



# Ab initio calculation of effective work functions for a TiN/HfO(2)/SiO(2)/Si transistor stack

Pierre-Yves Prodhomme, Fabien Fontaine-Vive, Abram Van Der Geest,  
Philippe Blaise, Jacky Even

## ► To cite this version:

Pierre-Yves Prodhomme, Fabien Fontaine-Vive, Abram Van Der Geest, Philippe Blaise, Jacky Even. Ab initio calculation of effective work functions for a TiN/HfO(2)/SiO(2)/Si transistor stack. Applied Physics Letters, American Institute of Physics, 2011, 99, pp.022101. <10.1063/1.3609869>. <hal-00662689>

**HAL Id: hal-00662689**

**<https://hal.archives-ouvertes.fr/hal-00662689>**

Submitted on 25 Jan 2012

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Ab initio calculation of effective work functions for a TiN/HfO<sub>2</sub>/SiO<sub>2</sub>/Si transistor stack

Pierre-Yves Prodhomme, Fabien Fontaine-Vive, Abram Van Der Geest, Philippe Blaise, and Jacky Even

Citation: *Appl. Phys. Lett.* **99**, 022101 (2011); doi: 10.1063/1.3609869

View online: <http://dx.doi.org/10.1063/1.3609869>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v99/i2>

Published by the [American Institute of Physics](#).

---

### Related Articles

One-shot spectrometer for several elements using an integrated conical crystal analyzer  
*Rev. Sci. Instrum.* **83**, 013112 (2012)

Analyzing a two-step polarization process in a pentacene/poly(vinylidene fluoride - trifluoroethylene) double-layer device using Maxwell-Wagner model  
*J. Appl. Phys.* **111**, 023706 (2012)

Micro-imprinted prism substrate for self-aligned short channel organic transistors on a flexible substrate  
*Appl. Phys. Lett.* **100**, 043301 (2012)

Micro-imprinted prism substrate for self-aligned short channel organic transistors on a flexible substrate  
*APL: Org. Electron. Photonics* **5**, 24 (2012)

Effect of channel widths on negative shift of threshold voltage, including stress-induced hump phenomenon in InGaZnO thin-film transistors under high-gate and drain bias stress  
*Appl. Phys. Lett.* **100**, 043503 (2012)

---

### Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: [http://apl.aip.org/about/about\\_the\\_journal](http://apl.aip.org/about/about_the_journal)

Top downloads: [http://apl.aip.org/features/most\\_downloaded](http://apl.aip.org/features/most_downloaded)

Information for Authors: <http://apl.aip.org/authors>

### ADVERTISEMENT

**AIPAdvances**

*Submit Now*

**Explore AIP's new  
open-access journal**

- **Article-level metrics  
now available**
- **Join the conversation!  
Rate & comment on articles**

## Ab initio calculation of effective work functions for a TiN/HfO<sub>2</sub>/SiO<sub>2</sub>/Si transistor stack

Pierre-Yves Prodhomme,<sup>1,2,a)</sup> Fabien Fontaine-Vive,<sup>1</sup> Abram Van Der Geest,<sup>1</sup> Philippe Blaise,<sup>1</sup> and Jacky Even<sup>2</sup>

<sup>1</sup>CEA-LETI, MINATEC Campus, 17 rue des Martyrs, 38054 Grenoble, France

<sup>2</sup>FOTON-INSA Laboratory, UMR 6082 au CNRS, INSA de Rennes, 20 Avenue des Buttes de Cosmes, CS 14315, 35043 Rennes Cedex, France

(Received 5 February 2011; accepted 21 June 2011; published online 11 July 2011)

*Ab initio* techniques are used to calculate the effective work function ( $W_{\text{eff}}$ ) of a TiN/HfO<sub>2</sub>/SiO<sub>2</sub>/Si stack representing a metal-oxide-semiconductor (MOS) transistor gate taking into account first order many body effects. The required band offsets were calculated at each interface varying its composition. Finally, the transitivity of local density approximation (LDA) calculated bulk band lineups were used and completed by many body perturbation theory (MBPT) bulk corrections for the terminating materials (Si and TiN) of the MOS stack. With these corrections the *ab initio* calculations predict a  $W_{\text{eff}}$  of a TiN metal gate on HfO<sub>2</sub> to be close to 5.0 eV. © 2011 American Institute of Physics. [doi:10.1063/1.3609869]

