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Computational calculation of the electronic and magnetic properties of 1x1-MN/GaN (M = V, Cr and Mn) multilayers

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We employed density functional theory (DFT) in order to study the electronic and magnetic properties of 1x1-MN/GaN (M = V, Cr, and Mn) multilayers, in the wurtzite-type hexagonal structure. The calculations were carried out using a method based on full-potential linearized augmented plane waves (FP-LAPW), employed exactly as implemented in Wien2k code. For the description of the electron-electron interaction, generalized gradient approximation (GGA) was used. We found that the VN/GaN multilayers exhibited a half-metallic ferromagnetic behavior and all 1x1-MN/GaN (M = V, Cr and Mn) multilayers have magnetic properties with a magnetic moment of 2, 3 and 4 μ_β per cell, respectively. Additionally, we found that the magnetic moment/cell multilayers increase linearly with an increase in the atomic number Z of the transition metal. Analysis of the density of states reveals that ferromagnetic behavior of the multilayers can be explained by the strong hybridization between states (V, Cr and Mn)-d and N-pcrossing of the Fermi level. The magnetism in the multilayers essentially comes from the d orbitals of the atoms of V, Cr and Mn.

Key words: DFT, 1x1-MN/GaN (M = V, Cr, and Mn) multilayers, structural and electronic properties.

INTRODUCTION

Gallium nitride, GaN, a semiconductor that crystallizes as wurtzite (Koide et al., 2005), is a material of great interest because of its wide potential application in technology, in light-emitting devices in the blue and near-ultraviolet ranges, diodes based on Schottky contact, and laser diodes (Nakamura, 1997; Morkoc et al., 1994). Its efficiency in blue, green, and yellow light-emitting emitting diodes, laser injection, and ultraviolet detectors is truly extraordinary (Steckl and Birkahn, 1998). The high value of the dielectric constant, high thermal conductivity, and favorable transport properties make it a good candidate for new applications in devices that must operate at high temperatures and in high-power electronic devices (Nakamura et al., 1994). In recent years, there has been great interest in the GaN compound, its alloys, and when doped with transition metal, due to their potential

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applications in diluted magnetic semiconductors (Dietl et al., 2000), as spin injectors, in magnetic memories, and in other spintronics applications (Zhang and Kuech, 1998; Dietl, 2002). At the same time, recent advances in techniques of the growth of materials and the ability to control the growth of semiconductor materials have opened the door to the manufacture of high-quality multilayers in different geometries and for different kinds of semiconductors. Rawat et al. (2009) demonstrated that it is possible to grow a multilayer of transition metal nitrides and GaN, despite the difference in the crystalline structures of NaCl, titanium nitride TiN, and GaN wurtzite. They grew a TiN/GaN multilayer using the reactive pulsed laser deposition technique (PLD), while Birch et al. (2006) grew a ScN/CrN multilayer epitaxially, using the magnetron sputerring technique. This fact shows that it is worthwhile to carry out theoretical studies of 1x1-MN/GaN (M = V, Cr, and Mn) multilayers that will provide information on the structural, electronic, and magnetic properties of these multilayers and enable the design of new devices that will contribute to the development of current semiconductor technology.

