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Physical Properties of TiNAlN Multilayer ab-initio Study

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Abstract

ab-*initio* calculations were carried out by means of the pseudopotential method, employing computational Quantum Wien2k code in the framework density functional theory, for study the structural and electronic properties of the 1x1-TiN/AlN multilayer. We found that the bulk modullus of the multilayer in high. In addition, the density states reveal that multilayer have a metallic behavior, this metallic behavior is mainly dominated by 3d-Ti orbitals.

Keywords: Density Functional Theory, structural and electronic properties, formation energy.

INTRODUCTIÓN

The multilayer of transition metal nitrides has generated very interest at present and over the past decades. Due to its superior physical and chemical properties, such as: good wear resistance, extreme hardness, high oxidation resistance, high melting point, high thermal stability, excellent thermal and electrical conductivity [1-6]. The multilayer is made of tow layered with the same crystal structure and with the minor mismatch between lattice constant, in despite of this last requirement, very transition metal multilayers has been although the lattices constant of the layered not match. On the other hand, the ground state of the TiN in cubic NaCl with a lattice constant of 4.24 Å [7-9], while the ground state of the AlN is hexagonal wurtzite type, but AlN have a metastable cubic NaCl type with a lattice constant of 4.05 Å [10, 11]. Although, in NaCl structure the lattices constant of the TiN and NaCl not match, (the lattice constants have a mismatch of ~ 4.5%), experimental studies [10, 12, 13] have shown that the TiN/AlN multilayer can be grown. However, the physical properties of the TiN/AlN multilayer are not sufficiently understood, for this reason, we present a detailed study based on density functional theory of the structural and electronic properties of the 1x1-TiN/AlN multilayer.

COMPUTATIONAL METHOD

We performed *ab*-initio calculations using full-potential linearized augmented plane wave (FP-LAPW) method within the framework density functional theory (DFT) [14, 15] as implemented in the Wien2k computational code [16]. The correlation and exchange energies were included with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [17]. The basis function was expanded up to cutoff parameter of $R_{MT}*K_{max} = 8$ (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). Brillouin zone integrations were performed with the special k-point method over a 160 Monkhorst-Pack mesh [18]. For the expansion of the potential in the interstitial region between muff-tin spheres, $G_{max} = 12$ was considered. The spherical harmonics for the charge density was expand up to $l_{max} = 10$ inside the atomic spheres. The radii muff-tin of the atoms were 1.6, 1.8, and 2.0 bohr, for N, Al, and Ti respectively. All the calculations were performed with spin polarization. To simulate the 1x1-TiN/AlN multilayer in the NaCl phase, we intercalate a layer of TiN and a layer of AlN in the direction [001], resulting a supercell belongs to space group 122 (*P4/mmm*) as show fig. 1. 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.

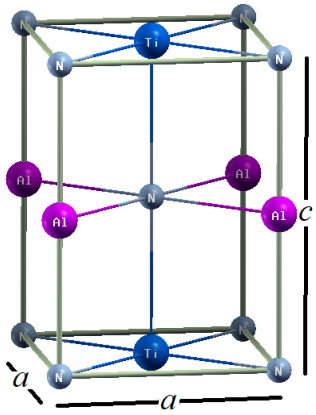

Figure 1. Conventional unit cell for 1x1-TiN/AlN multilayer. Source: Authors

RESULTS AND DISCUSSIONS

Structural properties

To evaluate the equilibrium structural parameters main such as lattice constant, ratio c/a, and bulk modullus of the binary AlN and CrN compounds and the TiN/GaN multilayer, the values energy-volume obtained after the relaxation process were fitted to the Murnaghan equation of state [19]. The equilibrium parameters are presented in table 1 along with available data reported experimental and theoretically for other authors.

Table 1: Lattice constant (a), ratio c/a, and bulk modulus

Compound	Phase	*a*(Å)	*c/a*	B_0 (GPa)
TiN	NaCl	4.2794 4.3200[a] 4.2600[c(exp)]	-	276.7402 297.0000[b] 277.2000[c(exp)]
TiN/AlN	NaCl	3.000	1.4142	250.5880
AlN	NaCl	4.0600 4,0700[d] 4.0500[e(exp)]	-	275.4246 254.3000[d] 295.0000[f(exp)]

[a] [20] Theoretical reference

[b] [21] Theoretical reference

[c] [22] experimental reference

[d] [23] Theoretical reference

[e] [5] experimental reference

[f] [24] experimental reference

We can see in the table 1 the calculated lattice constant and bulk modullus for TiN and AlN compounds are in good agreement with reported from other theoretical and experimental research's. For TiN the maximum discrepancies are ~ 0.95% and ~ 3.901%, respectively. While for AlN the lattice constant (4.06 Å) and bulk modulus (275.4246 GPa) are in excellent agreement with previous theoretically and experimental work, being the maximum discrepancy of ~ 0.25% and ~ 6.63%, respectively. These discrepancies are smaller, which show the reliability of our present calculation.