Reducing the scale of the metal-oxide-semiconductor (MOS) transistor has led the semiconductor industry to major changes in the MOS stack. First, the SiO<sub>2</sub> oxide has been replaced by a HfO<sub>2</sub> layer on top of a SiO<sub>2</sub> thin film, while TiN is a leading candidate to replace poly-silicon in the gate for the next generation of MOS transistor (22 nm and sub-22 nm). However, the control of the threshold voltage remains one of the major issues. The effective work function ( $W_{\text{eff}}$ ) of a metal in a MOS structure is one of the key properties governing this threshold voltage. The aim of this paper is to construct a milestone for the comparison between an ideal system and available experimental data.

During electrical capacitance-voltage (C-V) measurements,  $W_{\text{eff}}$  is usually estimated through:

$$W_{\text{eff}} = \phi_{\text{ms}} + \chi(\text{Si}) + \zeta(\text{Si}). \quad (1)$$

Here,  $\chi(\text{Si})$  is the electronic affinity of silicon,  $\zeta(\text{Si})$  is the difference between the conduction band and the Fermi energy of doped silicon, and  $\phi_{\text{ms}}$  is the difference between the metal Fermi energy and the semiconductor Fermi energy.  $\phi_{\text{ms}}$  is extracted from the flat-band voltage through modeling of the defect's charge distribution along the oxide.<sup>1</sup>

The valence band offset (VBO) between the metal and the semiconductor ( $\text{VBO}_{\text{ms}}$ ) is related to  $\phi_{\text{ms}}$  through  $\text{VBO}_{\text{ms}} + E_g(\text{Si}) = \phi_{\text{ms}} + \zeta(\text{Si})$ , where  $E_g(\text{Si})$  (1.1 eV) is the electronic gap of silicon. Combining this relation with Eq. (1) and considering the well-accepted value of  $\chi(\text{Si})$  (4.1 eV), the *ab initio*  $W_{\text{eff}}$  of a given metal can be evaluated through the equation

$$W_{\text{eff}}^{\text{ab initio}} = \text{VBO}_{\text{ms}}^{\text{ab initio}} + \chi(\text{Si}) + E_g(\text{Si}). \quad (2)$$

Then, one realizes that the *ab initio* quantity of primary importance is  $\text{VBO}_{\text{ms}}$ .

Evaluating the  $\text{VBO}_{\text{ms}}$  from first principles calculations is a challenge. On the one hand, the recent introduction of hafnium oxide requires the accurate treatment of the com-

plex chemistry of the interfaces. On the other hand, in order to reach a sufficient precision on electronic energies ( $\pm 0.1$  eV), one needs to compute the eigenvalues in many body perturbation theory (MBPT). However, this is out of reach for the treatment of a complete MOS stack within the GW approximation (GWA, where G stands for the Green's function and W for the screened potential). Fortunately, the interface's potential drop can be well estimated within the density functional theory (DFT) (Ref. 2) and coupled with the GW eigenvalues for the valence band states calculated only for each bulk material. These eigenvalues are calculated in reference to the electrostatic potential average<sup>3</sup> of each bulk. This reference potential is then aligned with the potential drop at the interface producing the band offset.<sup>2</sup> This technique is generally applicable for a sufficient material thickness (1 to 2 nm thickness for each slab) such that each material approaches a bulk state away from the interface.

In this manner, the first order implementation of GWA, called  $G_0W_0$ , has been applied to correct the band alignments along III-V heterojunctions. These corrections slightly improved the DFT results in the local density approximation (LDA), which were already in pretty good agreement with experiments.<sup>4,5</sup> Recently, this *ab initio* method has been applied to assess the band alignment at a junction between an oxide (SiO<sub>2</sub>, ZrO<sub>2</sub> or HfO<sub>2</sub>) and a semiconductor (Si) resulting in a close agreement with experiment unlike the LDA results.<sup>2,6</sup> In this paper, we use the same approach for each interface of a complete TiN/HfO<sub>2</sub>/SiO<sub>2</sub>/Si stack.

