **II. METHOD**

The total energy calculations have been performed with the density functional theory (DFT) within the generalized gradient approximation (GGA) (Ref. 21) for the exchangecorrelation potential, where the electron-ion interactions are described by *ab initio* norm-conserving fully separable Troullier–Martins<sup>22</sup> pseudopotentials in the Kleinman– Bylander form.<sup>23</sup> The total energy has been obtained by a fully self-consistent calculations by solving the standard Kohn–Shan (KS) equations. The KS orbitals are expanded using a linear combination of numerical pseudoatomic orbitals, implemented in the SIESTA code.<sup>24</sup>

In all calculations a split-valence double-zeta quality basis set enhanced with polarization function have been shown

<sup>&</sup>lt;sup>a)</sup>Electronic mail: tschmidt@infis.ufu.br.

to reproduce correctly the valence band and binding energies for both GaP and  $Ga_2O_3$  systems. The results have been compared to other first principles and experimental results.<sup>25,26</sup> To guarantee a good description of the charge density, a cutoff of 170 Ry for the grid integration was used to project the charge density in the real space and to calculate the selfconsistent Hamiltonian matrix elements.

It is well known that standard DFT calculations underestimate band gaps, due to a lower position for the conduction band energies. As we are interested here in energy dispersions of conduction bands, a band gap correction may be necessary in order to avoid any spurious interaction which can alter the conduction band energy. To describe correctly the empty states we also used a self-interaction correction (SIC) scheme,<sup>27</sup> which produces exchange parameters more accurate than standard GGA does. The SIC approach, implemented in the SIESTA code, have been used in some structures in order to confirm the main results, especially in those where we want to well describe the unoccupied bands.

Two types of nanowires have been studied in this work. One is aligned along the [111] direction (called here z direction), using the supercell approach, in which the periodicity length along the z direction is  $a\sqrt{3}$ , where a is the bulk lattice parameter. These [111] oriented wires present crystalline structure with six {110} planes forming a hexagonal crosssection on the xy planes. The other type of nanowire is aligned along the [110] direction, where the periodicity length is  $a\sqrt{2}/2$ . All the geometries were optimized until the remaining forces were less than 0.005 eV/Å. The Brillouin zone was sampled using up to five k-points along the nanowire axis. The bulk GaP band gap obtained using the standard GGA-DFT approximation gives a direct band gap of 2.00 eV and an indirect one of 1.70 eV, while by including the SIC approach we get 2.44 eV and 2.17 eV, respectively. As it is known standard DFT always gives smaller energy gaps, however, the SIC improves the value getting it close to the experimentally 2.78 eV and 2.26 eV for indirect and direct band gap, respectively.

### **III. RESULTS AND DISCUSSION**

In order to obtain the electronic properties of an ideal GaP nanowire without any surface effect, due to the presence of dangling bonds or surface defects, we first saturate the nanowire surface with hydrogen atoms in such way that all Ga and P atoms are fourfold coordinated. The GaP nanowires passivated with hydrogen atoms present crystalline structure as can be seen in Fig. 1, and they do not present any surface energy level inside or around the band gap, similarly as reported before for InP nanowires.<sup>28</sup> A calculation with a more realistic surface passivation with Ga2O3 will be discussed later. Initially we are only interested in the electronic structure of pristine GaP nanowires as a function of their diameters. We optimize the geometry of four nanowires aligned along the [111] direction [Fig. 1(a)] with diameters of 1.2, 1.7, 2.2, and 2.6 nm, in a supercell containing 68, 116, 176, and 239 atoms, respectively. Also we investigate two nano-



FIG. 1. (Color online) Structure of GaP nanowires aligned along the [111] (a) and [110] (b) directions. The biggest, the medium, and the smaller balls represent the Ga, P, and the H atoms, respectively.

wires aligned along the [110] direction [Fig. 1(b)] with diameters of 0.8 nm and 1.5 nm, containing 14 and 40 atoms, respectively.

