Ab initio invesgations of the electronic and magnetic behavior of 1x1-MnN/GaN superlattice under hydrostatic pressure

M J Espitia Rico, C Ortega López, and O Salcedo Parra

1 GEFEM - Grupo de Estudio en Temas de la Física, de la Estadística y la Matemática, Universidad Distrital Francisco José de Caldas, Bogotá, Colombia
2 Grupo Avanzado de Materiales y Sistemas Complejos, Universidad de Córdoba, Montería, Colombia
3 Facultad de Ingeniería, Universidad Nacional de Colombia, Bogotá, Colombia

E-mail: mespitiar@udistrital.edu.co

Abstract. In this paper, Ab-initio calculations are reported on the electronic and magnetic behavior of a 1x1-MnN/GaN superlattice in the wurtzite structure under hydrostatic pressure. The calculations were performed using the formalism of density functional theory with the generalized gradient approximations in the Perdew, Burke and Ernzerhof model, as well as the Wien2k computational package. The density of state shows that the electronic structure and the magnetic moment are affected by the hydrostatic pressure, because there is an abrupt change in the magnetic moment, which goes from 0 to 2.86 $\mu_B$ per cell under a pressure of $\sim 24.45$ GPa. When the pressure decreases to 0 GPa, the magnetic moment of the superlattice rises to 4.0 $\mu_B$ per cell. Therefore, the superlattice exhibits a half-metallic behavior for a pressure of 0 GPa, while it acquires a metallic behavior when pressure surpasses 24.45 GPa.

1. Introduction

The superlattices of transition metal nitrides of the semiconductor group III, such as aluminum nitride (AlN) or gallium nitride (GaN), have become an interesting subject for researchers. This recent interest is explained by the fact that superlattice combines the extraordinary properties of metal transition nitrides, such as a high degree of hardness, a high melting point, and excellent thermal and electrical conductivity [1], with the superior physical and chemical properties of the semiconductors in group III, such as high thermal stability, high thermal conductivity, high bulk modulus, low compressibility, and large direct band-gap energy [2]. At room temperature, the ground states of AlN and GaN are wurtzite, while the ground state of metal transition nitrides is cubic. Several forms of superlattices have been studied and grown. For example, a TiN/AlN superlattice was grown using magnetron sputtering [3] and plasma-enhanced chemical vapor deposition (CVD) [4] techniques, CrN/AlN has been grown via magnetron sputtering [5], TiN/GaN was fabricated using the reactive pulsed laser deposition technique [6], and the MnN/GaN superlattice was grown through molecular beam epitaxy [7] and CVD [8]. Several advantages of superlattices over the nitrides that make up the superlattice (metal transition nitrides and semiconductor nitrides) have been reported. Superlattices have enhanced hardness, increased thermal conductivity, improved oxidation resistance, and better chemical inertness [3-5]. Finally, some researchers predict that the superlattices of transition metal nitrides from group III can be used as diluted magnetic semiconductors [7,8]. These results prompted the study discussed hereby on the effects of hydrostatic pressure on the electronic and magnetic behavior of a 1x1-
MnN/GaN superlattice. The importance of this study lies in determining how pressure affects the electronic and magnetic properties of the superlattice. It can also determine the value of the transition pressure where the properties of the superlattice start to change. This information can be used in experimental research to manipulate the properties of the superlattice. Hence, the superlattice can have different applications for different pressure values.

2. Computational details
The structural, electronic, and magnetic properties of 1x1-MnN/GaN superlattices were investigated by means of ab-initio density functional theory [9], employing the full-potential plane wave method together with the generalized gradient approximation of GGA de Perdew-Burke-Ernzerhof [10]. The calculations were carried out with the wien2K code. We took a 10×10×8 k-point mesh generated with the Monkhorst-Pack method. For the parameter RmK\text{max}, we took a value of 8, where Rm is the smallest muffin-tin radius of the atomic sphere and K\text{max} is the maximum modulus of the vector k in the reciprocal space in the first Brillouin zone. The muffin-tin radii of Ga, Mn, and N atoms were 2.0, 1.85, and 1.6, respectively. The atomic positions in the unit cell were relaxed until the forces become smaller than 0.001 eV/Å. All the calculations were performed with spin polarization, and the criterion for the energy convergence for self-consistent field iteration was 10^{-5} eV/atom.

3. Results and discussions
3.1. Structural properties
The main equilibrium structural properties of lattice constant and bulk modulus were calculated for MnM, GaN, and the 1x1-MnN/GaN superlattice using the semi-empirical Murnaghan equation. Table 1 exhibits the calculated values of the lattice constant (a₀) and the bulk modulus (B₀) which are then compared with other theoretical and experimental values reported in the literature.

| Compound           | a₀ (Å)  | c/a    | B₀ (GPa) |
|--------------------|---------|--------|----------|
| GaN                | 3.215   | 1.639  | 186.52   |
|        3.221       | 1.629b  | 184.85b|
|        3.190c      | -       | 188.00d|
| MnN                | 4.271   |        | 291.50f  |
|        4.300f      | -       |        |
|        4.320g      | -       |        |
| 1x1-MnN/GaN       | 3.198   | 1.626  | 198.10   |

Theoretical reference [11,12,15,16].
Experimental reference [13,14,17].