The potential drops at each of the interfaces have been computed within DFT/LDA using the atomic orbital SIESTA software,<sup>7</sup> whereas the GWA computations have been carried out with the plane-waves ABINIT software.<sup>8</sup> To be consistent, identical Troullier-Martins pseudopotentials<sup>9</sup> for each atomic species have been used for Abinit and Siesta and were generated using the Fhi98pp and Atom programs<sup>7,10</sup> in the LDA.<sup>11</sup> Siesta calculations have been performed using a polarized double zeta, Polarized Double-Zeta (DZP) basis with an energy shift of 50 meV and a Meshcutoff of at least 100 Hartrees. A simulated anneal has also been carried out within

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: p.prodhomme@fkf.mpg.de.

Siesta as an heuristic method to relax the forces for each stack: from 1000 K to 100 K in 1 ps, followed by a conjugated gradient method to reduce the forces to less than 0.07 eV/Å.

All GWA calculations were performed at the  $G_0W_0$  level. The quasiparticles energies were carefully converged with respect to the energy cut-offs, the number of k-points in the Brillouin zone, and the number of bands used to compute the dielectric function and the self-energy. Thus, a numerical accuracy of  $\pm 0.1$  eV on the quasiparticles energies was reached. The Plasmon-Pole model proposed by Godby and Needs<sup>12</sup> was used to describe the dynamic dependence of the “screening” function.

Two types of Si/SiO<sub>2</sub> interfaces have each been simulated, one oxygen poor and one oxygen rich. These supercells contained a 22.2 Å long slab of  $\beta$ -cristobalite SiO<sub>2</sub> and a 24.3 Å long slab of diamond Si, both oriented with the (001) plane at the interface. The latter slab was compressed by 3% in the [100] and [010] directions. The simulated LDA value of the  $VBO_1^{LDA}$  is +3.0 eV (+2.8 eV) for the oxygen rich (poor) interface using the sign convention, where  $VBO > 0$  when the valence band maximum (VBM) of the material on the left is above the VBM of the material on the right. The  $G_0W_0$  corrections to the VBMs computed for each material are  $\delta\epsilon_v^{GW-LDA}(Si) = -0.6$  eV and  $\delta\epsilon_v^{GW-LDA}(SiO_2) = -1.9$  eV, which lead to a  $VBO_1^{GW}$  of  $+4.2 \pm 0.1$  eV. These results are in good agreement with the results published by Shaltaf *et al.*<sup>2</sup> (4.1 eV calculated within GWA starting from Generalized Gradient Approximation (GGA) electronic structures), and a little lower than experimental data ranging from 4.3 eV to 4.5 eV estimated by X-ray photoelectron spectroscopy (XRD).<sup>13,14</sup>

The SiO<sub>2</sub>/HfO<sub>2</sub> interface is the second interface of the complete stack (Figure 1) considered here. The HfO<sub>2</sub> slab was simulated in its monoclinic structure with  $P2_1/c$  symme-

try, which is its stablest phase at ambient pressure and temperature<sup>15,16</sup> with the (001) plane at the interface. The SiO<sub>2</sub> slab was again  $\beta$ -cristobalite and oriented with the (001) plane at the interface. The HfO<sub>2</sub> was stretched by 3.7% in the [100] direction and by 2.1% in the [010] direction to match the  $5.23 \times 5.23$  Å<sup>2</sup> square interface of the SiO<sub>2</sub>, which agrees with the other simulations in literature of SiO<sub>2</sub> in the stack.<sup>2,17</sup> The supercell contained seven HfO<sub>2</sub> layers and ten SiO<sub>2</sub> tetrahedron. At the interface after relaxation, 3 oxygens were each three times coordinated with both Si and Hf. The potential along the stack shown in Figure 1 exhibits a large potential drop of 5.2 eV, which is expected since the electric permittivity and the average valence electronic density are much higher in hafnia than in silica. At the LDA level, the  $VBO_2^{LDA}$  is +0.4 eV, which is qualitatively wrong with respect to XPS measurements,<sup>13</sup> i.e., the VBM of SiO<sub>2</sub> is measured below the VBM of HfO<sub>2</sub>. Some DFT calculations of the HfO<sub>2</sub>/SiO<sub>2</sub> interface at the LDA level have also been performed by Sharia *et al.* showing that the valence band offset is highly dependent on the interface stoichiometry.<sup>17</sup> Using our  $G_0W_0$  correction for SiO<sub>2</sub> (−1.9 eV) and for HfO<sub>2</sub> (−0.5 eV close to the value of Grüning *et al.*<sup>6</sup> of −0.4 eV), the LDA band offset is reversed producing a  $VBO_2^{GW}$  of −1.0 eV. This is qualitatively and quantitatively in good agreement with XPS measurements<sup>13</sup> of  $1.05 \pm 0.1$  eV.

