VN/TiN, CrN/TiN and MnN/TiN Superlattices,

New Materials for Hard Coatings:

A Computational Study

Miguel J. Espitia R.

Universidad Distrital "Francisco José de Caldas"
Bogotá, Colombia

John Hernán Díaz Forero

Universidad Distrital "Francisco José de Caldas"
Bogotá, Colombia

Octavio José Salcedo Parra

Universidad Distrital "Francisco José de Caldas"
Universidad Nacional de Colombia, sede Bogotá
Bogotá, Colombia

Abstract

The work focused on ab initio study of structural, electronic and magnetic properties of VN/TiN, CrN/TiN and MnN/TiN superlattices in the sodium chloride structure (NaCl). Determine the bulk modulus of the VN/TiN, CrN/TiN and MnN/TiN superlattices and, comparing the bulk modulus of the superlattices with that of the binary compounds TiN, VN, CrN y MnN. Computational calculations were executed with Quantum ESPRESSO code using the pseudopotential-plane wave method in the frame Density Functional theory. 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. We determine the structural, electronic and magnetic properties of the VN/TiN, CrN/TiN y MnN/TiN multilayers and, we found that the multilayers possess greater hardness than the individual binary compounds.

Keywords: Multilayers, ultrahard materials, structural properties and electronic properties

1 Introduction

In recent years there has been a great interest in the development of new and better ultrahard materials. The interest in the study of new ultrahard materials is motivated not only by its great technological importance and its potential applications but also in the search of the understanding of the mechanisms responsible for its extreme hardness. Within this new classification of ultrahard materials the multilayers of transition metal nitrides have attracted the attention of various research groups, due to their extraordinary physical and chemical properties such as: high melting point, high hardness, high wear resistance, oxidation and corrosion, good electrical conductivity and in some cases with good ferromagnetic properties [1], [2], [3]. Experimental studies have shown that the multilayers manufactured with transition metal nitrides have hardness that exceeds that of the binary compounds that constitute them. This has been found in the multilayers VN / AlN [4], AlN / TiN [5], NbN / TiN, MoN / TiN and TaN / TiN [6] grown by magnetron sputtering. The reasons why the multilayers of transition metal nitrides have high hardnesses are not yet completely clear. It is at this point where the theoretical calculations play an important role because from them you can build models that allow a greater understanding of the physical properties of the new materials. For this reason, in this article we carried out a DFT study of the structural and electronic properties of the multilayers of transition metal nitrides VN / TiN, CrN / TiN and MnN / TiN in order to characterize them structurally and electronically and to explain the origin of its hardness.

2 Computational Method

The ab initio calculations of the total energy were executed within the framework of the DFT Density Functional Theory [7], as implemented in the Quantum ESPRESSO computational code [8]. The effects of exchange and correlation between the electrons were included by means of the Generalized Gradient Approach GGA-PBE. The Kohn-Sham equations are solved with a kiss of flat waves and using ultra-soft pseudopotentials for the atoms of titanium, vanadium, chromium, manganese and nitrogen. For flat waves a cutting energy of 40 Ry is taken, while a cut of 400 Ry is used for the charge density. A 6x6x4 k-point mesh is used for the first Brillouin zone, using the special Monkhorst-Pack scheme. The calculations are made with polarized spin due to the presence of V, Cr and Mn

atoms in the multilayers. The structural relaxation process ends when the magnitude of the force acting on each atom is 1 mRy/Å and the convergence in energy is of the order of 10^{-4} Ry.

To calculate the network constant, the cohesion energy and the volume module of each multilayer, the calculated values are adjusted with Murnaghan's equation of state, equation 1.

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

Where: E_0 is the cohesion energy, B_0 is the volume module, its first derivative is B_0' and B_0' is equilibrium volume of the cell of the unit cell.

