International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 18 (2018) pp. 14018-14021

Transition Phase, Structural and Electronic Properties of CrN/AlN Superlattice under Hydrostatic Pressure

Miguel J. Espitia R.[1], John H. Díaz F.[1], Octavio José Salcedo Parra[2,3]

[1]*GEFEM Group, Universidad Distrital "Francisco José de Caldas", Bogotá, Colombia.*

[2]*Internet Inteligente Research Group, Universidad Distrital "Francisco José de Caldas", Bogotá, Colombia.*

[3]*Faculty of Engineering - Universidad Nacional de Colombia, Bogotá D.C., Colombia.*

Abstract

In this paper we performed first-principles total energy calculations using the pseudopotential method, in order to investigate the structural and electronic properties of CrN/AlN superlattice. The calculations were carry out in the sodium chloride (NaCl) and wurtzite phases because these are the ground states of the binary CrN and AlN compounds, respectively. The structural properties study predicts a transition phase from wurtzite to NaCl phase by means external pressure, the calculated transition pressure was 5.0 GPa. The electronic properties calculations reveal that in the wurtzite phase the superlattice have a half-metallic ferromagnetic behavior, but in the NaCl phase obtained by the application of external pressure, the superlattice loses its half-metallic character and acquires a metallic behavior. The calculated values of magnetic moment were 3.0 μ_β/cell and 2.91 μ_β/cell in the wurtzite and NaCl, respectively. These magnetic properties come from hybridization and polarization between metallic Cr-3d and nonmetallic 2p-N. For this magnetic behavior CrN/AlN superlattice in the wurtzite phase is a good candidate to be used as diluted magnetic semiconductor material with potential application in the spintronic field.

Keywords: Density Functional Theory, structural and electronic properties, transition pressure.

INTRODUCTIÓN

The superlattices based on nitrides has been studied theoretical and experimentally, due to superior properties as high hardness, large bulk modulus, high melting point, and mechanical stability [1-3]. The superlattices has potential applications in hard coating, devices that operate at high temperatures and high frequencies [3-8]. For very superlattices such as TiN/GaN [4], CrN/NbN [5], TiN/AlN [6,7], VN/AlN, VN/TiN [8], these applications are reality. On the other hand, recently there is very interest in the investigation of the possible applications of the metal transition nitrides superlattices due to potential application in spintronics devices. Tien *et al* [9] and Tytko *et al* [10] in 2017 grew by means magnetron sputtering technique the CrN/AlN superlattice. However, all the physical processes that occur between the layers of CrN and AlN are not sufficiently understood, for these reasons, in this paper we did a detailed study of the structural and electronic properties of the CrN/AlN superlattice in the NaCl and wurtzite phases.

COMPUTATIONAL METHOD

In the framework of density functional theory [11, 12] using the pseudopotential method [13, 14] as implemented in the Quantum ESPRESSO computational code [15], the first-principles calculations were performed. The exchange and correlation interaction were included with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [16]. The basis function was expanded up to kinetic energy cutoff of 40 Ry and charge density was of 400 Ry. Brillouin zone integrations were performed with the special k-point method over a 140 Monkhorst-Pack mesh [17]. The CrN/AlN superlattice in the NaCl and wurtzite phase were modeled interlacing a CrN layer and an AlN layer. The figure 1 show the tow phase for the superlattice. All the calculations we carry out with spin polarization. We performed relax type calculations, in which all atoms in the supercell move in the three directions. the optimization process ended when the forces became smaller than 10^{-4} eV/Å. The convergence threshold for self-consistent field iteration was 10^{-5} eV.

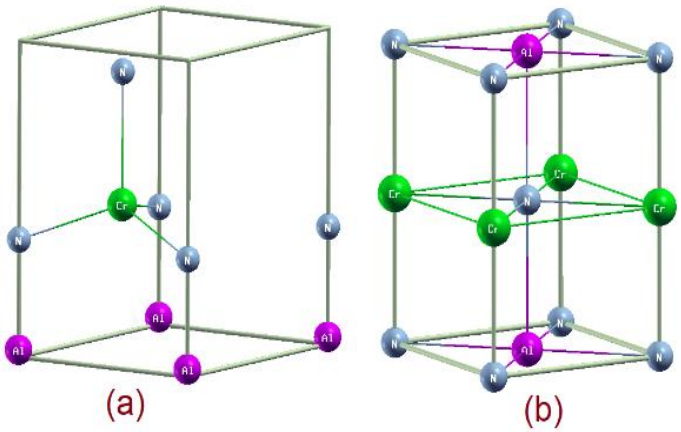

Figure 1. Conventional cell used for the CrN/AlN superlattice (a) wurtzite phase, and (b) NaCl phase. Source: Authors

RESULTS AND DISCUSSIONS

Structural properties

Under ambient of pressure and temperature, AlN crystallizes in the hexagonal wurtzite phase [19, 19], while the CrN crystalizes in the cubic NaCl phase [21]. In spite of that binary compounds have different crystalline structures, the CrN/AlN superlattice has been grown experimentally [9, 10]. For this reason, the superlattice was modeled in two phases. First, we calculated the equilibrium parameter of the AlN and CrN after relaxation process. The table 1 show lattice constant, ratio c/a, bulk modullus and total energy of the binary compounds, which are compared with available data reported theoretical and experimentally.