The TiN/HfO<sub>2</sub> interface is the final interface of the stack. Constructing this interface requires a specific procedure because of the large lattice mismatch. First, a slab of 6 layers of monoclinic HfO<sub>2</sub> surrounded by vacuum oriented in the direction perpendicular to the (001) plane containing three unit cells in the [100] direction and one unit cell in the [010] direction was generated. During molecular dynamic simulations, several TiN layers were successively added to the surface. We found that the positions of the interfacial

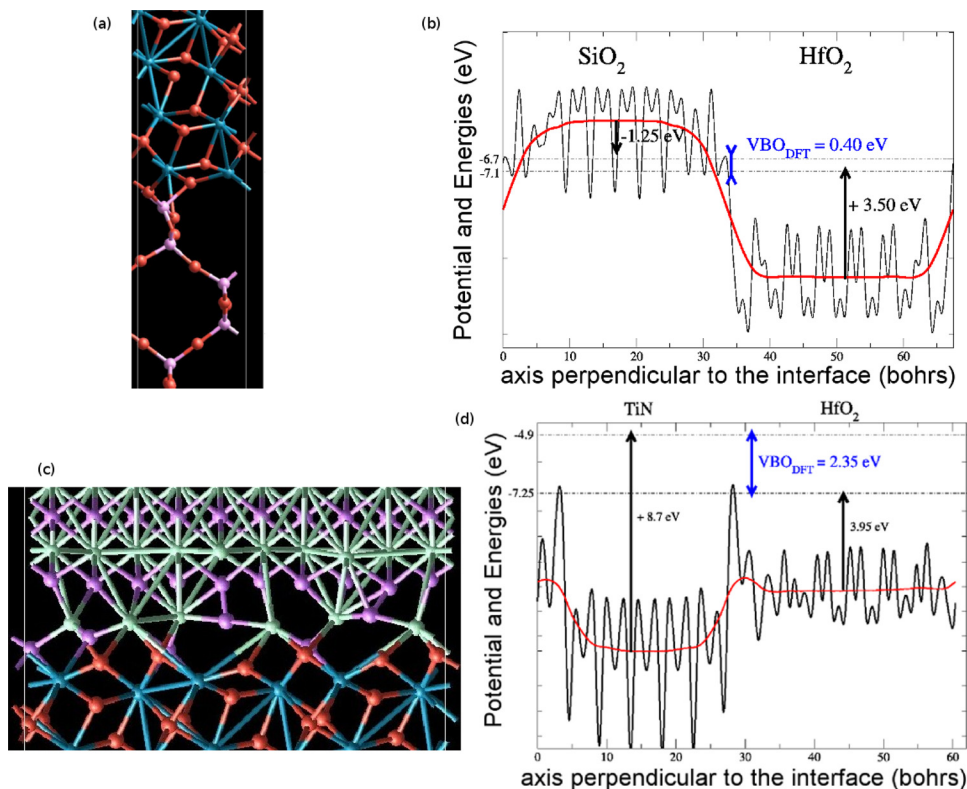


FIG. 1. (Color online) O rich SiO<sub>2</sub>/HfO<sub>2</sub> interface (a) and nitridized TiN/HfO<sub>2</sub> interface (c): N in purple, Ti in turquoise, Hf in blue, Si in pink, and O in red. Potential projected along the HfO<sub>2</sub>/SiO<sub>2</sub> (b) and the TiN/HfO<sub>2</sub> (d) superlattices (black line) and smoothed by a double convolution (red line). The black arrows indicate the shifts of the eigenenergies with respect to the averaged potential in the bulk. The blue arrow indicates the  $VBO^{LDA}$ .



TABLE I. Valence band (VBO) and conduction band (CBO) offsets with the resulting effective work function. The sign of the band offset is positive when the VBM of the material on the left is above the VBM of the material on the right.

