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Full Length Research Paper

First principles study of the relative stability and electronic properties of the VN/GaN/VN interlayer

Miguel Espitia J. R.[1]*, Jonh Díaz F.[1] and César Ortega L.[2]

[1]Grupo GEFEM, Universidad Distrital Francisco José de Caldas, Bogotá, Colombia.
[2]Grupo Avanzado de Materiales y Sistemas Complejos GAMASCO, Departamento de Física, Universidad de Córdoba, Montería Colombia.

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Using first principles total-energy calculations within the framework of density functional theory, the relative stability and the structural and electronic properties of a VN/GaN/VN interlayer in sodium chloride (NaCl), cesium chloride (CsCl), nickel arsenide (NiAs), zinc-blende, and wurtzite structures were studied. The calculations were carried out using a method based on pseudopotential, employed exactly as implemented in Quantum-ESPRESSO code. From total energy minimization, it was found out that the global energy minimum of VN/GaN/VN is obtained for the wurtzite structure. Additionally, at high pressure, our calculations show the possibility of phase transition from the wurtzite to the NaCl structure. For the wurtzite phase, the density of states analyses revealed that the interlayer exhibits a half-metallic behavior with a magnetic moment of 2.0 μ_β/V-atom. This property essentially comes from the polarization of states V-d and N-p crossing of the Fermi level. Due this property, the interlayer can potentially be used in the field of spintronics as spin injectors.

Key words: Density functional theory (DFT), interlayers, structural and electronic properties.

INTRODUCTION

The group III nitrides such as gallium nitride (GaN) have been the subject of many intense investigations in the last years. This interest is partly motivated by their promising applications for optical devices (Nakamura, 1997) and in high-voltage, high-power, and high-temperature microwave applications (Wagner and Bechstedt, 2002; Nakamura et al., 1994). They are wide-band-gap semiconductors and are used for short-wavelength electroluminescent devices. Additionally, heterostructures based on the surface growth of oxides on GaN are used in various applications, such as high-efficiency blue and green light-emitting devices, ultraviolet light-emitting diodes, metal-oxide-semiconductor field-effect transistors and field-effect transistors (Binari et al., 1997; Ping et al., 1998; Dang et al., 1999). Recently, pioneering theoretical research carried out by Espitia et al. (2015a) has shown that graphene on the GaN(0001) surface is stable and the Dirac cones remain intact.

The ground state of GaN is the wurtzite structure. However, depending on the substrate and the growth

*Corresponding author. E-mail: mespitiar@udistrital.edu.co.

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conditions, a zinc-blende phase can be formed (Yeh et al., 1992). The difference in total energy between the zinc-blende and wurtzite structures is very small (~10 meV/atom), which explains why the two structures can be obtained experimentally. Additionally, this last year, there has been a great deal of interest in developing new and improved ultrahard materials using the group III nitrides and a metal transition ion. Experimental studies show that these superhard compounds can be grown; for example, a TiN/GaN multilayer was grown via reactive pulsed laser deposition (Rawat and Sands, 2006), while the AlN/VN superlattice was grown via reactive sputtering (Kim et al., 2001). On the other hand, the combination of the semiconductor properties of GaN and the magnetic properties of the transition metal ions is of great current interest, because of their potential applications in diluted magnetic semiconductors (DMS) (Yao et al., 2012; Sato et al., 2013; Cudris et al., 2016). The study of such ultrahard structures or those with magnetic properties is clearly of high technological relevance, but it is also fundamentally interesting with regard to understanding the mechanisms responsible for the extreme hardness and the magnetic properties. Achieving super hardness or specific magnetic properties involves the ability to deliberately create stable and metastable structures according to one's desire on an atomic level. The realization of this objective is becoming increasingly achievable due to advancement in experimental techniques as well as to theoretical methods that are able to reliably predict the relative stability and the atomic and electronic properties of increasingly complex structures.

For this reason, in this paper, a detailed theoretical calculation of the structural and electronic properties of VN/GaN/VN was reported in order to determine the energetically most favorable structure. To his end, the results of the calculated structural and magnetic properties in the wurtzite, zinc-blende, rock-salt, cesium chloride (CsCl), and nickel arsenide (NiAs) structures at zero temperature were presented.