One of the first response to the confinement effects in nanowires is that the band gap is enlarged with respect to the bulk band gap. Particularly for GaP nanowires, a new effect which is the transition from the bulk indirect band gap to a nanowire direct one is believed also to be due to the confinement effects as we will explain below. In Fig. 2 we plot the bottom of the conduction band (CBM) for four GaP nanowires aligned along [111] direction with different diameters, where the reference for the top of valence band (VBM) was keep at zero. The back dotted line is the bulk CBM result. In order to guarantee that the reduced band gaps obtained in standard DFT calculations do not affect the dispersion energies, the results presented in this figure were obtained using the GGA-SIC scheme that, as described in Sec. II, is more accurate to calculate band gaps. The energy dispersions for calculations where no self-interaction is included are very similar to those presented in Fig. 2, only the band gaps are reduced as compared to results using SIC scheme.

We note from Fig. 2 that for the bulk, as it is expected, part of the  $\Gamma$ -L and  $\Gamma$ -X bands are lower in energy than the  $\Gamma$ point. On the other hand for the nanowires aligned along the [111] direction the  $\Gamma$ -L' as well  $\Gamma$ -X' are always upper in energy than the  $\Gamma$  point. For the [111] oriented nanowires the L' point is three times shorter than the L point of the bulk first Brillouin zone (since the modulus of the smaller reciprocal vector of the nanowire along the z direction is  $2\pi/a\sqrt{3}$ , while for the [111] direction of the bulk this modulus is  $2\pi\sqrt{3}/a$ ). The X' point of the nanowire also does not belong to the bulk first Brillouin zone, but it is folded along the strongly confined xy plane (in which the folding depend on the nanowire diameter) and along the z direction. In this way



FIG. 2. (Color online) Energy dispersions at the CBM for nanowires with different diameters aligned along the [111] direction. Also the bulk dispersion is included (dotted line). The energies are with respect to the VBM. This result have been obtained using SIC.

the almost symmetric dispersion observed in Fig. 2 is due to the dispersion mainly guided by the folding along the  $\Gamma$ -L' (or z direction). For all nanowires aligned along the [111] direction studied here the band gap is direct, and the energy band gap difference between the direct and indirect one does not obey a simple function of the nanowire diameter. So, we cannot predict exactly for which diameter the transition to indirect one will occur as is in the bulk phase, but by making a simple linear extrapolation we observe that this transition will occur for diameters greater than 4 nm.

If the GaP nanowire is aligned along the [110] direction the energy band gap is always indirect. As we can see from Fig. 3, the folded L' and X' are always lower in energy than the  $\Gamma$ -point. Due to the foldings both points L' and X' have the same energy. Also we observe that along the nanowire axis ([110] direction or  $\Gamma$ -K'), as showed inset of the Fig. 3, the nanowire band gaps are also indirect.

As we reported before<sup>28</sup> unpassivated nanowires present energy levels inside the band gap, due to the nonsaturated surface dangling bonds. In order to understand the effects on the electronic structure, particularly in the transition indirect/ direct band gap, we study the properties of an outer oxide on the surface of [111] oriented GaP nanowire. We started from a completely hydrogen passivated nanowire (an ideal wire without dangling bonds), then we started to change H for O atoms. By assuming that we have a source of  $O_2$  and  $H_2$ molecules, we can obtain the formation energy per additional oxygen atom by computing the number *m* of atomic oxygens taken from the  $O_2$  reservoir and the number *n* of atomic hydrogens taken from the surface of the nanowire to the  $H_2$ reservoir



FIG. 3. (Color online) Energy dispersions at the CBM for nanowires aligned along the [110] direction for two diameters. Inset is the dispersion along the nanowire direction.

$$\Delta E_F = E_{nw+mO-nH} - E_{nw} - m\mu_O + n\mu_H,$$

where  $E_{nw+mO-nH}$  is the total energy of the nanowire, where m oxygens have been added and n hydrogens have been removed.  $E_{nw}$  is the total energy of the hydrogen passivated nanowire, and  $\mu_{\rm O}$  and  $\mu_{\rm H}$  are the chemical potentials of the atomic oxygen and hydrogen, respectively. These chemical potentials have been calculated as the energy to take an atom from the reservoir of the O<sub>2</sub> and H<sub>2</sub> molecules, respectively. If  $E[O_2]$  and  $E[H_2]$  are the energies of the ground states of H<sub>2</sub> and O<sub>2</sub> molecules,  $\mu_{O} = (1/2)E[O_2]$ and  $\mu_{\rm H}$  $=(1/2)E[H_2]$  are the chemical potentials, respectively. The ground state for the  $O_2$  molecule is a spin triplet state. We compute the formation energy of five potential sites for the O atom on the surface of [111] oriented GaP nanowire. The results are summarized in Table I. Although most of these formation energies per adsorbed O atom are negatives, it is not expected a chemisorbed oxidation process in GaP nanowires. That is because the calculated binding energy per atom for the  $O_2$  molecule is -2.93 eV. So, the oxidation can only occurs at high temperatures. Experimentally it has been observed that the oxidation of GaP nanocrystals takes place for temperatures higher than 400 °C,<sup>19</sup> and it is known that for bulk GaP the completed oxidation occurs for temperatures higher than 800 °C. As our formation energies for the oxygens are calculated starting from hydrogen passivated nanowires, it is expected that the oxidation of unpassivated