Interfaces	Si/SiO <sub>2</sub>		SiO <sub>2</sub> /HfO <sub>2</sub>	HfO <sub>2</sub> /TiN		Si/TiN	W <sub>eff</sub> (TiN)
	O rich	O poor		Nitridized	Oxidized		
VBO(LDA)	+3.0	+2.8	+0.4	-2.4	-2.5	[+0.7, +1.0]	[5.9, 6.2]
VBO(G <sub>0</sub> W <sub>0</sub> )	+4.3	+4.1	-1.0	-3.3	-3.4	[-0.3, 0.0]	[4.9, 5.2]
CBO(G <sub>0</sub> W <sub>0</sub> )	-3.2	-3.4	+1.6	+2.7	+2.6	[+0.8, +1.1]	

atoms from TiN were influenced by the underlying HfO<sub>2</sub> slab arranging themselves in almost the same structure as the oxide (at  $\pm 0.3$  Å of the atom sites). Thanks to this observation, when we constructed our TiN/HfO<sub>2</sub> stack model, the Ti atoms at the interface were placed in the sites of the hafnium and the nitrogens in the oxygen sites. The stack was finalized by adding a face-centered-cubic TiN slab oriented with the (111) surface plane on top of the interfacial TiN layer, which minimizes the mismatch between the slabs. Indeed, it has been pointed out experimentally that the (111) growth direction lowers the film strain.<sup>18,19</sup> In our case, the TiN is 1.8% stretched out in the  $[1\bar{1}0]$  direction and 0.5% compressed in the  $[11\bar{2}]$  direction and contained 6 TiN layers expanded by 1% in the  $[111]$  direction in order to keep the average electronic density of the TiN bulk. Two types of interfaces were computed: one “nitridized” with oxygen sites of HfO<sub>2</sub> substituted by N at the interface (Figure 1), the second “oxidized,” with six O replacing the six N at the interface. The VBO<sub>3</sub><sup>LDA</sup> obtained for these two interfaces are -2.4 eV (Figure 1) and -2.5 eV, respectively. Previous DFT calculations have been done on TiN/HfO<sub>2</sub> stacks but cannot be compared with ours since they were computed in the generalized gradient approximation.<sup>20</sup> The quasiparticle correction to the LDA Fermi energy of TiN was calculated to be  $\delta\epsilon_v^{GW-LDA}(TiN) = +0.4$  eV.

The valence band alignments along the whole stack at the LDA and G<sub>0</sub>W<sub>0</sub> levels where

$$VBO_{ms} = VBO_1 + VBO_2 + VBO_3 \quad (3)$$

are depicted in Table I. Also included in Table I are the conduction band alignments calculated by using our G<sub>0</sub>W<sub>0</sub> band gaps for Si (1.1 eV), SiO<sub>2</sub> (8.6 eV), and HfO<sub>2</sub> (6.0 eV). The VBO<sub>ms</sub><sup>LDA</sup> ranges between -1.0 eV and -0.7 eV depending on the chemistry of the interfaces which would correspond to a work function of between 6.2 eV and 5.9 eV. This is in qualitative disagreement with the experimental W<sub>eff</sub> which is usually equal to or below 5 eV. It is worthy of note that in order to calculate the VBO between the two materials on the extremities of the stack one only needs to compute the GW energies for the top and the bottom slabs because for the intermediate slabs the corrections vanish yielding,

$$VBO_{ms}^{GW} = VBO_{ms}^{LDA} + \delta\epsilon_v^{GW-LDA}(Si) + \delta\epsilon_v^{GW-LDA}(TiN). \quad (4)$$

VBO<sub>ms</sub><sup>GW</sup> ranges from 0.0 eV to 0.3 eV depending on the chemistry of the interfaces, and one finally obtains an *ab initio* W<sub>eff</sub> evaluated in the MBPT framework ranging from 5.2 eV to 4.9 eV (i.e., P+ in jargon of the semiconductors industry). The W<sub>eff</sub> for (111) oriented TiN is in agreement with those measured during cold growth process which mostly does not

modify the TiN stoichiometry.<sup>1,21</sup> We also point out that the GW corrections applied with a coherent methodology are mandatory in order to obtain qualitatively correct results for the evaluations of VBOs and W<sub>eff</sub> in a MOS stack.