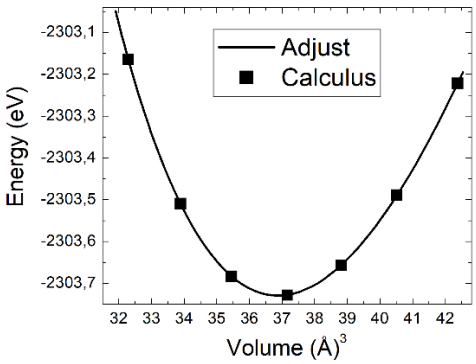

Figure 2. Total energy vs volume. Source: Authors

In the table 1 we note that the value of the bulk modullus of 1x1-TiN/AlN multilayer is high, of the same order of magnitude than the bulk modullus of the binary compounds TiN and AlN, therefore the 1x1-TiN/AlN is quite rigid. This property opens the doors to multilayer for possible applications in hard coatings. In order to check the energy stability of the multilayer we calculated the formation energy, which is defined as the difference between the total energy of the TiN/AlN multilayer, and the total energy of the binary compounds in their ground states, that is, TiN in NaCl and AlN in wurtzite (E_{TiN}^{NaCl} and $E_{AlN}^{Wurtzite}$, respectively); therefore, the energy of formation is given by [25-27]:

$$E_f = E_{TiN/AlN} - (1-x)E_{TiN}^{NaCl} - xE_{AlN}^{Wurtzite} \quad (1)$$

In this case, x = 0.50 because the concentration is 1x1 or 50-50, the total energies are: -2306.7291 eV, -3722.8784 eV, and -866.6618 eV, respectively. The calculated value of formation energy was ~ -1.96 eV. The formation energy is negative, hence the 1x1-TiN/AlN is stable and the moderate value indicate that can be grown easily.

Electronic Properties

To evaluate the band structure and density of states (DOS) of the 1x1-TiN/AlN multilayer the equilibrium lattice constant shown in table 1 was used. The band structure and DOS are presented in fig. 3(a)-(b), respectively. The AlN is a semiconductor material, the band structure show that due to the union of the AlN monolayer with the TiN monolayer, the AlN loses its semiconductor properties, the 1x1-TiN/AlN multilayer have a metallic behavior. The fig. 3(b) show the total and partial DOS. The DOS confirm again that the multilayer have a metallic character. The 1x1-TiN/AlN multilayer in NaCl structure not have magnetism properties because the spin-up channel is symmetric to spin-down channel. In the valence band near the Fermi Level the metallic behavior is mainly dominated by 3d-Ti orbitals.

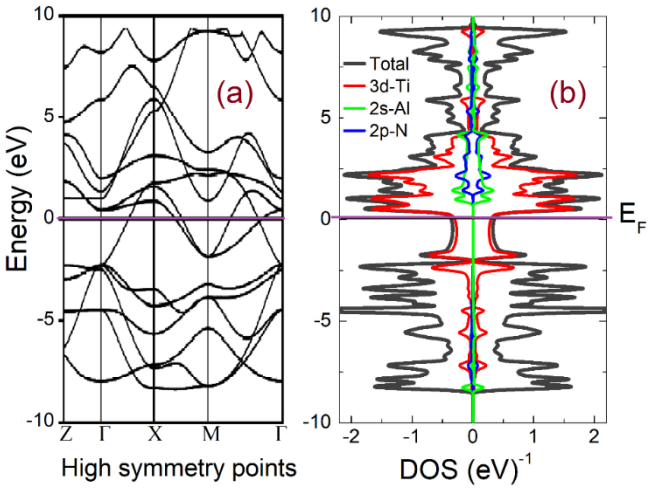

Figure 3. (a) Band structure and (b) total and partial 1x1-TiN/AlN multilayer. Source: Authors.

CONCLUSIONS

This ferromagnetic behavior is mainly dominated by 3d-Cr orbital with a minor contribution of 2p-N orbitals. we studied the structural and electronic properties of 1x1-TiN/AlN multilayer in the NaCl structure, using computational calculation in the framework of the density functional theory. For the structural properties, we found that the bulk modullus of the multilayer is high, this indicate that the multilayer is quite rigid and could be used as hard coating. The density state calculations show that multilayer exhibit a metallic character. This metallic behavior is mainly dominated by 3d-Ti orbitals.

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