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Structure and stability of transition metal nitride interfaces from first-principles: AlN/VN, AlN/TiN, and VN/TiN

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ABSTRACT

We perform first-principle density-functional theory calculations using the full-potential linearized augmented plane wave method to investigate the formation, atomic and electronic structure, and stability of the metal–nitride interface systems, (1 0 0) AlN/TiN, AlN/VN, and VN/TiN in the rocksalt structure. We also determine the surface, interface, and strain energies, of the constituent materials, as well as the layer-dependent interaction energy between the adlayer surface and the interface. We find that this latter interaction, while typically not taken into account, plays an important role in terms of the formation energy for the initial stages of film growth. Using these energy quantities we calculate the film formation energy as a function of thicknesses, where we find that the growth of TiN on VN has the lowest formation energy, followed respectively by AlN on VN, and AlN on TiN. The formation energy of the latter two systems is notably higher due to the significantly higher energy of the metastable rocksalt phase of AlN compared to the stable wurtzite structure. From our calculations, together with experiment, we can predict the values of the interface energy of wurtzite-AlN on VN(1 0 0) and TiN(1 0 0).

1. Introduction

There has been much interest in recent years aimed at developing new and improved super- and ultrahard materials [1–8]. Such structures are clearly of high technological relevance but are also fundamentally interesting with regard to understanding the mechanisms responsible for the extreme hardness. One approach of achieving superhardness (e.g. 40 GPa) involves the ability to deliberately stabilize metastable and stable structures according to desire on an atomic level. This affords tremendous potential for the control of the physical, chemical, and mechanical properties of a system. The realization of this objective is becoming increasingly achievable due to advancement in new experimental techniques as well as to theoretical methods that are able to reliably predict the atomic and electronic properties of increasingly complex structures. Strained-layer superlattices are an example, in particular, where precise control of the grown materials can be obtained, and where often the formed structures are not in thermodynamic equilibrium but are "epitaxially stabilized" in a metastable state. Such man-made structures have no analogue in nature and exhibit properties that are neither observed for the constituents nor their alloys.

In this respect, transition metal nitride superlattices of nanoscale dimensions are of great technological interest, e.g., in the area of wear-resistant coatings for mechanical applications such as cutting tools, not only due to the unique physical properties of their constituent compounds, which include high mechanical hardness, wear resistance, chemical inertness, good electrical conductivity, and in some, relatively high superconducting transition temperatures, but also because these fabricated structures can exhibit enhanced hardness that far exceeds that of the constituent materials. This was demonstrated for VN/TiN superlattices by Helmersson et al. [9] as well as for other systems, e.g., Nb/TiN [10], and magnetic structures, e.g. Mo/NbN [11]. Furthermore, for AlN/VN [12–14] and AlN/TiN [15] superlattices, it has been found that only for the *metastable* rocksalt phase of AlN does the hardness enhancement occur. In this case, only relatively thin regions of AlN can be stabilized in the rocksalt structure. At a critical thickness a phase transition occurs and AlN transforms into the stable wurtzite structure, resulting in a loss of hardness. Thus, it is of high interest and importance to understand the factors that govern the delicate energy balance between various contributions which determine the behavior of the system.

An alternative design concept for obtaining super- and ultrahard, and thermally stable, coatings exploits the natural formation, through spinodal decomposition, of a strong interface between nanocrystalline (*nc*) and amorphous regions (*a*) e.g. the "*nc*-TiN/*a*-Si_3N_4" system [16–18]. In these nanocomposites, the crystalline regions are separated by a very thin layer of SiN_x and exhibit a

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maximum hardness when the crystalline TiN regions are of the order of 3–4 nm in diameter. The interfaces are thought to prevent grain boundary sliding and dislocation propagation, and to contribute to the found significant enhancement in the hardness as compared to the pure constituents.