We think that our results can be used to adjust the parameters of the model used to simulate the whole MOS device. Second, by comparing our “ideal” model system (no defects and a perfect stoichiometry) with the dispersion of the experimental values (from 4.2 to 4.9 eV) assessed by C-V measurements,<sup>1,22</sup> we think that our values can be used as a reference to study the impact of the fine chemistry in such a gate stack. Finally, in this paper, we show that the W<sub>eff</sub> is an accessible and reliable *ab initio* quantity and that this type of calculation is promising to help the understanding of the W<sub>eff</sub> for nanodevices in microelectronics.

<sup>1</sup>A. Kuriyama, O. Faynot, L. Brevard, A. Tozzo, L. Clerc, S. Deleonibus, J. Mitard, V. Vidal, S. Cristoloveanu, and H. Iwai, *Solid-State Device Research Conference, 2006. Proceeding of the 36th European ESSDERC 2006*, (2006), pp. 109–112, ISSN 1930-8876.

<sup>2</sup>R. Shaltaf, G.-M. Rignanese, X. Gonze, F. Giustino, and A. Pasquarello, *Phys. Rev. Lett.* **100**, 186401 (2008).

<sup>3</sup>J. Junquera, M. H. Cohen, and K. M. Rabe, *J. Phys.: Condens. Matter* **19**, 213203 (2007).

<sup>4</sup>S. Zhang, M. L. Cohen, S. G. Louie, D. Tomanek, and M. S. Hybertsen, *Phys. Rev. B* **41**, 10058 (1990).

<sup>5</sup>C. G. Van de Walle and R. M. Martin, *Phys. Rev. B* **34**, 5621 (1986).

<sup>6</sup>M. Grüning, R. Shaltaf, and G.-M. Rignanese, *Phys. Rev. B* **81**, 035330 (2010).

<sup>7</sup>J. Soler, O. Artacho, J. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).

<sup>8</sup>X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Cote, T. Deutsch, L. Genovese, Ph. Ghosez, M. Giantomassi, S. Goedecker, D. R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. J. T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. J. Verstraete, G. Zerah, and J. W. Zwanziger, *Computer Phys. Commun.* **180**, 2582-2615 (2009).

<sup>9</sup>N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).

<sup>10</sup>M. Fuchs and M. Scheffler, *Comput. Phys. Commun.* **119**, 67 (1999).

<sup>11</sup>D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).

<sup>12</sup>R. W. Godby and R. J. Needs, *Phys. Rev. Lett.* **62**, 1169 (1989).

<sup>13</sup>S. Sayan, E. Garfunkel, and S. Suzer, *Appl. Phys. Lett.* **80**, 2135 (2002).

<sup>14</sup>J. L. Alay and M. Hirose, *J. Appl. Phys.* **81**, 1606 (1997).

<sup>15</sup>J. Leger, A. Atouf, P. Tomaszewski, and A. Pereira, *Phys. Rev. B* **48**, 93 (1993).

<sup>16</sup>J. Lowther, J. dewhurst, J. Leger, and J. Haines, *Phys. Rev. B* **60**, 14485 (1999).

<sup>17</sup>O. Sharia, A. A. Demkov, G. Bersuker, and B. H. Lee, *Phys. Rev. B* **75**, 035306 (2007).

<sup>18</sup>U. C. Oh and J. H. Je, *J. Appl. Phys.* **74**, 1692 (1993).

<sup>19</sup>J. H. Je, D. Y. Noh, H. K. Kim, and K. S. Liang, *J. Appl. Phys.* **81**, 6126 (1997).

<sup>20</sup>L. R. C. Fonseca and A. A. Knizhnik, *Phys. Rev. B* **74**, 195304 (2006).

<sup>21</sup>L. Wu, H. Y. Yu, X. Li, K. L. Pey, J. S. Pan, J. W. Chai, Y. S. Chiu, C. T. Lin, J. H. Xu, H. J. Wann, X. F. Yu, D. Y. Lee, K. Y. Hsu, and H. J. Tao, *Appl. Phys. Lett.* **96**, 113510 (2010).

<sup>22</sup>M. Charbonnier, C. Leroux, V. Cosnier, P. Besson, E. Martinez, N. Benedetto, C. Licitra, N. Rochat, C. Gaumer, K. Kaja, G. Ghibaudo, F. Martin, and G. Reimbold, *IEEE Trans. Electron Devices* **57**, 1809 (2010).