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DFT Study of Structural and Electronic Properties of TiN/AlN/TiN Interlayer

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Abstract

First-principles calculations were carried out by means of the pseudopotential method, employing computational Quantum ESPRESO code within density functional theory, for study the structural and electronic properties of the TiN/AlN/TiN interlayer in the rock-salt (NaCl) structure. We found that the bulk modullus of the interlayer is high. In addition, we found that interlayer is energetically stable, with a formation energy of – 2.0 eV/cell. The density states reveal that interlayer have a metallic behavior, this metallic behavior come from hybridization between 3d-Ti and 2p-N orbitals, which are responsible of the high hardness of interlayer.

Keywords: DFT calculations, interlayer, structural and electronic properties, formation energy.

INTRODUCCTION

There is a great interest in the study of photon detector due to applications in different fields of technological importance, such as for X-ray in satellite astronomy, in X-ray medical examination, and in material analysis as component analyzer [1]. Some semiconductor materials as aluminum nitride (AlN) has been used in the photon detector technology. Actually, the scientific community are investigating the next generation of photon detector named superconducting tunnel junctions, which will improve the limitations of the semiconductor detectors as its low energy resolution, because the superconducting tunnel junctions have high energy resolution and wide energy range [1]. Several superconducting tunnel junctions has been successfully obtained, the NbN/AlN/NbN it was grown by means magnetron sputtering technique [2] and recently, Nakayama *et al* [1] grown the TiN/AlN/TiN junction. However, the physical properties, the energetic stability and the change that occur in the AlN and TiN are not sufficiently understood. For these reasons, we present a detailed study based on density functional theory of the structural and electronic properties of the TiN/AlN/TiN junction.

METHODOLGY

We performed first-principles calculations using pseudopotential method [3, 4] within of framework density functional theory (DFT) [5, 6] as implemented in the Quantum ESPRESSO computational code [7]. The correlation and exchange energies were included with the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [8]. For the expansion of the electronic function in plane waves, we used values of kinetic energy cutoff and charge density of 40 Ry and 400 Ry, respectively. Brillouin zone integrations were performed with the special k-point method over a 4×4×6 Monkhorst-Pack mesh [9] for a unit cell. To simulate the TiN/AlN/TiN interlayer in the NaCl- phase, we intercalate two AlN layers between two TiN layers in the direction [001], resulting a supercell belongs to space group 122 (*P4/mmm*). The figure 1 show the unit cell obtained after of relaxation process. 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.

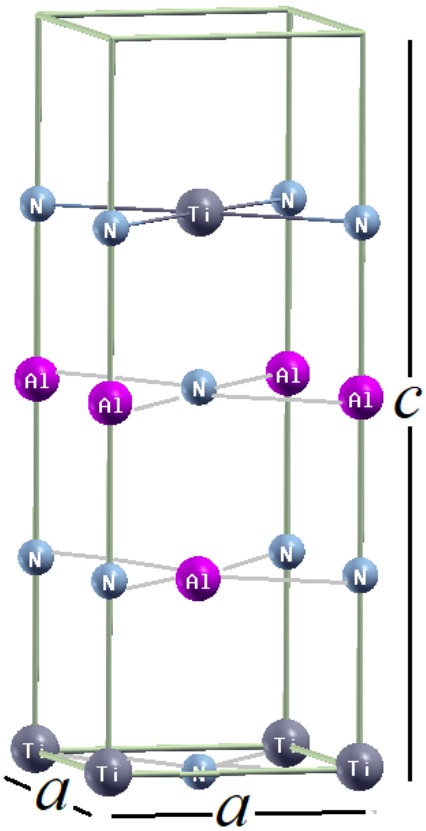

Figure 1. Unit cell for TiN/AlN/TiN interlayer obtained after relaxation process.

RESULTS AND DISCUSSIONS

Structural properties

Table 1. Lattice constant (*a*), ratio c/*a*, and bulk modullus.

Compound	Phase	*a*(Å)	*c/a*	B_0 (GPa)
TiN	NaCl	4.279 4.320[a] 4.2600[c(exp)]	-	276.740 297.00[b] 277.200[c(exp)]
AlN	NaCl	4.060 4,070[d] 4.050[e(exp)]	-	275.424 254.300[d] 295.000[f(exp)]
TiN/AlN/TiN	NaCl	3.00	$2\sqrt{2}$	257.849

[a] [11] Theoretical reference

[b] [12] Theoretical reference

[c] [13] experimental reference

[d] [14] Theoretical reference

[e] [15] experimental reference

[f] [16] experimental reference

The values energy vs volume calculated after relaxation process were fitted with Murnaghan equation of state [10], in order to evaluate the equilibrium structural parameters main such as, lattice constant, ratio c/a, and bulk modullus of the binary TiN and AlN compounds in the NaCl phase and the TiN/AlN/TiN interlayer, The equilibrium parameters are listed in table 1 along with available data reported experimental and theoretically for other authors.