In the present paper we perform first-principles density-functional theory calculations to investigate the strained (1 0 0) AlN/VN, AlN/TiN, and VN/TiN systems, which form sharp epitaxial interfaces and represent ideal structures for fundamental study [9,12–15,19]. In particular, we analyze the role and magnitude of the different energy contributions constituting the adlayer formation energy, namely, film and substrate surface energy, interface energy, strain energy, and a layer-dependent surface–adlayer-interface interaction energy, which all together ultimately dictate the nature and stability of the structures. The paper is organized as follows: In Section 2 details of the calculation method are described along with the definitions of various quantities. In Section 3 results are presented for the atomic and electronic properties, and energetics of the bulk, surfaces, and interfaces. Section 4 contains investigations of the adlayer formation energy as a function of layer thickness, and the conclusions are given in Section 5.

2. Calculation method

The total energy calculations are performed using the all-electron full-potential linearized augmented plane-wave (FLAPW) method [20–22] and the local-density approximation for the exchange-correlation functional [23]. Angular momenta up to $l_{max} = 8$ in the muffin-tin spheres are used for both wave functions and charge density in the self-consistent procedure. The respective muffin-tin radii for N, V, Al, and Ti are 1.4, 2.2, 2.0, and 2.4 Bohr. We use an energy cutoff of 16.4 Ry for the plane-wave expansion of the wave-function in the interstitial region and a Monkhorst–Pack **k**-point set of $10 \times 10 \times 2$ for calculations of surface and interface properties. For the bulk calculations we take equivalent **k**-points to maximize the accuracy. Five layers of each material are used for the interface systems. The surface energies are obtained using eleven layers in the "two-dimensional" film geometry of the FLAPW method. Atomic relaxation of all atoms is performed and we consider the structures fully relaxed when the force on each atom is less than 1 mRy/Bohr. Convergence tests were carried out with regard to **k**-points and the number of substrate layers, in order to ensure the accuracy of our calculations [24].

In a simple model, when one material is grown on another, the type of structure that forms depends on the energies of the surface of the epitaxial layer, $\sigma_{\rm ad}$, that of the substrate surface, $\sigma_{\rm sub}$, and the interface energy between the substrate and the layers, $E_{\rm int}$: If $\sigma_{\rm ad} + E_{\rm int} < \sigma_{\rm sub}$, i.e. if $\sigma_{\rm ad} - \sigma_{\rm sub} + E_{\rm int} < 0$, then the system is stable against break-up of the layer and "layer-by-layer" (Frank–van-der-Merwe) growth results. If $\sigma_{\rm ad} + E_{\rm int} > \sigma_{\rm sub}$, i.e. if $\sigma_{\rm ad} - \sigma_{\rm sub} + E_{\rm int} > 0$, then the system is unstable and either island formation will occur from the first layer (Volmer–Weber, island growth mode) or if the initial layer is constrained by the substrate, then only after several layers have grown epitaxially will subsequent layers break-up into islands (Stranski–Krastanov, layer plus island growth mode) [25]. If the epitaxial layer is strained, then the so-called formation energy, E_f, of the film will include a contribution from this strain energy, $E_{\rm strain}$, which will increase with increasing layers, that is,

$$E_f(h) \simeq \sigma_{\rm ad} - \sigma_{\rm sub} + E_{\rm int} + hE_{\rm strain}. \tag{1}$$

Here h is the number of layers and $E_{\rm strain}$ is the strain energy per unit cell of an adlayer. For a *small* number of adlayers this equation may break down because the surface energy of the adlayer cannot be assumed to have reached the value corresponding to a thick adlayer. We therefore add a layer-dependent term, $E_{i-s}(h)$, to Eq. (1) that represents the interaction energy between the interface and the surface of the adlayer [26], which must tend to zero as h becomes large. The resulting expression for the adlayer dependent formation energy is then,