3 Results

3.1 Structural properties

The 1x1-(VN/TiN, CrN/TiN and MnN/TiN) multilayers were modeled in the NaCl structure by interlaying a VN layer (CrN, MnN) and a TiN layer along the z axis. Figure 1 shows the crystalline structure of each multilayer obtained after the structural relaxation. It was found that the multilayers crystallize in a tetragonal structure with spatial group 123 (P4/mmm).
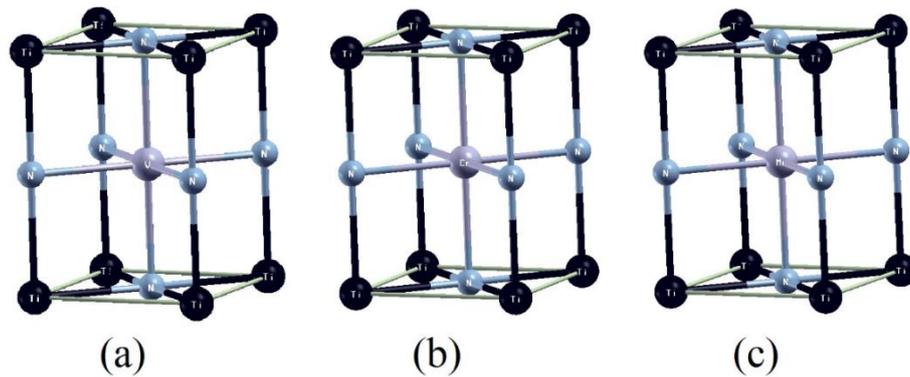

Figure 1. Unitary cells of the multilayers (a) VN / TiN, (b) CrN / TiN and (c) MnN / TiN obtained after structural relaxation. Source: authors

To obtain the structural parameters such as: the network constant a_0, the equilibrium volume (V_0), the volume module (B_0) and the cohesion energy (E_0) of the binary compounds TiN, VN, CrN and MnN and of the three multilayers VN / TiN, CrN / TiN and MnN / TiN; cohesion energy was calculated as a function of volume, the calculated values were adjusted to the Murnaghan state equation.

Figure 2 shows the energy-volume curves of the multilayers VN/TiN, CrN/TiN and MnN/TiN.
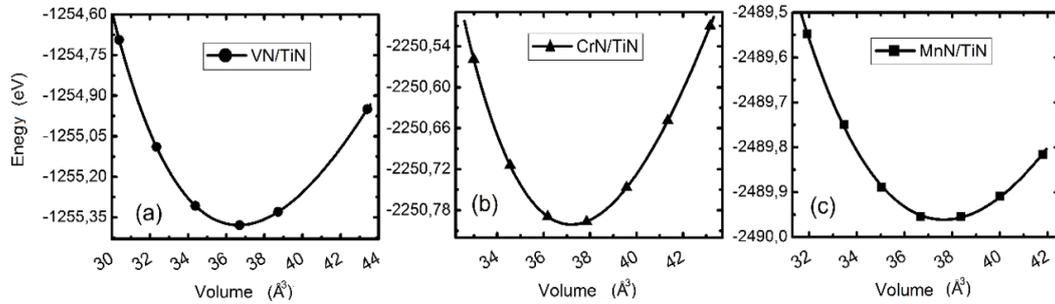

Figure 2. Total energy as a function of volume for the multilayers (a) VN / TiN, (b) CrN / TiN and (c) MnN / TiN. The points are the calculated values and the continuous curve is the adjustment to Murnaghan. Source: authors

Figure 2 shows that the NaCl structure is a stable or metastable phase for each of the multilayers, because each curve has a minimum energy value.

Table 1 shows the values of the network constant, the volume module, the equilibrium volume and the cohesion energy of the binary compounds, calculated in this work and theoretical and experimental values reported by other authors.

Table 1. Structural parameters of the compounds TiN, VN, CrN and MnN

Ccompounds	a_0 [(Å]	V_0 [Å^3]	B_0 [GPa]	E_0 [eV]
TiN	4,242	19,189	272,74	- 1861,439
	4,250[a]	-	277,20[a]	-
	4,247[b]	-	288,00[b]	-
VN	4,122	17,521	304,90	- 1298,579
	4,129[c]	-	306,10[c]	-
	4,140[b]	-	305,3[d]	-
CrN	4,150	18,392	202,20	- 2640,185
	4,140[e]		204,15[f]	-
MnN	4,268	19,695	289,50	- 3118,353
	4,256[g]	-	291,00[c]	-

As can be seen in table 1, the values of the network constants of the binary compounds calculated in this work agree quite well with the values reported in the literature, because they differ by less than 1%. Additionally, the values of the volume modules are in good agreement with those reported by other authors, with the maximum discrepancy of 5.29% for the TiN, 0.4% for the VN and 0.51% for the MnN.

