Research of the structural and electronic properties of VN/AlN/VN and AlN/VN/AlN based on DFT calculation

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Abstract. We investigated the structural, electronic, and magnetic properties of AlN/VN/AlN and VN/AlN/VN interlayers in the wurtzite structure, via first-principles calculations using the pseudopotential method within density functional theory (DFT) as implemented in the Quantum ESPRESSO code. The total energy calculation showed that the VN/AlN/VN interlayer is energetically more favorable than the AlN/VN/AlN one. Analysis of the density of states showed that the interlayers exhibit a metallic behavior that essentially comes from the hybridization and polarization of states V-d and N-p across the Fermi level. The interlayers exhibit magnetic properties, with a magnetic moment of 4μB/cell. Due to these properties, the superlattices can potentially be used in the field of spintronics.

1. Introduction
Aluminum nitride (AlN) normally crystallizes in the wurtzite structure [1, 2]. This material has recently attracted the attention of researchers due to its excellent properties, and has been widely used in the design of light-emitting diodes (LEDs) and laser diodes (LDs) [3] and in electronic packaging material, and has been applied to optical disks as well as lithographic photo masks [4-6]. Due to its stability at high temperature, high degree of thermal conductivity, low thermal expansion, and high resistance to gases and chemicals [7], it has been used in many electronic devices that must function at high temperature and high power and in corrosive environments. Over the last few years, AlN has received extensive attention because of its possible use as a diluted magnetic semiconductor (DMS) with potential applications in the field of spintronics. There is also interest in various applications in spintronics (e.g. electro-optical switches and spin injectors) [8]. In the present paper, we study the structural and electronic properties of AlN/VN/AlN and VN/AlN/VN interlayers in the wurtzite structure.

2. Computational method
Calculations were performed using periodic density functional theory (DFT) as implemented in the plane-wave self-consistent field (PWscf) code in the Quantum ESPRESSO package [9]. The exchange and correlation energies were modeled according to the generalized gradient approximation (GGA) with the Perdew Burke Ernzerhof (PBE) gradient-corrected functional [10]. Electron-ion interactions were dealt with using the pseudopotential method [11, 12]. The electron wave functions were expanded into plane waves with a kinetic-energy cutoff of 40Ry. For the charge density, a kinetic energy cutoff of 400Ry was used. A 6×6×3 Monkhorst-Pack mesh [13] was used to generate the k-
To calculate the lattice constant, the bulk modulus, and the total energy of each studied compound, the calculated data were fit to the Murnaghan equation of state [14], Equation (1).

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

(1)

where \( B_0 \) is the bulk modulus and its first derivative is \( B_0' \), \( V_0 \) is the equilibrium volume of the cell, and \( E_0 \) is the binding energy. In order to study the relative stability of AlN/VN/AlN and VN/AlN/VN interlayers, the energy of formation was calculated. For a ternary compound, the formation energy is defined as the difference between the total energy of the ternary \( M = \text{AlN/VN/AlN} \) (or \( M = \text{VN/AlN/VN} \)) and the total energy of the binary compounds VN-NaCl and AlN-wurtzite in their ground state. Therefore, the formation energy is given by Equation (2) [15, 16].

\[
\Delta E_f = E_{\text{wurtzite}}^M - \left(1 - x\right)E_{\text{NaCl}}^{\text{VN}} - xE_{\text{AlN}}^{\text{wurtzite}}
\]

(2)

The interlayer is modeled as sandwiching two layers of AlN between two layers of VN (or VN between two layers of AlN), and was modeled according to the special quasirandom structures approach [17]. The disorder aspects were ignored.

3. Results and discussions

3.1. Structural properties

In order to obtain the structural properties in the ground state, such as the equilibrium lattice constant \( a_0 \), the bulk modulus \( B_0 \), the \( c/a \) ratio, the total energy \( E_0 \), and the magnetic moment (\( \mu \)) per cell of AlN/VN/AlN and VN/AlN/VN interlayers in the wurtzite structure, the total energy of the compound was minimized as a function of cell volume. The results were fit to the Murnaghan equation of state, Equation (1). Figure 1 shows the total energy-volume curves for the interlayers.