TABLE I. Formation energies (in electron volt) and bond lengths (in angstrom) of the O adsorbed on the surface of [111] oriented GaP nanowire.

Structure	Ga—O—P	Ga—O—Ga	Ga=0	P=0	P—0
$\Delta E_F$	-1.05	-0.56	-0.49	0.05	-0.02
Bond length	1.90/1.52	1.93	1.72	1.54	1.59

[This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to ] IP 128.235.251.160 On: Fri. 19 Dec 2014 12:47:08



FIG. 4. (Color online) Schematic representation of an outer Ga<sub>2</sub>O<sub>3</sub> layer on the surface of [111] oriented GaP nanowire. The biggest, the medium, and the smaller balls represent the Ga, P, and the O atoms, respectively.

GaP nanowires will present lower formation energies. Also it is interesting to observe from these formation energies that they are smaller as compared to those obtained for InP nanowires.<sup>28</sup> So the oxidation in InP nanowires will take place easier than in GaP nanowires.

The bond lengths (b) of the oxygens when adsorbed on the surface of GaP nanowires present three family bonds: (i) single Ga—O bond,  $b \approx 1.9$  Å; (ii) single P—O bond,  $b \approx 1.5$  Å; and (iii) double Ga=O bond,  $b \approx 1.7$  Å. The single Ga—O bond lengths are in the range of our calculated  $\beta$  phase of the Ga<sub>2</sub>O<sub>3</sub>, 1.87 Å–2.11 Å. And the P—O bond lengths are close to that of the PO<sub>4</sub> group average bond lengths, 1.54 Å. The structure for more O atoms on the surface of the GaP nanowire will be discussed later.

Next, we try to elucidate the effects on the electronic structure of [111] oriented GaP nanowires due to an oxide cap layer (Fig. 4). In order to understand step by step how the oxide is attached on the GaP nanowire surface, we increase one by one the number of oxygens and gallium atoms on the GaP nanowire, and compute the cohesive energy and the electronic structure. The cohesive energy has been computed as the energy difference between the atomic species (sum of the Ga, P, and O isolated atomic energies) and the GaP nanowire with m oxygens adsorbed on its surface. As we can see from Fig. 5, the system becomes more stable as the number of the oxygens m increases, reaching a value



FIG. 5. Cohesive energy as a function of the number of adsorbed O atoms on the GaP nanowire surface per unit cell.



FIG. 6. (Color online) Schematic representation for a GaP nanowire in a stage where an amorphous oxide cap layer is forming on the surface of the nanowire. This configuration is for m=9 from Fig. 5. The atom representation is the same as that of Fig. 4.

around 3.4 eV. For hydrogen saturated GaP nanowire the cohesive energy is 3.02 eV and the GaP bulk cohesive energy is 3.81 eV. The stabilization can be understood by the formation of a structure which is getting close to the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> structure, as we can see in Fig. 6, but the oxide present an amorphous structure.

For the crystalline  $\beta$  phase one can separate the bond angles in two classes for each species.<sup>29</sup> O—Ga<sub>I</sub>—O: 108– 118°, O—Ga<sub>II</sub>—O: 81–103°, Ga—O—Ga (tetrahedral): 112-123°, and Ga-O-Ga (octahedral): 94-103°. The structure of the gallium oxide layer keeps the Ga<sub>2</sub>O<sub>3</sub> stoichiometry, but is not the crystalline  $\beta$  phase, because the bond angles vary almost continuously from 88° to 135° for Ga—O—Ga and 81° to 124° for O—Ga—O. The Ga—O bond lengths of the oxide layer are also quite close to that of the crystalline  $\beta$  phase. We calculate the crystalline structure of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, obtaining five families of bond lengths ranging from 1.87 Å to 2.11 Å, which comes from two-types of Ga atoms and three-types of O atoms, in agreement with the Geller work.<sup>29</sup> For the oxide cap layer we obtain tens of different bond lengths ranging from 1.81 Å to 2.13 Å. So, what is formed on the nanowire surface is an amorphous oxide structure close to the fourfold and sixfold coordinated O and Ga atoms, respectively, of the crystalline  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> structure. This result is in agreement with experiments where is obtained, or amorphous, or polycrystalline outer Ga<sub>2</sub>O<sub>3</sub> oxide layers.<sup>16,17</sup>