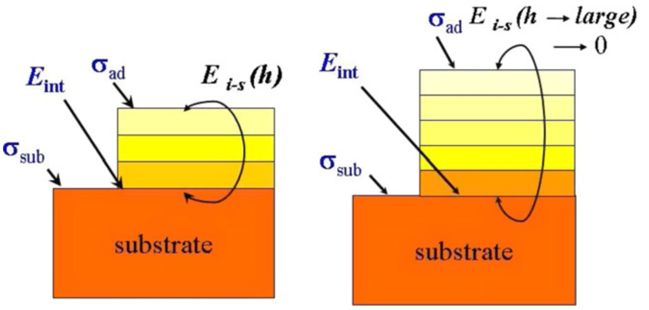

Fig. 1. Illustration of adlayers on a substrate and the associated energy quantities. Left: a small number of adlayer h and right, as h becomes large, the adlayer-surface–interface interaction, E_{i-s}, becomes negligible.

$$E_f(h) = \sigma_{\rm ad} - \sigma_{\rm sub} + E_{\rm int} + E_{i-s}(h) + hE_{\rm strain}. \tag{2}$$

In the present work, using first-principles calculations we determine these various energy quantities for the three systems, (1 0 0) AlN/VN, AlN/TiN, VN/TiN. Through *direct* calculation of the formation energy (cf. Eq. (3)) for systems with a few adlayers, we can determine the quantity $E_{i-s}(h)$ and investigate its importance as compared to the more simple expression (Eq. (1)) which neglects this contribution.

The formation energy of h adlayers on a substrate can be calculated directly from first-principles as,

$$E_f^{\rm direct}(h) = \frac{1}{2}(E^{\rm tot}_{{\rm ad}/sub} - E^{\rm tot}_{\rm sub} - 2hE^{\rm tot}_{{\rm ad}.bulk}), \tag{3}$$

where $E^{\rm tot}_{{\rm ad}/sub}$ is the total energy of the h-adlayer/substrate system, $E^{\rm tot}_{\rm sub}$ is the total energy of the substrate, and $E^{\rm tot}_{{\rm ad}.bulk}$ is the bulk total energy of the adlayer material at the equilibrium lattice constant. The factors 1/2 and 2 arise due to the fact that inversion symmetry is employed in the calculations and the adlayers are created on both sides of the substrate slab.

The expressions for the surface energy of the substrate and the (thick) adlayer film are given below,

$$\sigma_{\rm sub} = \frac{1}{2}(E^{\rm tot}_{\rm sub} - nE^{\rm tot}_{\rm bulk}), \tag{4}$$

$$\sigma_{\rm ad} = \frac{1}{2}(E^{\rm tot}_{{\rm str}-ad.slab} - nE^{\rm tot}_{{\rm str}-ad.bulk}), \tag{5}$$

where n is the number of layers used to calculate the surface energy and $E^{\rm tot}_{{\rm str}-ad.bulk}$ and $E^{\rm tot}_{{\rm str}-ad.slab}$ are the total energies of a strained bulk stoichiometric unit of the adlayer material, and the slab of strained adlayer material, respectively. The strain and interface energies are defined as,

$$E_{\rm strain} = E^{\rm tot}_{{\rm str}-ad.bulk} - E^{\rm tot}_{{\rm ad}.bulk}, \tag{6}$$

$$E_{\rm int} = \frac{1}{2}(E^{\rm tot}_{\rm interf} - nE^{\rm tot}_{\rm bulk} - mE^{\rm tot}_{{\rm str}-ad.bulk}), \tag{7}$$

where $E^{\rm tot}_{\rm bulk}$ and $E^{\rm tot}_{\rm interf}$ are the calculated total energies of a bulk stoichiometric unit of the substrate material and the interface system, consisting of n substrate layers and m layers of the adlayer material. The various energy quantities are illustrated in Fig. 1. Using the expressions Eq. (3) to Eq. (7), and in the limit of a large number of adlayers h, Eq. (1) can be derived.[1] The term $E_{i-s}(h)$ is determined as the difference between Eqs. (1) and (3). Once $E_{i-s}(h)$ is found, Eq.

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[1] From the substitution of $E^{\rm tot}_{\rm sub}$ from Eq. (4) and $E^{\rm tot}_{{\rm ad}.bulk}$ from Eq. (6) into Eq. (3),