COMPUTATIONAL METHODS

The calculations were carried out within the framework of density functional theory (DFT), and full potential augmented plane wave (FP-LAPW) was used as implemented in the Wien2k software package (Schwarz et al., 2010). The exchange and correlation effects of the electrons were dealt with using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) (Perdew et al., 1997). In the LAPW method, the cell is divided into two types of regions, namely spheres centered at the atomic nuclear sites and an interstitial region between non-overlapping areas. Within the atomic spheres, wave functions are replaced by atomic functions, whereas in the interstitial region, the functions are expanded in the form of plane waves. The charge density and potential expand to form spherical harmonics up to l_{max} = 10 inside the atomic spheres, and the wave function in the interstitial region expands in the form of plane waves with a cutoff parameter $R_{MT}K_{max}$ = 8, where R_{MT} is the smallest radius of the atomic level within the unit cell and K_{max} is the magnitude of the largest k vector of the reciprocal lattice. To ensure convergence in the integration of the first Brillouin zone, 1600 points were used, which corresponds to 140 k-points at the irreducible part of the first Brillouin. The integrals over the Brillouin zone were solved using the special approximation of k points provided by Monkhorst and Pack (1976). Self-consistency was achieved by requiring that the convergence of the total energy be less than 10^{-4} Ry. To achieve expansion of the potential in the interstitial region, G_{max} was considered to be = 12. The corresponding muffin-tin radii were 1.6 bohr for N, 1.95 bohr for Ga, and 1.85 for V, Cr and Mn. Calculations were performed taking into consideration the spin polarization caused by the presence of V, Cr and Mn in the superlattice.

To calculate the lattice constant, the minimum volume, the bulk modulus, and the cohesive energy of the two structures studied, calculations were fit to the Murnaghan equation of state (Murnaghan, 1944),Equation (1)

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

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.

In other to study the relative stability of 1x1-MN/GaN (M = V, Cr, and Mn) multilayers in a 50-50 concentration, namely, *x* = 50% GaN molecules and *x* = 50% MN (M = V, Cr, and Mn) molecules, the energy of formation was calculated. For the ternary compound, the formation energy is defined as the difference between the total energy of the ternary phase $M_{1-x}Ga_xN$ and the total energy of the binary compounds in their ground state (more stable phase: fme) MN and GaN wurtzite, namely, E_{MN}^{fme} and $E_{GaN}^{wurtzita}$, respectively. Therefore, the formation energy is given by Equation (2)(Zhang and Veprek, 2007; Sheng et al., 2008).

$$\Delta E_f = E_{M_{1-x}Ga_xN}^{fme} - (1-x)E_{MN}^{fme} - xE_{GaN}^{wurtzita} \quad (2)$$

The 1x1-MN/GaN multilayer were modeled according to special quasirandom structures approach (Zunger et al., 1990) and the disorder aspects were ignored. The 1x1-MN/GaN multilayer an hexagonal unit cell with alternating [0001] layers of MN (V, Cr and Mn) and GaN in conventional wurtzite structure was employed, as show in Figure 1. Where a and c are the lattice constants, *u* denotes the dimensionless parameter of the internal structure and the positions of the atoms are: for Ga or M (0,0,0), (1/3,2/3,1/2) and N (0,0,*u*), (1/3,2/3,*u*+1/2).

RESULTS AND DISCUSSION

Structural properties

The multilayers were modeled in the wurtzite structure belonging to space group 156 (P3m1), interspersing a monolayer of GaN and one of MN (M = V, Cr and Mn) along the z axis. Figure 2 shows the energy as a function of the volume of 1x1- MN/GaN (M = V, Cr and Mn) multilayers. The calculated total energy was fit to Murnaghan's equation of state. It can be noted that each of the curves has a minimum energy value, and thus the crystallization phase of the multilayers is stable or metastable.

The lattice constant, the c/a value, the bulk modulus (B_0), the minimum volume (V_0), the minimum energy (E_0), the magnetic moment (μ_β) per cell, and the energy of formation of 1x1-MN/GaN (M = V, Cr and Mn) multilayers are shown in Table 1. Table 2 shows the values of the structural parameters of the binary compounds VN, CrN, MnN and GaN, calculated and reported by other authors.The calculated lattice constant for each of the binary compounds accords well with values reported theoretically and experimentally, since it differs by less than one percent. The values of the bulk modules of the multilayers 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 hard coatings. On the other hand, despite the difference in the crystalline structure between VN NaCl, zinc blend of CrN, MnN, and GaN wurtzite, joining of the layers of the 1x1-MN/GaN (M = V, Cr and Mn) compounds with GaN to form a multilayer does