The organization of the paper is as follows: section 2 presents a description of the pseudopotential method used, with some computational details. Section 3 presents the calculated results, with discussion of the structural properties. The transition phase was studied and the energy formation was calculated, and for the most stable structure, the energetically most favorable magnetic phase was calculated. Finally, the electronic properties of the wurtzite structure were studied. In section 4, some conclusions were drawn.

COMPUTATIONAL METHODS

The calculations were performed within the density functional theory (DFT) framework using the Quantum-ESPRESSO package (Giannozzi et al., 2009). The correlation and exchange effects of the electrons were treated using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) (Perdew et al., 1996). Electron–ion interactions were treated with the pseudopotential method (Vanderbilt, 1990; Laasonen et al., 1993). The electron wave functions were expanded into plane waves with a kinetic-energy cutoff of 40 Ry. For the charge density, a kinetic energy cutoff of 400 Ry was used. A 6 × 6 × 4 Monkhorst-Pack mesh (Monkhorst and Pack, 1976) was used to generate the k-points in the unit cell. The calculations were performed taking into account the spin polarization.

To calculate the lattice constant, the minimum volume, the bulk modulus, and the cohesive energy of the two structures studied, calculations were adjusted to the Murnaghan equation of state (Murnaghan, 1944):

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left[\frac{\left(V_0/V\right)^{B'}}{B_0'-1} + 1\right] - \frac{B_0 V_0}{B_0'-1} \quad (1)$$

where B_0 is the bulk modulus, its first derivative is B'_0, V_0 is the equilibrium volume of the cell, and E_0 represents the cohesive energy.

The electronic configurations used in the present calculations are [Ar] $3d^{10}4s^24p^1$ for the Ga, [Ar]$3d^34s^2$ for the V, and [He] $2s^22p^3$ for the N. In each of the five phases, the interlayer is modeled as sandwiching two layers of GaN between two layers VN.

RESULTS AND DISCUSSION

Structural properties

To determine the structural properties in the ground state, such as the lattice constant (a), the bulk modulus (B_0), the c/a ratio, and the total energy (E_0) of the VN/GaN/VN interlayer in the CsCl, NaCl, NiAs, zinc-blende, and wurtzite structures, the total energy was calculated as a function of the volume, and the results were fit to the Murnaghan equation of state. Figure 1 shows the energy-volume curves.

In Figure 1, it can be noted that the five structures considered in this study are metastable, because in each of the energy-volume curves there is a minimum energy value. In Figure 1, one can clearly see that the wurtzite phase is the energetically most favorable structure, because it has the lowest minimum energy value. Additionally, we can see that the curve corresponding to the wurtzite phase crosses the curve of the NaCl structure of smallest equilibrium volume. This indicates a high-pressure phase transition from the wurtzite to the NaCl structure. To analyze the phase transformation under high pressure, we used the Gibbs free energy, given by Mujica et al. (2003): $G = U + PV - TS$; where U is the internal energy, P is the pressure, V is the volume, T is the temperature, and S is the entropy. Since the calculations are in ground state (T = 0 degree K), the last term of the Gibbs energy can be neglected, and by working with the enthalpy, the Gibbs free energy reduces to $H = U + PV$ (Mancera et al., 2004; Espitia et al., 2015b). This equation was used for the five crystal structures considered in this paper; however, the possible existence of other stable or metastable structures for a VN/GaN/VN interlayer cannot be excluded.

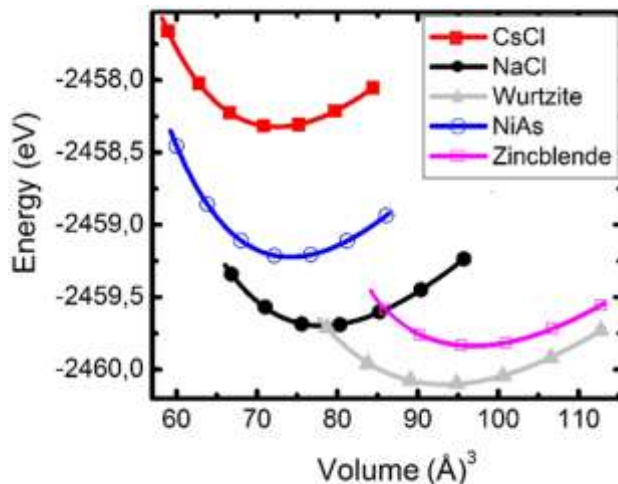

Figure 1. Total energy as a function of unit-cell volume for the CsCl, NaCl, wurtzite, NiAs, and zinc-blende structures of VN/GaN/V interlayer.