Table 1: Lattice constant (a), ratio c/a, bulk modullus, and total energy of CrN and AlN compounds

Compound	*a*(Å)	*c/a*	B_0 (GPa)	E_0 (eV/atom)
AlN-(wurtzite)	3.120 3.123[a] 3.110[c]	1.610 1.604[b] 1.601[c]	192.15 192.93[b] 185.00[c]	-1765.3238
CrN-(NaCl)	4.16 4,13[d] 4.08[e] 4,15[f(exp)]	-	308 310[d]	-1320.1436

[a] [18] Theoretical reference

[b] [19] Theoretical reference

[c] [20] experimental reference

[d] [21] Theoretical reference

[e] [22] Theoretical reference

[f] [23] experimental reference

We can see in the table 1, the calculated lattice constant and bulk modulus for AlN are in good agreement with obtained from other theoretical and experimental studies, because the maximum discrepancies are ~ 0.32% and ~ 3.86%, respectively. While for CrN the lattice constant (4.16 Å) and bulk modulus (308 GPa) are in excellent agreement with previous theoretically and experimental work, being the maximum discrepancy of ~ 1.9% and ~ 0.65%, respectively. These discrepancies are smaller, which show the reliability of our present calculation.

In the table 2 are listed the equilibrium parameters of CrN/AlN superlattice in the NaCl and wurtzite structures.

Table 2: Lattice constant (*a*), ratio c/*a*, equilibrium volume, bulk modullus, and total energy of the CrN/AlN superlattice

Phase	a (Å)	c/a	V_0 (Å^3)	B_0 (GPa)	E_0(eV)	μ_β
NaCl	2.9940	1.414	35.284	188.998	-1541.3870	3.00
Wurtzite	3.1561	1.613	43.927	188.711	-1541.3225	3.00

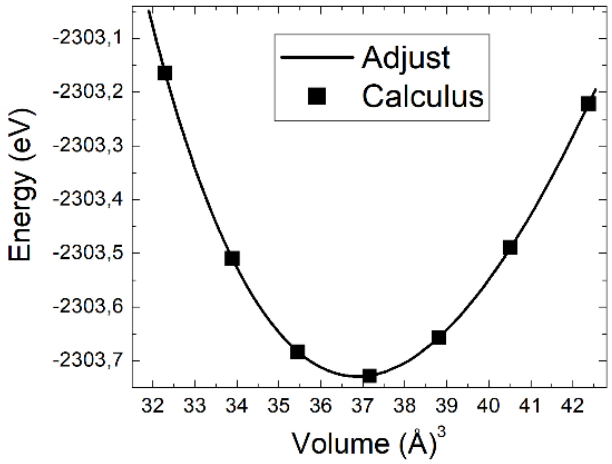

Figure 2. Total energy vs volume. Source: Authors

In the table 2 we note that the bulk modullus of superlattice is high, very close to the bulk modullus of AlN, therefore the CrN/AlN superlattice is quite rigid and can be used as hard coating material. Additionally, we can see that the bulk modullus is the same (~ 189 GPa) in the NaCl and wurtzite phase, although the two structures have different equilibrium volumes 35.284 Å^3 and 43.927 Å^3, respectively. Therefore, the superlattice preserve their rigidity (~ 189 GPa) in two phases because the bulk modullus is an intensive property.

In order to compute the energy stability, we calculated the formation energy of CrN/AlN in both phases. The formation energy is defined as the difference between the total energy of the superlattice and the total energy of the binary compound in their ground states, namely, AlN-wurtzite and CrN-NaCl. The formation energy is [24,25]:

$$E_f = E_{CrN/AlN}^{phase} - (1-x)E_{CrN}^{NaCl} - xE_{AlN}^{wurtzite} \quad (1)$$

The calculated values for the formation energy of the superlattice were 1.3467 eV and 1.4112 eV in the NaCl and wurtzite phases, respectively. The NaCl is the most stable phase for the superlattice because has the minor value of the formation energy.

In order to check a possible phase transition under high pressure, the Gibbs free energy $G = E + PV - TS$ was used. The calculations were performed in ground state (T = 0 °K), the term TS of the Gibbs energy is zero. Gibbs free energy reduces to $G = H = E + PV$ [25, 26], where H is the enthalpy. We use this equation for NaCl and wurtzite phases, nevertheless, it can exist other stable or metastable structures for CrN/AlN superlattice.