We now turn to the electronic structure when atomic oxygens are adsorbed on GaP nanowire surface. Also we want to understand the influence of an oxide cap layer on the electronic structure of [111] oriented GaP nanowires. The presence of O atoms on the GaP nanowire surface introduces empty or occupied levels inside the band gap. When the O is binding with two Ga atoms, or between a Ga and a P atom, or makes single or double bond with P atoms it introduces unoccupied levels inside the nanowire band gap. Otherwise when the O makes single or double bond with Ga atoms, an occupied level appears in the band gap. The O impurity level is strongly localized for all systems described above. By increasing the number of O atoms on the [111] oriented GaP nanowire surface, which turns the system more stable, the oxygen levels move toward the valence band (for occupied levels) or toward the conduction band (for unoccupied lev-

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to ] IP: 128.235.251.160 On: Fri. 19 Dec 2014 12:47:08



FIG. 7. (Color online) (a) Schematic representation of the band structure around the band gap for the GaP nanowires with m O atoms adsorbed on the surface. m=0 is for a H passivated nanowire. (b) Schematic diagram of the band structure for Ga<sub>2</sub>O<sub>3</sub> cap layer on the GaP nanowire. The horizontal dashed line is a guide to separate occupied from unoccupied states.

els). A schematic representation of the electronic structure for many configurations with different number of O atoms are shown in Fig. 7(a). On the left of this figure, for m=0, is the band gap for a hydrogen saturated GaP nanowire, when no surface levels appear inside the band gap. We observe from this figure that, although there are energy levels inside the band gap for all configurations, the occupied levels are getting close to the valence band as the number of oxygens m increases. Otherwise the empty levels form a band around the GaP conduction band, which comes from the formation of the oxide cap layer. As schematically shown in Fig. 7(b), a conduction band offset takes place due to the GaP/Ga2O3 heterojunction of about 0.2 eV. This result can explain the exponentially current increasing observed in *n*-type  $GaP/Ga_2O_3$  core shell nanowires,<sup>8</sup> where a lowering of the barrier for the electrons will occur since electrons will be transferred from the core GaP to the outer Ga<sub>2</sub>O<sub>3</sub> layer. The fact that [111] oriented GaP nanowires present a direct band gap when the diameters are just few nanometers, and the oxide  $Ga_2O_3$  CBM is located at the  $\Gamma$  point, turns this nanostructured core-shell GaP/Ga2O3 system a potential structure for optical applications too.

In summary our calculations show that the band gap of GaP nanowires, besides to be enlarged with respect to the bulk indirect band gap, can be transformed to a direct band gap, when their diameters are in a range of few nanometers. According to our results this transformation to a direct band gap is mainly due to confinement effects and it occurs for nanowires aligned along the [111] direction. For [110] oriented nanowires the band gap is always indirect. The results also show that the formation of oxide layers on the surface of [111] oriented GaP nanowires is a stable process and it introduces a small conduction band offset due to the GaP/Ga<sub>2</sub>O<sub>3</sub> heterojunction, keeping direct band gap nanowires.

#### ACKNOWLEDGMENTS

This work was supported by the Brazilian agencies FAPEMIG, CAPES, and CNPq. We would like to thank Matheus P. Lima from Instituto de Física at Universidade de São Paulo for valuable discussions on self-interaction correction calculations.