We can see in the table 1, the lattice constant and bulk modullus values for TiN and AlN compounds calculated here, are in good agreement with reported from other theoretical and experimental researches. 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.

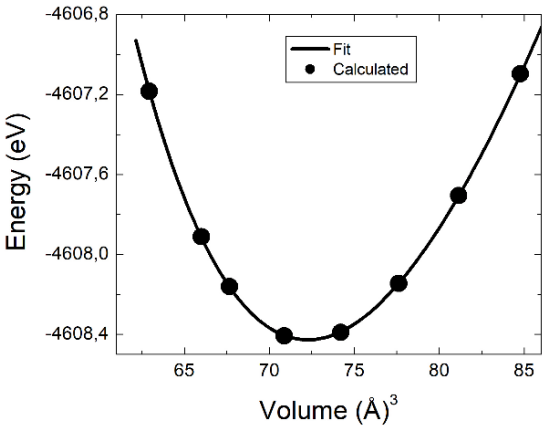

Figure 2. Total energy vs volume

The figure 2 show the energy-volume curve for TiN/AlN/TiN interlayer. The points are calculated values and the curve continues is the fit with Murnaghan equation. As we can see in the figure 2, the energy-volume curve has a local minimum value, therefore the TiN/AlN/TiN interlayer in the NaCl phase is stable or metastable. In addition, In the table 1 we note that the value of the bulk modullus of TiN/AlN/TiN interlayer is high, hence the interlayer is quite rigid. This property opens the doors to interlayer for possible applications in hard coatings. In order to check the energy stability of the interlayer we calculated the formation energy, which is defined as the difference between the total energy of the TiN/AlN/TiN interlayer, 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 [17-19]:

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

In this case, x = 0.50 because the concentration is 50-50 namely, there are two TiN layers and two AlN layers. The calculated value of formation energy was ~ -2.0 eV/cell. The formation energy is negative; hence the TiN/AlN/TiN interlayer is stable, and the moderate value indicate that can be grown easily.

Electronic Properties

The density of states (DOS) of TiN/AlN/TiN interlayer was calculated using the equilibrium lattice constant listed in table 1. The DOS is show in figure 3. It is well known that, the AlN is a semiconductor material, but as we can see in the DOS due to the union of the AlN with the TiN (TiN/AlN/TiN junction), the AlN loses its semiconductor properties, the TiN/AlN/TiN interlayer have a metallic behavior.

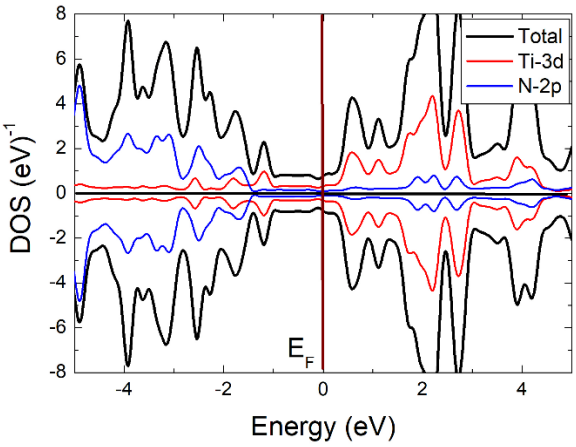

Figure 3. Total and partial TiN/AlN/TiN interlayer

The TiN/AlN/TiN interlayer 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 and 2p-N

orbitals in lesser contribution. Additionally, there is a strong hybridization between metallic 3d-Ti states and nonmetallic 2p-N states, which according to the theory proposed by Jhi et al [20] results in strong covalent bonding p-d, which is responsible of the high hardness of the TiN/AlN/TiN interlayer.

CONCLUSIONS

We studied the structural and electronic properties of TiN/AlN/TiN interlayer in the NaCl structure, using computational calculation within of density functional theory. For the structural properties, we found that the bulk modullus of the interlayer is high, this indicate that the interlayer is quite rigid and could be used as hard coating. The interlayer is energetically stable with a formation energy of –2.0 eV/cell. The density state calculations show that interlayer exhibit a metallic character caused by hybridization between metallic 3d-Ti orbitals and nonmetallic 2p-N orbitals.

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