![Figure 1. Total energy as a function of the volume for the AlN/VN/AlN and VN/AlN/VN interlayers.](image-url)

The VN/AlN/VN interlayer has a lower minimum value of total energy than the AlN/VN/AlN interlayer; therefore, the VN/AlN/VN interlayer is energetically more stable.

The lattice constant, the \( c/a \) value, the bulk modulus \( B_0 \), the total energy \( E_0 \), and the magnetic moment (\( \mu_0 \)) per cell are listed in Table 1.
We note that the values of the bulk modulus of the interlayers are high. These values are close to the bulk module of AlN [17] and VN in the wurtzite structure [18]; hence the interlayers are quite rigid, making them good candidates for possible applications in devices operated at high temperature and high power, as well as in hard coatings. The energy difference between VN/AlN/VN and AlN/VN/AlN is -273.2meV, so in the ground state the VN/AlN/VN interlayer has lower energy than the AlN/VN/AlN. In order to verify the relative stability of the VN/AlN/VN and AlN/VN/AlN interlayers, we calculated the corresponding formation energy, using Equation (2). We calculated the total energy $E_{VN}$ and $E_{wurtzite}$ in their ground states. The values are -2631.48eV and -2715.234eV, respectively. Table 2 shows the calculated values of the formation energy $E_f$.

According to the results shown in Table 2, the smallest value of the energy of formation corresponds to the VN/AlN/VN interlayer; therefore, it is the most energetically stable structure. Additionally, the moderate formation-energy values indicate that the compounds can easily be grown experimentally. These results for the energy of formation are important, because if one knows these values, growing conditions can be improved, and therefore a VN/AlN/VN interlayer of excellent quality can be grown.

Figure 2 shows the crystal structure of the VN/AlN/VN interlayer obtained after structural relaxation. For both the VN/AlN/VN interlayer and the AlN/VN/AlN interlayer, the space group obtained is the same: tetragonal structure 156 (P3m1).

**Figure 2.** Unit cell of the VN/AlN/VN interlayer after structural relaxation.
3.2. Electronic properties

Figure 3 shows the total density of states (TDOS) and partial density of states (PDOS) of the orbitals that contribute most near the Fermi level of the VN/AlN/VN interlayer. The calculations were performed with spin polarization up and down.

![Graph showing total and partial density of states of the VN/AlN/VN interlayer in the wurtzite structure.](image)

**Figure 3.** Total and partial density of states of the VN/AlN/VN interlayer in the wurtzite structure.

The interlayer exhibits a metallic behavior due to the fact that the valence orbitals cross the Fermi level. This metallic behavior is determined by the V-3d state. The interlayer exhibits magnetic properties, with a total magnetic moment of $4\mu_B$ per supercell. Since there are two vanadium atoms in the supercell, this corresponds to $2\mu_B$/V-atom. The magnetic moment is due to the $V^{3+}$ configuration (with electronic configuration [Ar]3d$^2$). This implies that when the V atom is in the interlayer, it gives up three electrons, and two valence electrons remain (d$^2$ configuration). These valence electrons couple, and as a result the two electrons produce a total magnetic moment of $2\mu_B$/V atom. Touati et al. [19] reported a valence of $V^{3+}$ for infrared luminescence in V-doped GaN samples grown with MOVPE on a sapphire substrate.

4. Conclusions

We carried out a study of AlN/VN/AlN and VN/AlN/VN interlayers using density functional theory (DFT) within the pseudopotential framework. The total energy calculation showed that the VN/AlN/VN interlayer is more energetically favorable than the AlN/VN/AlN one. The values of the bulk modules of the interlayers are high, close to the bulk modules of AlN and VN in the wurtzite structure. This 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 in hard coatings. Analysis of the density of states shows that the interlayers exhibit a metallic behavior that essentially comes from the polarization of V-3d states that cross the Fermi level. The interlayers exhibit magnetic properties, with a magnetic moment of $4\mu_B$/cell. Due these properties, the interlayer can potentially be used in the field of spintronics.
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