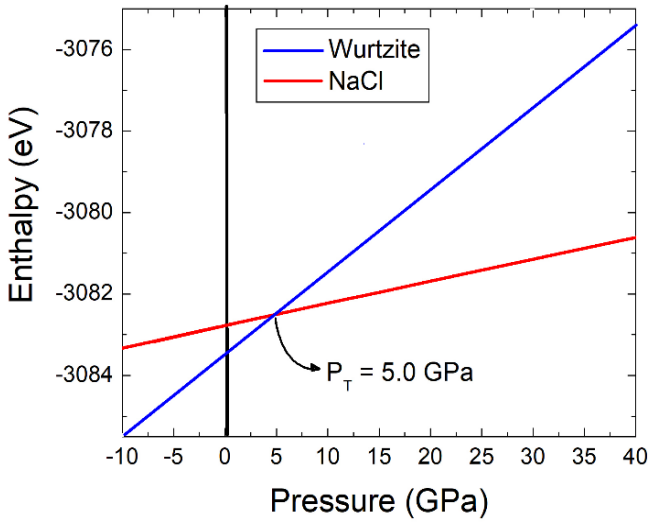

Figure 2. Enthalpy vs pressure in the NaCl and wurtzite phases of CrN/AlN superlattice. Source: Authors

The enthalpy vs pressure for the wurtzite and NaCl phases is illustrated in the figure 1. We observe that due to hydrostatic pressure the CrN/AlN will change from a wurtzite structure to NaCl at a transition pressure P_T = 5.0 GPa. Additionally, before the transition pressure ($P < P_T$) the lowest values of enthalpy belong to the wurtzite phase. Therefore, within this pressure range the wurtzite phase is most stable that NaCl phase. For higher values of the transition pressure ($P > P_T$), the lowest values of enthalpy corresponding to NaCl phase. Hence, within this pressure range, NaCl is the most stable phase. At the transition pressure, the enthalpies of both structures have the same value. But there is a volume reduction of about 17.75%, from 42.899 Å^3 in the wurtzite phase to 35.284 Å^3 NaCl phase.

Electronic Properties

The equilibrium lattices constant listed in the table 2 were using to evaluate the total and partial density of states (DOS) of CrN/AlN superlattice in the wurtzite and NaCl phases. The DOS are illustrated in fig. 3(a)-(b), respectively. As we can see in the fig. 3(a) for wurtzite phase the superlattice have a half-metallic ferromagnetic behavior, because near the Fermi Level the spin-up are metallic and spin-down are semiconductors. Therefore, the superlattice in the wurtzite phase have a polarization of 100% of the conduction carriers, which is a requirement for spin injector [27, 28], hence the CrN/AlN in the wurtzite phase is a good candidate for diluted magnetic semiconductor with potential application in spintronic. The calculated total magnetic moment was 3.0 μ_β/cell. We note that the magnetic moment is integer which again confirms the half-metallic character of superlattice in wurtzite phase. This magnetic behavior come from hybridization and polarization between of Cr-3d and N-2p orbitals.

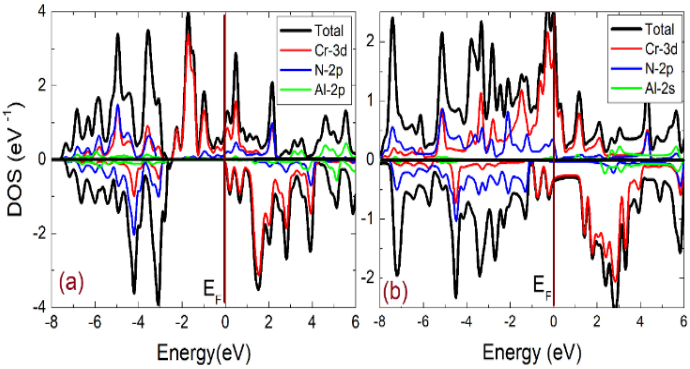

Figure 3. Total and partial DOS of CrN/AlN superlattice, (a) wurtzite phase and (b) NaCl phase. Source: Authors.

The DOS of superlattice in the NaCl phase is show in the fig.3(b). We note that due to transition phase the superlattice losses the half-metallic behavior and acquire a metallic character in the NaCl phase, with a total magnetic moment of 2.91 μ_β/cell. This magnetic moment comes from of the strong hybridization between metallic stated Cr-3d and nonmetallic states N-2p.