As seen in Table 1, the lattice constant (3.215 Å) for the GaN compound is highly consistent with the experimental (3.190 Å) and theoretical (3.221 Å) values reported by other authors. Similarly, the MnN compound exhibits a consistency between the computed lattice constant (4.271 Å) and the reported values both theoretically (4.300 Å) and experimentally (4.320 Å). The maximum deviations for MnN and GaN were 0.67% and 0.78%, respectively. These discrepancies represent less than 1% which guarantees the reliability of our calculations. For the 1×1-MnN/GnN superlattice, the values calculated for the lattice constant and c/a ratio were 3.198 Å and 1.626, respectively. The obtained bulk modulus was 198.10 GPa, which is larger than the bulk modulus of GaN and thus represents an improvement in hardness with respect to GaN-wurtzite.
3.2. Electronic properties

In order to analyze the effects of pressure on the magnetic properties of a 1×1-MnN/GaN superlattice, the variation of the magnetic moment was determined compared to the lattice constant (and therefore to pressure, since each pressure value has a corresponding lattice constant). Figure 1 illustrates the results.

![Figure 1. Variation of the magnetic moment vs lattice constant.](image)

The Figure 1 shows an abrupt change in the magnetic moment of the superlattice, since it goes from 0 to 2.86 µβ/cell with a lattice constant of 3.156 Å (pressure of ~ 24.45 GPa). Additionally, the same figure reveals that the lattice constant increases until it reaches the equilibrium value of 3.198 Å (or alternatively, the pressure decreases until its equilibrium pressure reaches 0 GPa). The magnetic moment reaches a \(4\) integer number of 4.0 µβ/cell. This is relevant because it implies that magnetic properties can be changed experimentally.

![Figure 2. DOS to equilibrium pressure P = 0 GPa.](image)

To study the effects of pressure on the electronic properties of 1×1-MnN/GaN superlattice, the density of state at equilibrium pressure (P = 0 GPa) and high pressure (P = 24.45 GPa and \(a = 3.156\) Å) were calculated. Figure 2 shows the total density of state (DOS) and partial density of state of the atomic orbital that constitutes the major contribution to the superlattice at P = 0 GPa. The superlattice has a half-metallic ferromagnetic character given this pressure, since the spin-up state is metallic and the spin-down state is semiconductor. The largest contribution to this behavior comes from the d-Mn orbitals. At a pressure of 0 GPa, the superlattice has an integer magnetic moment of 4.0 µβ/cell, once again confirming the half-metallic character of the 1×1-MnN/GaN superlattice.

Figure 3 shows the total density (DOS) of state and partial density of state of the atomic orbital that represents the largest contribution to the superlattice at a high pressure of P = 24.45 GPa. At this pressure level, the superlattice has a metallic character, since it has spin-up and spin-down states across the Fermi level. The main contribution to this behavior comes from d-Mn orbitals.
Figure 3. DOS high pressure of $P = 24.45$ GPa.

4. Conclusions
In summary, ab initio calculations were carried out in order to study the electronic and magnetic behavior of a 1x1-MnN/GaN superlattice in the wurtzite structure under hydrostatic pressure. It was found that pressure affects the magnetic properties of the superlattice, revealed by an abrupt change in the magnetic moment, which goes from 0 to 2.86 $\mu_B$/cell at a pressure of $\sim 24.45$ GPa and a lattice constant of 3.156 Å. Additionally, when pressure reaches 0 GPa, the superlattice has a half-metallic character and a magnetic moment of 4.0 $\mu_B$. In a high-pressure scenario ($P = 25.50$ GPa), the superlattice has a metallic character with a magnetic moment of 2.86 $\mu_B$/cell.

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References
[1] Arbouche O, Belgoumène B, Soudini B and Driz M 2009 Computational Materials Science 47 (2) 432
[2] Janika J, Drygas M, Czosnek C, Kaminska M, Palczewska M and Paine R 2004 Journal of Physics and Chemistry of Solids 65 639
[3] Thobor A, Rousselot C, Clement C, Takadoum J, Martin N, Sanjines R and Levy F 2000 Surface and Coating Technology 124 210
[4] Lim J W, Lee S H and Lee J J 2003 Surface and Coating Technology 169 170
[5] Lin J, Moore J J, Mishra B, Pinkas M, Zhang X H and Sproul W D 2009 Thin Solid Films 517 5798
[6] Rawat V and Sands T 2006 Journal of Applied Physics 100 064901
[7] Chen Z, Su Y, Yang Z, Zhang B, Xu K, Yanga X, Pan Y and Zhang G 2007 Journal of Crystal Growth 298 254
[8] Sonoda S, Shimizu S, Sasaki T, Yamamoto Y and Hori H 2002 Journal of Crystal Growth 237 239
[9] Kohn W and Sham L 1965 Physical Review A 140 1133
[10] Perdew J, Burke K and Emzerhof M 1996 Physical Review Letter 77 3865
[11] Espitia Rico M J, Moreno Armenta M G, Rodriguez J A and Takeuchi N 2016 Journal of Physics: Conference Series 687 012048
[12] Rufinus J 2007 Journal of Magnetism and Magnetic Materials 310 1666
[13] Serrano J, Rubio A, Herández A, Muñoz A and Mujica A 2000 Physics Review B 62 16612
[14] Christensen N E 1998 Electronic structure calculations for semiconductors under pressure High pressure in semiconductor physics vol 54, ed Suski T and Paul W (San Diego: Academic Press) chapter 2 p 49
[15] Espitia M J, Casiano G and Ortega L 2014 International Journal of Physical Science 9(24) 538
[16] Paiva R, Alves J, Nogueira R, Leite J and Scolfaro J 2005 Journal of Magnetism and Magnetic Materials 288 384
[17] Janotti A, Wei S and Bellaiche L 2009 Applied Physics Letter 82 766