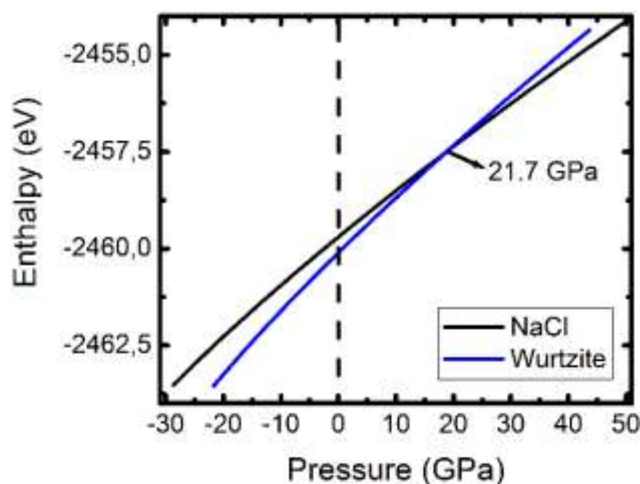

Figure 2. Enthalpy as a function of pressure in the NaCl and wurtzite phases of VN/GaN/VN interlayer.

Figure 2 shows enthalpy as a function of pressure for the NaCl and wurtzite phases. It was noted that the compound will transform from a wurtzite structure to NaCl at a transition pressure P_T = 21.7 GPa. Note that before the transition ($P < P_T$), the lowest values of enthalpy correspond to the wurtzite phase. This shows the relative stability of the wurtzite phase within this pressure range, while for higher values of the transition pressure ($P > P_T$), the NaCl phase has the lowest values of enthalpy. Therefore, within this pressure range, NaCl is the most stable phase. At the transition pressure, the enthalpies of both structures are equal. Across the transition, there is a volume reduction of about 14.3%, from 92.122 Å^3 to 78.07 Å^3. Similar transitions, from the wurtzite to the NaCl structures, have been observed experimentally and predicted theoretically for GaN (Arbouche et al., 2009; Perlin et al., 1992), and they have been theoretically predicted in other compounds (López et al., 2008; Báez et al., 2013).

The lattice constant a_0, the c/a value, the bulk modulus (B_0), and the total energy (E_0) of the binary compounds GaN and VN calculated in the ground state, wurtzite for GaN and NaCl for VN, are shown in Table 1, while Table 2 shows the structural parameters of VN/GaN/VN calculated in the phases CsCl, NaCl, NiAs, wurtzite, and zinc-blende.

Table 1 compares the experimental and theoretical data available from the literature. We can see that the

Table 1. Lattice constant, c/a ratio, bulk modulus, and total energy of the binary compounds GaN and VN.

Compound	Phase	a_0 (Å)	c/a	B_0 (GPa)	E_0 (eV)
GaN	Wurtzite	3.205	1.64	175.33	-2513.12
		3.22[a]	1.634[a]	176.54[a]	
		3.19[b]	-	188[b]	
VN	NaCl	4.10	-	228	-2409.48
		4.06[c]	-	233[d]	
		4.14[e]	-	-	

[a]Theoretical Reference (Arbouche et al., 2009), [b]Experimental Reference (Shultz and Thiemann, 1977), [c]Theoretical Reference (Stampfl and Freeman, 2012), [d]Experimental Reference (Stampfl et al., 2001). [e]Theoretical Reference (Carlson et al., 1986).

Table 2. Lattice constant, c/a ratio, equilibrium volume, bulk modulus, total energy, and magnetic moment per cell of the VN/GaN/VN interlayer.