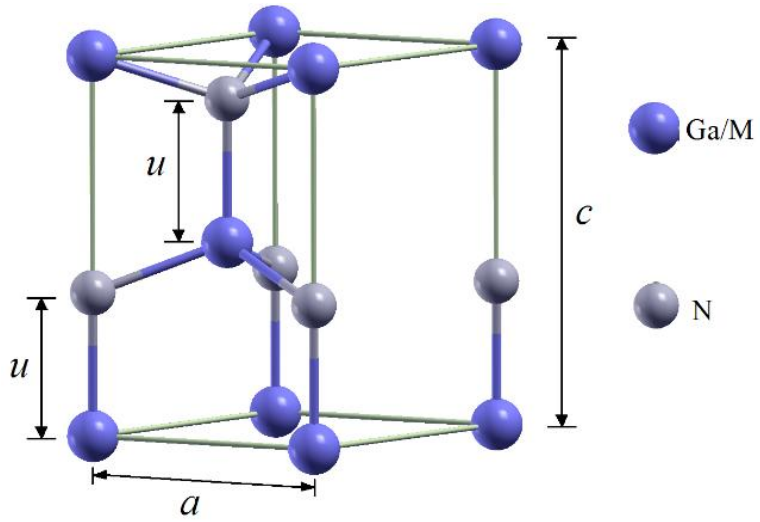

Figure 1. Unit cell 1x1-MN/GaN (M = V, Cr and Mn) multilayers.

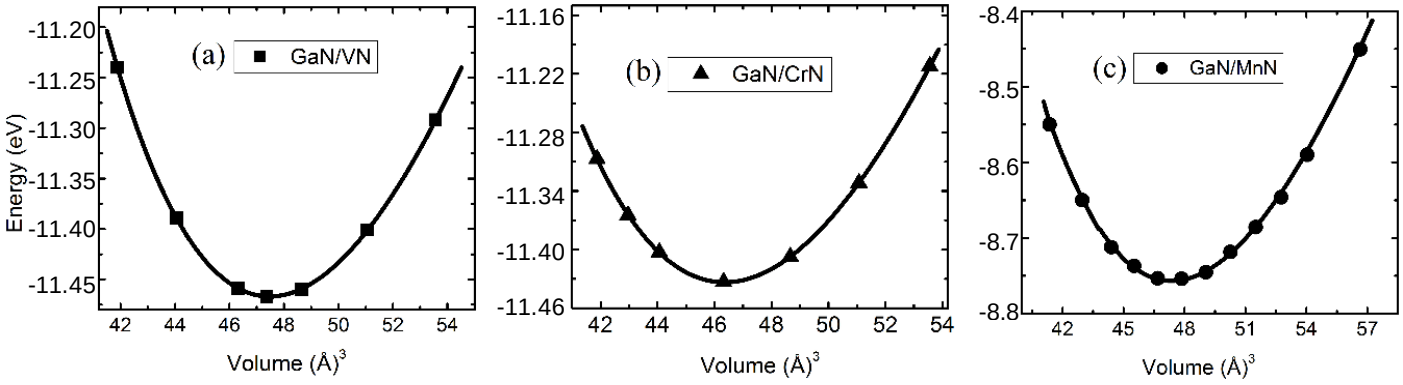

Figure 2. Total energyas a function ofvolume for 1x1-(a) VN/GaN, (b) CrN/GaN, (c) MnN/GaN multilayers.

Table 1. Structural and magnetic parameters and the energy of formation ΔE_f of 1x1-MN/GaN (M = V, Cr and Mn) multilayers.

Multilayer	a_0 (Å)	c/a	V_0 (Å^3)	B_0 (GPa)	E_0 (eV)	μ (μ_B)	ΔE_f (eV)
VN/GaN	3.227 3.267[a]	1.631	47.41	176.07	- 11.47	~2.0	+ 0.621
CrN/GaN	3.210	1.628	47.19	191.50	- 11.48	~3.0	+ 0.461
MnN/GaN	3.190	1.626	46.31	181.00	- 8.570	~4.0	+ 0.403

not change the GaN wurtzite structure, as seen in Table 1 in the value of the lattice constant and the c/a value of the multilayers, which are very close to the value of the lattice constant and the c/a value of GaN in Table 2.