- <sup>1</sup>M. Gudiksen, L. Lauhon, J. Wang, D. Smith, and C. Lieber, Nature (London) **415**, 617 (2002).
- <sup>2</sup>H. Yu, J. Li, R. A. Loomis, L.-W. Wang, and W. E. Buhro, Nature Mater. **2**, 517 (2003).
- <sup>3</sup>J. Bao, D. C. Bell, F. Capasso, J. B. Wagner, T. Martensson, J. Tragardh, and L. Samuelson, Nano Lett. **8**, 836 (2008).
- <sup>4</sup>C. Tang, S. Fan, M. L. de la Chapelle, H. Dang, and P. Li, Adv. Mater. (Weinheim, Ger.) **12**, 1346 (2000).
- <sup>5</sup>H. W. Seo, S. Y. Bae, J. Park, H. Yang, M. Kang, S. Kim, J. C. Park, and S. Y. Lee, Appl. Phys. Lett. **82**, 3752 (2003).
- <sup>6</sup>K. A. Dick, K. Deppert, M. W. Larsson, T. Martensson, W. Seifert, L. R. Wallenberg, and L. Samuelson, Nature Mater. 3, 380 (2004).
- <sup>7</sup>B. D. Liu, Y. Bando, C. C. Tang, D. Golberg, R. G. Xie, and T. Sekiguchi, Appl. Phys. Lett. **86**, 083107 (2005).
- <sup>8</sup>B. K. Kim, J. J. Kim, J.-O. Lee, K. J. Kong, H. J. Seo, and C. J. Lee, Phys. Rev. B **71**, 153313 (2005).
- <sup>9</sup>Z. Gu, M. P. Paranthaman, and Z. Pan, Cryst. Growth Des. 9, 525 (2009).
- <sup>10</sup>R. G. Humphreys, U. Rossler, and M. Cardona, Phys. Rev. B **18**, 5590 (1978).
- <sup>11</sup>B. Gil, M. Baj, J. Camassel, H. Mathieu, C. Benoit à la Guillaume, N. Mestres, and J. Pascual, Phys. Rev. B 29, 3398 (1984).
- <sup>12</sup>P. Grivickas, M. D. McCluskey, and Y. M. Gupta, Appl. Phys. Lett. 92, 142104 (2008).
- <sup>13</sup>T. M. Schmidt, R. H. Miwa, P. Venezuela, and A. Fazzio, Phys. Rev. B 72, 193404 (2005).
- <sup>14</sup>Z. Ikonić, G. P. Srivastava, and J. C. Inkson, Phys. Rev. B 48, 17181 (1993).
- <sup>15</sup>R. E. Algra, M. A. Verheijen, M. T. Borgström, L. F. Feiner, G. Immink, W. J. P. van Enckevort, E. Vlieg, and E. P. A. M. Bakkers, Nature (London) **456**, 369 (2008).
- <sup>16</sup>B.-K. Kim, H. Oh, E.-K. Jeon, S.-R. Kim, J.-R. Kim, J.-J. Kim, J.-O. Lee, and C. J. Lee, Appl. Phys. A: Mater. Sci. Process. 85, 255 (2006).
- <sup>17</sup>B. D. Liu, Y. Bando, C. C. Tang, and F. F. Xu, Appl. Phys. A: Mater. Sci. Process. 80, 1585 (2005).
- <sup>18</sup>W. S. Shi, Y. F. Zheng, N. Wang, C. S. Lee, and S. T. Lee, J. Vac. Sci. Technol. B **19**, 1115 (2001).
- <sup>19</sup>S. Gao, Y. Zhu, and X. Tian, Inorg. Chem. **42**, 5442 (2003).
- <sup>20</sup>M. Mattila, T. Hakkarainen, H. Lipsanen, H. Jiang, and E. I. Kauppinen, Appl. Phys. Lett. **90**, 033101 (2007).
- <sup>21</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- <sup>22</sup>N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
- <sup>23</sup>L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982).
- <sup>24</sup>J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002).
- <sup>25</sup>A. Höglund, C. W. M. Castleton, and S. Mirbt, Phys. Rev. B 72, 195213 (2005).
- <sup>26</sup>H. He, R. Orlando, M. A. Blanco, R. Pandey, E. Amzallag, I. Baraille, and M. Rérat, Phys. Rev. B **74**, 195123 (2006).
- <sup>27</sup>A. Filippetti and N. A. Spaldin, Phys. Rev. B 67, 125109 (2003).
- <sup>28</sup>T. M. Schmidt, Appl. Phys. Lett. **89**, 123117 (2006).
- <sup>29</sup>S. Geller, J. Chem. Phys. 33, 676 (1960).