Phase	a_0 (Å)	c/a	V_0 (Å^3)	B_0 (GPa)	E_0 (eV)
CsCl	2.648	-	72.120	228.060	-2458.323
NaCl	2.923	1.414	78.070	211.794	-2459.697
NiAs	2.864	1.81	74.157	247.487	-2459.622
Wurtzite	3.193	1.64	92.122	161.746	-2460.201
Zinc-blende	4.505	-	96.966	177.940	-2460.035

equilibrium lattice constant a_0 of the binary compounds GaN and VN calculated in this paper is in very good agreement with theoretical references (Arbouche et al., 2009; Stampfl and Freeman, 2012; Carlson et al., 1986) and experimental references (Shultz and Thiemann, 1977; Stampfl et al., 2001), since it differs by less than one percent. On other the hand, despite the difference between the crystal structures wurtzite, GaN, and NaCl VN, experimental and theoretical studies show that the GaN:V system can be grown. Souissi et al. (2005) report on the vanadium doping of a GaN layer grown using the metal-organic vapor phase epitaxy technique (MOVPE), and González et al. (2007) studied the structural properties of $Ga_{1-x}V_xN$ using DFT.

In Table 2, it can see be seen that the phase with the lowest value of energy corresponds to the wurtzite structure. Additionally, it can see also been seen that the values of the bulk modules of the VN/GaN/VN interlayer are higher, which confirms that they are quite rigid, making them good candidates for possible applications in devices operated at high temperature and high power, as well as in hard coatings.

In order to verify the relative stability of the VN/GaN/VN interlayer with reference to the terminal phases, the corresponding formation energy was calculated, which is expressed as the difference between the total energy of the ternary VN/GaN/VN phases, $E_{VN/GaN/VN}^{phase}$ and the reference states of wurtzite GaN, $E_{GaN}^{wurtzite}$ and NaCl of VN, E_{VN}^{NaCl} (Zhang and Veprek; Vargas-Hernández et al., 2015; Ortega et al., 2016):

$$E_f = E_{VN/GaN/VN}^{phase} - xE_{GaN}^{wurtzita} - (1-x)\, E_{VN}^{NaCl}$$

For all interlayers x = 0.5, because there are the same number of molecules of GaN and VN. Table 3 shows the values of formation energy E_f calculated in each of the five phases considered in this study.

According to the results shown in Table 3, the smallest value of energy of formation that corresponds to the VN/GaN/VN interlayer is the wurtzite phase; therefore, it is the most energetically stable structure. This confirms the result obtained earlier. Additionally, the moderate formation energy values indicate that the compounds can easily be grown experimentally.

These results for the energy of formation are important, because knowing these values, growing conditions can be improved and therefore a VN/GaN/VN interlayer of excellent quality can be grown.

For the most stable phase, the wurtzite structure, the total energy variation as a function of the volume of the ferromagnetic (FM) and antiferromagnetic (AFM) phases were calculated in order to determine the most favorable magnetic phase of the interlayer. Figure 3 shows the energy-volume curve for the VN/GaN/VN interlayer in the wurtzite structure in the FM and AFM states. In the ground state, the total energy difference between the FM

Table 3. Formation energy.

Compound	Phase	E_f (eV)
VN/GaN/VN	CsCl	2.977
	NaCl	1.603
	NiAS	1.678
	Wurtzite	1.099
	Zinc-blende	1.265

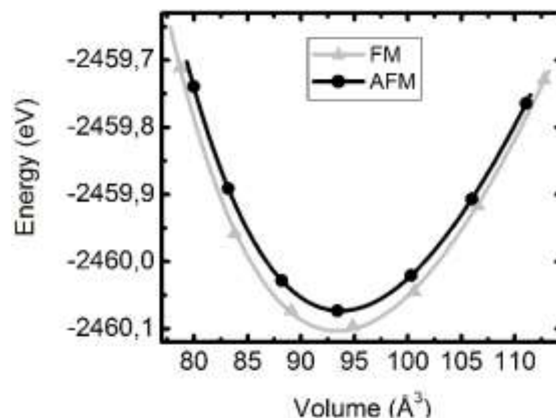

Figure 3. Total energy as a function of unit-cell volume for the wurtzite structures of VN/GaN/VN interlayer in the FM and AFM phases.

and AFM states ($\Delta E = E_{FM} - E_{AFM}$) was - 0.03 eV. The FM state was more energetically favorable than the AFM state.