In order to verify the relative stability of the multilayer, we calculated the energy of formation of each multilayer. For this purpose, we calculated the total energy E_0 (Table 2) of the binary compounds VN, CrN, MnN and GaN in their ground states. Table 1 shows the values of formation energy ΔE_f calculated using Equation 2.

The energy of VN, CrN, MnN and GaN binary compounds in their ground state is negative, whereas, according to the results of Table 2, the value of the energy of formation of each multilayer is positive.

Table 2. Structural parameters of binary compounds VN, CrN, MnN and GaN in ground state.

Binary	a_0 (Å)	c/a	B_0 (GPa)	E_0 (eV)
VN	4.129 4.127[b] 4.139[c]	-	306.01 305.3[c]	- 15.25
CrN	4.148 4.146[b] 4.135[c]	-	211.15 204.15	- 14.95
MnN	4.271 4.256[d]	-	291.5	- 9.524
GaN	3.222 3.221[f] 3.190[g]	1.629 1.631[f]	184.50 170.56[f] 188.00[g]	- 8.933

A (González et al., 2009) Theoretical, b (Liangcai et al., 2013) Theoretical, c (International center for diffraction data, 2007) Experimental, d (Suzuki et al., 2000) Experimental, e (Lukashev and Lambrecht, 2004) Theoretical, f (Shultz and Thiemann, 1977) Theoretical, g (Arbouche et al., 2009) Experimental.

Therefore, 1x1-MN/GaN (M = V, Cr and Mn) multilayers are metastable. This means that the multilayer cannot grow under equilibrium conditions, so in order to grow them, it is necessary to supply power to the system, as Rawat et al. (2009) did in order to grow a 1x1-TiN/GaN multilayer using the reactive pulsed laser deposition technique (PLD). These results for the energy of formation are important, because through knowing these values, growing conditions can be improved, and therefore 1x1- MN/GaN (M = V, Cr and Mn) multilayers of excellent quality can be grown.

Table 1 shows that energy of formation of the 1x1-MN/GaN (M = V, Cr and Mn) multilayer. The smallest value of the energy of formation corresponds to the 1x1-MnN/GaN multilayer; therefore, it is the most energetically stable.

Electronic properties

Figure 3(a), (b) and (c) shows the calculated band structures of 1x1-MN/GaN (M = V, Cr and Mn) multilayers in their ferromagnetic state phase. Figure 4b and 4c shows that the 1x1-CrN/GaN and 1x1-MnN/GaN multilayers are not half-metallic behavior due valence and conduction bands cross the Fermi level, however 1x1-VN/GaN multilayer is half-metallic and ferromagnetic, since in the valence band near the Fermi level the majority spin (spin-up) is metallic, and the minority spin (spin-down) is semiconducting. The 1x1-VN/GaN multilayer exhibit 100% polarization of the conduction carriers in the ground state, which is required in spin injection. This suggests that it can be used efficiently for injection of spin polarized charge carriers.

Figure 4(a), (b) and (c) show the total density of states (TDOS) and partial density of states (PDOS) of the orbitals that more contribute near the Fermi level of 1x1-MN/GaN (M = V, Cr, and Mn) multilayers in the ground state. The calculations were performed with spin polarization up and down.

Figures 4a confirm the half-metallic and ferromagnetic nature of 1x1-VN/GaN multilayer, since the up-spin density is metallic, whereas the down-spin density is of semiconductor character, namely, the spin-up channel is completely occupied and the spin-down channel is completely empty. Whereas that 1x1-CrN/GaN and 1x1-MnN/GaN have metallic behavior of the two spin channels.