CONCLUSIONS

We studied the structural and electronic properties of CrN/AlN in wurtzite and NaCl phases, we used first-principles calculations by means density functional theory. We found that the superlattice have the same bulk modullus in the two phases, with a value ~ 189 GPa. This values very close to bulk modullus of AlN compound. In other words, we found that the CrN/AlN superlattice preserve their rigidity in the wurtzite and NaCl phases. The density of state show that in the wurtzite phase, the superlattice have a half-metallic ferromagnetic behavior with magnetic moment of 3.0 μ_β/cell. Hence, the superlattice in the wurtzite phase is a good candidate for application in the spintronic field. On the other hand, the superlattice in NaCl phase have a metallic magnetic character, with a magnetic moment of 2.91 μ_β/cell. These properties are a consequence of hybridization between Cr-3d and N-2p orbital.

ACKNOWLEDGEMENTS

The authors are very grateful to the Investigations center of the Universidad Distrital Francisco José de Caldas for its financial support

REFERENCES

[1] M. J. Espitia R., C. Ortega López, G. Casiano Jiménez, Revista Colombiana de Física, Vol. 43, No. 2 de 2011

[2] A. Zaoui, S. Kacimi, B. Bouhafs and A. Roula. PHYSICA B, 358 (2005) 63-71.

[3] M. Guemmaz, G moraitiz, A. Mosser, M. A. Khan. ReladPhenom, 83 (1997) 173- 175.

[4] Vijay Rawat and Timothy Sands, Jour.Appl. Phys. 100 (2006) 064901

[5] Juliano Avelar Araujo, Roberto Martins Souza, Nelson Batista de Lima, André Paulo Tschiptschin, Materials Research. 2017; 20(1): 200-209

[6] Anne Thobor, Christophe Rousselot, Christine Clement, Jamal Takadoum, Nicolas Martin, Rosendo Sanjines, Francis Levy, Surface and Coatings Technology 124 (2000) 210–221

[7] Vipin Chawla, David Holec, Paul H. Mayrhofer, Computational Materials Science 55 (2012) 211–216

[8] C. Stampfl, A.J. Freeman, Applied Surface Science 258 (2012) 5638– 5645

[9] Shih-Kang Tien, Jenq-GongDuh, Jyh-WeiLee, Surface and Coatings Technology, 201(9-11) 2007 5138-5142

[10] Darius Tytko, Pyuck‑Pa Choi, Dierk Raabe, Tytko et al. Nano Convergence (2017) 4:15

[11] Hohenberg, P., Kohn, W.: Phys. Rev. B 136, 864 (1964)

[12] Kohn, W., Sham, L.J.: Phys. Rev. A 140, 1133 (1965)

[13] Vanderbilt D 1990 Phys. Rev. B 41 7892

[14] Laasonen K, Pasquarello A, Car R, Lee C and Vanderbilt D 1993 Phys. Rev. B 47 10142

[15] Giannozzi P, Baroni S and Bonin N 2009 J. Phys. Condens. Matter 21 395502 http://www.quantum-espresso.org

[16] Perdew J, Burke K and Ernzerhof M 1996 Physical Review Letter 77 3865

[17] H. Monkhorst, J. Pack, Special points for Brillouin-zone integrations, Phys Rev B, 13 (1976) 5188.

[18] J.F. Murillo G, César Ortega López, Miguel J. Espitia R, Results in Physics 5 (2015) 281–285

[19] Warner JM, Bechstedt F., Phys. Rev. B 2002; 66:15202.

[20] Schulz H, Thieman KH. Solid State Commun. 1977;23:815.

[21] Zhu Ming and Ke-Hong Wang, Modern Physics Letters B, 29(04):1550009, 2015.

[22] Marco Marin-Suarez and Et al. Leidy L. Alzate-Vargas, Jorge David, Mauricio Arroyave-Franco, Mario E. Vélez, Physica Status Solidi (A) Applications and Materials Science, 215(1):1 (2018)

[23] P. Subramanya Herle, M. S. Hegde, N. Y. Vasathacharya, Sam Philip, M. V. Rama Rao, and T. Sripathi. Journal of Solid State Chemistry, 134(1):120{127, 1997.

[24] C. Vargas-Hernández, Miguel J. Espitia R, R.E. Báez Cruz, Computational Condensed Matter 4 (2015) 1-5

[25] C Ortega López, G Casiano Jiménez, M J Espitia, Journal of Physics: Conference Series 687 (2016) 012052

[26] J. H. Díaz, M. J. Espitia R, J. A. Rodríguez Martínez, Journal of Physics: Conference Series 743 (2016) 012004

[27] Gladys Casiano Jiménez, César Ortega López, Miguel J. Espitia R, Journal ofMagnetism and Magnetic Materials 402 (2016) 56–160

[28] Miguel J. Espitia R, John H. Díaz F, Jairo Arbey Rodríguez Martínez, Solid State Communications 244 (2016) 23–27