Electronic properties

The theoretical lattice constants a_0 and the c/a ratio of the interlayer in the most energetically favorable phase, the wurtzite structure, shown in Table 1, were used to calculate the spin-polarized density of states (DOS) along the high-symmetry direction in the first Brillouin zone.

Figure 4 shows the total and partial spin-polarized density of states (TDOS and PDOS, respectively) of the VN/GaN/VN interlayer in the wurtzite structure. The TDOS results show that the interlayer is half-metallic and ferromagnetic. This result occurs because in the valence band near the Fermi level, the majority spins (spin-up) are metallic, and the minority spins (spin-down) are semiconductors. This interlayer has a spin polarization of 100% of the conduction carriers in the ground state, which is a requirement for spin injectors (Vargas-Hernández et al., 2015; Espitia et al., 2016). This finding suggests that the interlayer can be efficiently used as a spin injector. Figure 4 shows that in the valence band near the Fermi level, the spin-up density (the majority spins) is mainly dominated by the V-3d states and to a lesser extent by the N-2p states, which cross the Fermi level. The interlayer has a magnetic moment of 4 μ_β per supercell. Since there are two vanadium atoms in the supercell, this corresponds to 2 μ_β /V-atom. The magnetic moment is due to the V^{3+} configuration (with electronic configuration $[Ar]3d^2$). This implies that when the V atom is in the interlayer, it gives up three electrons, and two valence electrons remain (d^2 configuration). These valence electrons couple ferromagnetically, and as a result the two electrons produce a total magnetic moment of 2 μ_β/atom-V. Touati et al. (2008) reported a valence of V^{3+} for infrared luminescence in V-doped GaN samples grown with MOVPE on a sapphire substrate. The calculated magnetic moment for VN/GaN/VN in the wurtzite structure is an integer; therefore, this confirms that the interlayer is ferromagnetic and half-metallic.

Conclusions

The first principles calculations to determine the structural, electronic, and magnetic properties of a VN/GaN/VN interlayer for CsCl, NaCl, NiAs, zinc-blende, and wurtzite structures, within the framework of density functional theory with the approach of the generalized

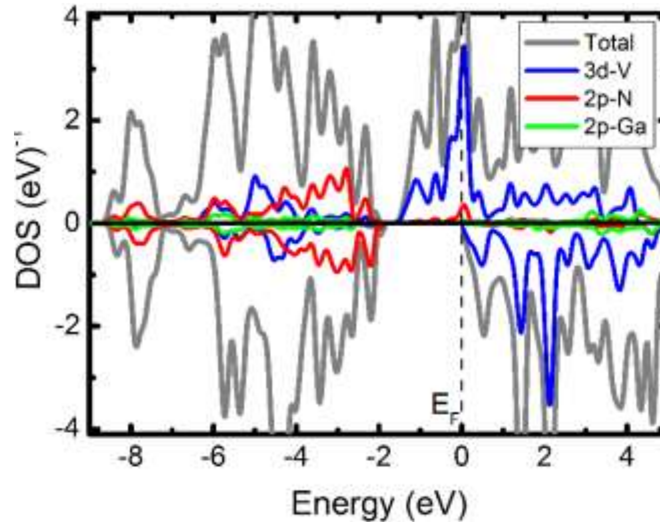

Figure 4. Partial and total density of states for VN/GaN/VN wurtzite structure.

gradient approximation (GGA) were reported. From the computation of the total energy versus unit-cell volume, the wurtzite structure was found to be preferred at ambient pressure. It was found out that the transition pressure for the wurtzite to the NaCl phase was about 21.7 GPa. The interlayer has a half-metallic behavior with a magnetic moment of 2 μ_{β}/V-atom. The ground-state ferromagnetic behavior comes from the polarization of the V-3d and N-2p orbitals, which cross the Femi level. These compounds are good candidates for potential applications in spintronics and can be used as spin injectors.

Conflict of Interests

The authors have not declared any conflict of interests.

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