The 1x1-MN/GaN(M = V, Cr, and Mn) multilayers, have magnetic behavior with magnetic moments of 2, 3 and 4 μ_β respectively, is mainly determined by the orbitals (M = V, Cr, and Mn)-d, and to a lesser extent by the N-p orbitals that cross the Fermi level. However, as seen in Figure 4, the contribution of the N-p (up-spin) orbital near the Fermi level increases with the increase in the atomic number Z of the transition metal in the multilayer, the contribution of orbital N-p being lower in the VN/GaN and higher in the CrN/GaN multilayer. Additionally, according to the theory by Jhi et al. (1999), the hybridization of the metallic states (M = V, Cr, and Mn)-d and nonmetallic electrons N- p that cross the Fermi level results in a strong covalent bond, which is responsible for the high degree of stiffness of the multilayer.

Figure 5 shows the variation of the magnetic moment as a function of the atomic number of the transition metal present in the1x1-MN/GaN (M = V, Cr, and Mn) multilayer, with Z = 23, 24 and 25 respectively. It can be observed that the magnetic moment increases linearly with an increase in the atomic number.

This increase in the magnetic moment value can

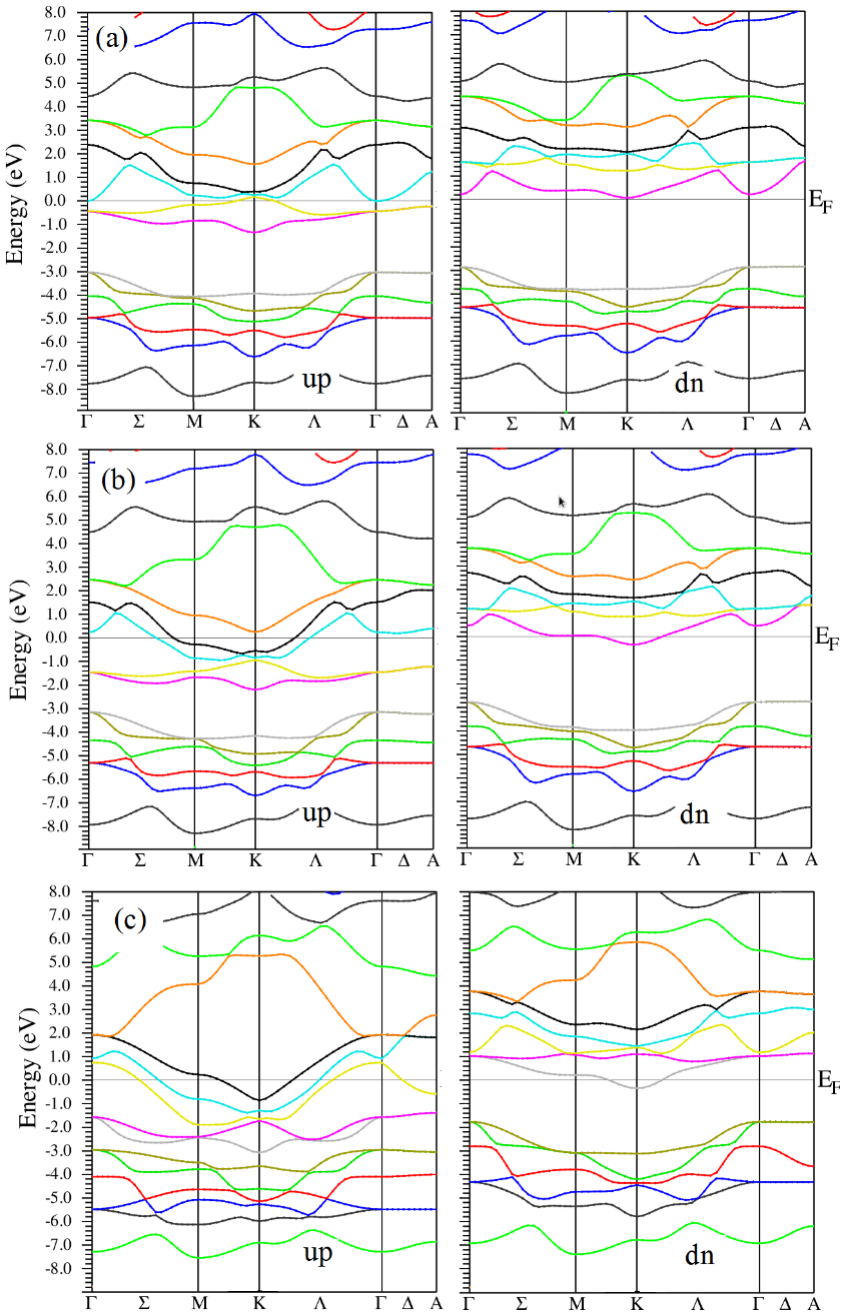

Figure 3. Band structure (a) 1x1-VN/GaN, (b) 1x1-CrN/GaN and (c) 1x1-MnN/GaN.

understood as follows: the magnetic moments of 2, 3 and 4 μ_β are due V^{3+}, Cr^{3+} and Mn^{3+} configuration, respectively; with electronic configurations V^{3+} =:[Ar]$3d^2$, Cr^{3+} =:[Ar]$3d^3$ and Mn^{3+} =:[Ar]$3d^4$; because, when the V, Cr and Mn atoms are in the multilayer each atom gives three electrons. Then, the V atom remain two valence electrons, Cr atoms three and Mn atom four valence electrons (configurations d^2, d^3 and d^4, respectively). This valence electrons couple ferromagnetically, as result the two electrons produce a total magnetic moment of 2 μ_β/atom-V, the three electrons produce a total magnetic moment of 3 μ_β/atom-Cr and the four electrons produce a total magnetic moment of 4 μ_β/atom-Mn.

Conclusions

We reported first principles calculations to determine the structural, electronic, and magnetic properties of a 1x1-MN/GaN (M = V, Cr, and Mn) multilayer. The calculated