Table 2 lists the values of the structural parameters and the magnetic moment per cell of the multilayers VN/TiN, CrN/TiN and MnN/TiN in the NaCl structure calculated in this work.

Table 2. Structural parameters of multilayers VN/TiN, CrN/TiN and MnN/TiN

Multilayer	a_0 [Å]	c/a	V_0 [Å^3]	B_0 [GPa]	E_0 [eV]	μ (μ_β/cell)
VN/TiN	3,000	1,414	37,655	338,50	- 1255,378	1,10
CrN/TiN	2,990	1,412	37,190	329,25	- 2250,801	2,80
MnN/TiN	2,971	1,411	36,645	323.,51	- 2489,961	3,40

It is observed that the calculated values of the network constants of the three multilayers are close to the same value of 3.0 Å, this can be attributed to the small difference between the atomic radii of the V ions (1.34Å), Cr (1.27Å) and Mn (1.26 Å). Additionally, the values of the volume modules of the multilayers VN/TiN, CrN/TiN and MnN/TiN are high, 338.50 GPa, 329.25 GPa and 323.51 GPa, respectively. These values are greater than the volume modules of the individual binary compounds TiN, VN, CrN and MnN shown in Table 1. This result indicates that the multilayers VN/TiN, CrN/TiN and MnN/TiN have greater rigidity than the binary compounds, so these multilayers can present a better performance in hard coatings than the binary compounds that form them. Additionally, due to their high rigidity they can be potentially used in devices that must operate at high power, high frequencies and high temperatures.

3.1 Electronic properties

The theoretical network constants shown in Table 2 were used to calculate the DOS state density along the high symmetry paths in the irreducible volume in the first Brillouin zone of the multilayers VN/TiN, CrN/TiN and MnN/TiN. Figure 3 shows the total state density (TDOS) and the orbitals that most build near the Fermi level (PDOS partial state density) of the multilayers in the NaCl structure.
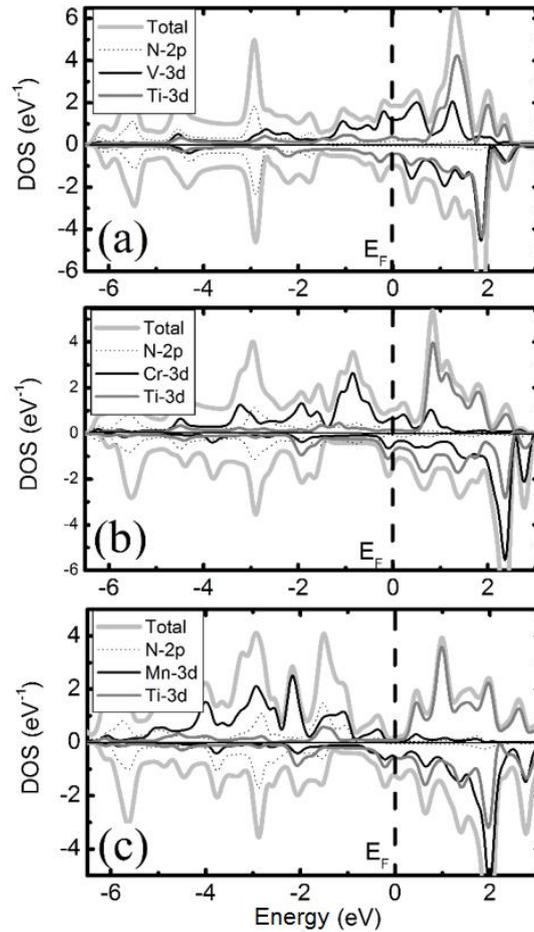
Figure 3. Total and partial state density of the multilayers (a) VN/TiN, (b) CrN/TiN and (c) MnN/TiN. Source: authors

Multilayers have a conductive behavior, because in the valence band near the Fermi level, both the spin density (spin up) and the spin density (spin spin) are metallic, that is, both spin channels they cross at Fermi level. The metallic character of each multilayer is determined by the states 3d-V (3d-Cr and 3d-Mn) in higher contribution and by the 3d-Ti and 2p-N states in lower contribution. The multilayers VN/TiN, CrN/TiN and MnN/TiN have ferromagnetic properties with magnetic moments of 1.10 μ_β, 2.80 μ_β and 3.40 μ_β per cell, respectively. In order to understand the mechanism that stabilizes the ferromagnetic state in each multilayer, the contribution of each atom to the total magnetic moment is calculated. For the multilayer VN / TiN it was found that the main contribution to the magnetic moment (0.85 μ_β) comes from the 3d-V orbital, while the atoms of N atoms and the Ti atom contribute a small part to the total magnetic moment 0.17 μ_β and 0.07 μ_β respectively. For multilayer CrN/TiN the contribution is 2.53μ_β for the Cr atom and 0.19 μ_β and 0.08 μ_β for the N and Ti atoms respectively. While for the multilayer MnN / TiN the contribution of the Mn atom is 3.13 μ_β and it is 0.171μ_β,

and 0.085 μ_β for the N and Ti atoms, respectively. These results indicate that, in each multilayer, the main contribution to the total magnetic moment comes from the 3d states of the atoms of V, Cr and Mn. Therefore, the transition metal atoms V, Cr and Mn induce a finite magnetization in the neighboring atoms of N and Ti, which is reflected in the hybridization of the 3d-V states (3d-Cr, 3d-Mn) and the 2p-N and 3d-Ti states. Consequently, 2p-3d hybridization is responsible for the ferromagnetic coupling in multilayers.

Additionally, in each multilayer the hybridization between the metal states 3d-V (3d-Cr, 3d-Mn) and the non-metallic states 2p-N that cross the Fermi level, they result in a strong covalent bond responsible for the high rigidity of the multilayers [16], [17] and therefore they are responsible for the high hardness of the multilayers.

4 Conclusion

In this work, by means of studies by first principles, the structural and electronic properties of the multilayers VN / TiN, CrN / TiN and MnN / TiN were calculated. It was found that the volume modules of the multilayers are larger than the modules of the individual binary compounds TiN, VN, CrN and MnN that form them, therefore the multilayers are more rigid and consequently they are excellent candidates for applications in hard coatings and in devices that must work high temperatures and high powers. The analysis of the density of states shows that the multilayers VN / TiN, CrN / TiN and MnN / TiN have a metallic behavior with magnetic moments of 1.1 μ_β, 2.8 μ_β and 3.4 μ_β, respectively. The magnetic properties come from the hybridization between the 3d-V states (3d-Cr, 3d-Mn) in higher contribution and the 2p-N and 3d-Ti states in smaller proportion. Finally, the hardness of the multilayers comes from the covalent bonds between the metallic states 3d-V (3d-Cr, 3d-Mn) and the non-metallic states 2p-N.

References

[1] A. J. Freeman, C. Stamplf, Structure and stability of transition metal nitride interfaces from first-principles AlN/VN and AlN/TiN, *Applied Surface Science*, **258** (2012), 5638– 5645.
https://doi.org/10.1016/j.apsusc.2012.02.046

[2] V. Chawla, D. Holec and P. H. Mayrhofer, Stabilization criteria for cubic AlN in TiN/AlN and CrN/AlN bi-layer systems, *Journal Physics D: Applied Physics*, **46** (2013), no. 4, 045305.
https://doi.org/10.1088/0022-3727/46/4/045305

[3] J. Lin, J. J. Moore, B. Mishra, M. Pinkas and W. D. Sproul, Nano-structured CrN/AlN multilayer coatings synthesized by pulsed closed field unbalanced magnetron sputtering, *Surface & Coatings Technology*, **204** (2009), 936–940. https://doi.org/10.1016/j.surfcoat.2009.04.013