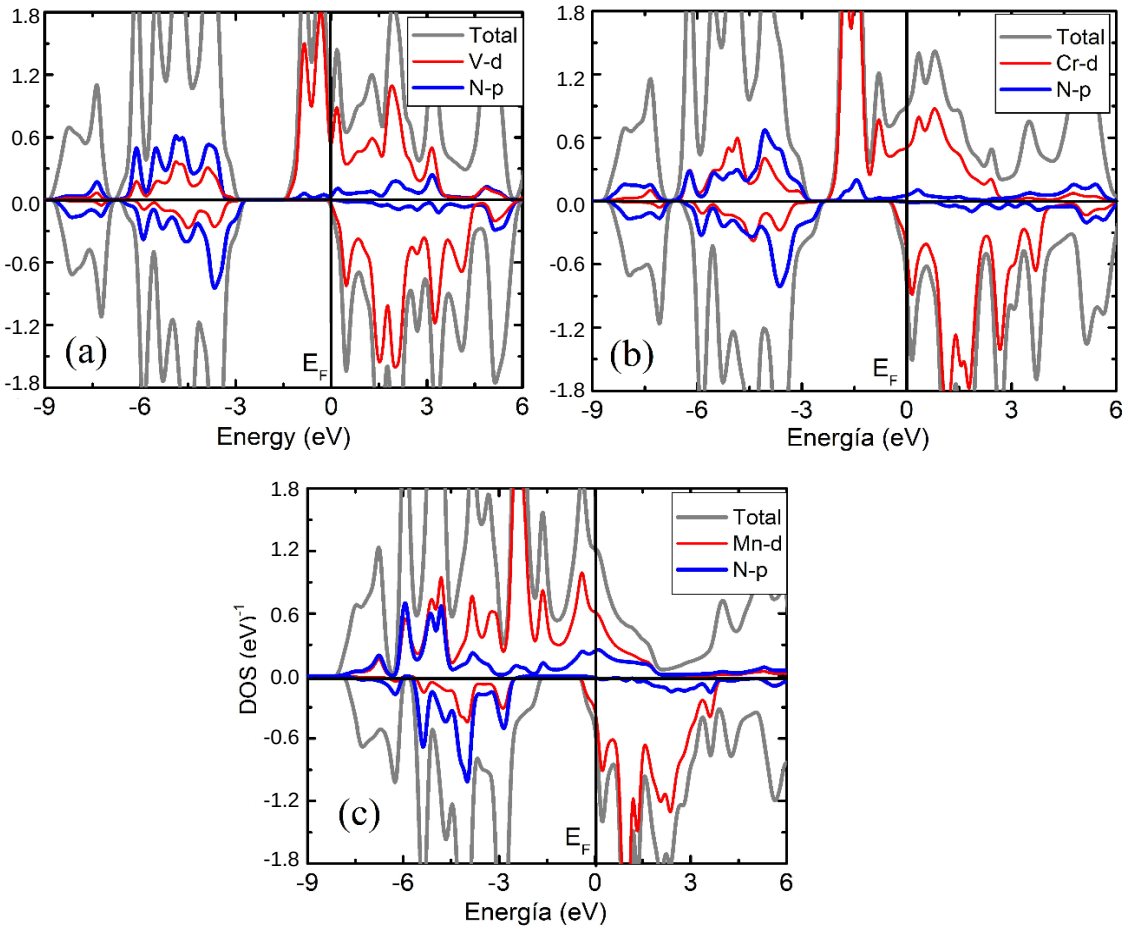

Figure 4. Total and partial density of states of 1x1 (a) VN/GaN, (b) CrN/GaN, (c) MnN/GaN multilayers.

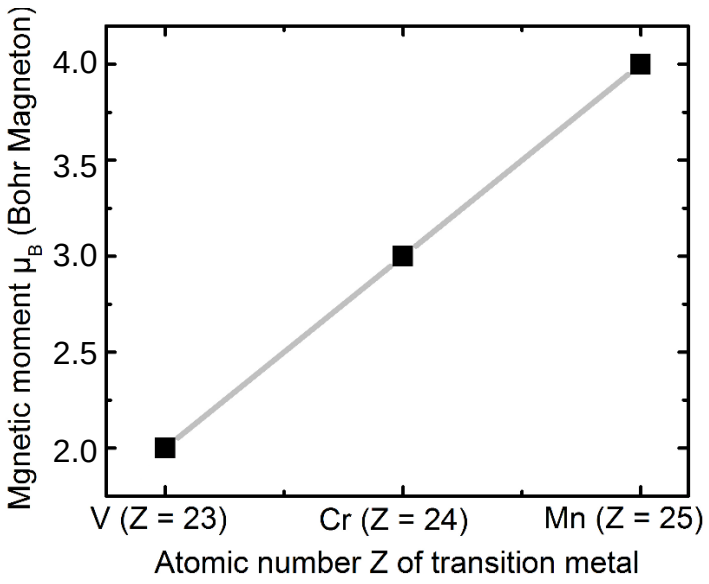

Figure 5. Magnetic moment as a function of the atomic number of the transition metal present in the1x1-MN/GaN (M = V, Cr, and Mn) multilayer. The line is a visual guide.

values of the bulk modules were quite high; therefore, the multilayers are quite rigid, which makes them attractive for potential applications at high temperatures and for hard coatings. Also, we found that the magnetic moment increases linearly with an increase in the atomic number of the transition metal present in the multilayer. On the basis of the density of states, we found that the multilayer exhibits a half metallic behavior, due to the orbital M-*d*(M = V, Cr, andMn) andN-*p* that cross the Fermi level in each corresponding multilayer. Finally, we found that 1x1-MN/GaN (M = V, Cr, and Mn) multilayers exhibit magnetic properties with magnetic moments 2, 3 and 4 μ_β, respectively. These properties show that multilayers are good candidates for possible applications in diluted magnetic semiconductors, spin injectors, and other spintronics applications.

Conflict of Interest

The authors have not declared any conflict of interest

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