[4] J. -K. Park and Y. -J. Ba, Increase of hardness and oxidation resistance of VN coating by nanoscale multilayered structurization with AlN, *Materials Letters*, **62** (2008), no. 16, 2528–2530. https://doi.org/10.1016/j.matlet.2007.12.040

[5] I. W. Kim, Q. Li, L. D. Marks abd S. A. Barnett, Critical thickness for transformation of epitaxially stabilized cubic AlN in superlattices, *Appl. Phys. Lett.*, **78** (2008), 892-894. https://doi.org/10.1063/1.1345831

[6] M. Nordin, M. Larsson and S. Hogmark, Mechanical and tribological properties of multilayered PVD TiN/CrN, TiN/MoN, TiN/NbN and TiN/TaN coatings on cemented carbide, *Surface and Coatings Technology*, **106** (2000), no. 2, 234–241. https://doi.org/10.1016/s0257-8972(98)00544-1

[7] G. A.-R. Garzón and J. R. Martínez, YInN: nueva perspectiva. Estudio de sus propiedades estructurales y electrónicas desde primeros principios, *Tecnura*, **8** (2005), no. 16, 1-14.

[8] P. Giannozzi and S. Baroni, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *Journal Physics: Condensed Matter*, **21** (2009), 395502. https://doi.org/10.1088/0953-8984/21/39/395502

[9] Miguel J. Espitia-Rico, Gladys Casiano-Jiménez, César Ortega-López, Nicolás De la Espriella-Vélez, Luis Sánchez-Pacheco, A Comparative study TiC/TiN and TiN/CN multilayers, *DYNA*, **81** (2014), no. 188, 160-165. https://doi.org/10.15446/dyna.v81n188.41637

[10] C. Stampfl, W. Mannstadt, R. Asahi and J. Freeman, Electronic structure and physical properties of early transition metal mononitrides: Density functional theory LDA, GGA, and screened-exchange LDA FLAPW calculations, *Physical Review B*, **63** (2001), 55106. https://doi.org/10.1103/physrevb.63.155106

[11] R. M. Espitia, J. G. Casiano and C. Ortega, Computaional of the electronic and magnetic properties of 1x1-MN/GaN (M = V, Cr and Mn) multilayers, *International Journal of Physical Science*, **9** (2014), no. 24, 538-544.

[12] R. González, W. López and J. Rodríguez, Estudio AB initio de las propiedades estructurales y electrónicas del nitruro de vanadio VN, *Ciencia e Ingeniería Neogranadina*, **17** (2007), no. 1, 23-33. https://doi.org/10.18359/rcin.1082

[13] I. Povstugar, P. P. Choi and J. P. Ahn, T. Darius and D. Raabe, Interface-directed spinodal decomposition in TiAlN/CrN multilayer hard coatings studied by atom probe tomography, *Acta Materialia*, **61** (2013), 7534–7542. https://doi.org/10.1016/j.actamat.2013.08.028

[14] W. Lopez, C. Ortega and J. Casiano, Estabilidad Relativa del compuesto CrN, *Revista Colombiana de Física*, **41** (2009), no. 3, 580-583

[15] K. Suzuki, T. Kaneko, H. Yoshida, Y. Obi, H. Fujimori and H. Morita, Crystal structure and magnetic properties of the compound MnN, *Journal of Alloys and Compounds*, **306** (2000), no. 2, 66–71. https://doi.org/10.1016/s0925-8388(00)00794-5

[16] H. Jhi, J. Ihm, S. Louie and M. L. Cohen, Electronic mechanism of hardness enhancement in transition-metal carbonitrides, *Nature*, **399** (2000), 132–134. https://doi.org/10.1038/20148

[17] C. Vargas-Hernández, Miguel J. Espitia R, R.E. Báez Cruz, Half-metallic ferromagnetism of ZnxMn1-xO compounds: A first-principles study, *Computational Condensed Matter*, **4** (2015), 1-5. https://doi.org/10.1016/j.cocom.2015.04.001