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Interface-induced electronic structure toughening of nitride superlattices

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ABSTRACT

We report on first-principles study of uniaxial strength for brittle cleavage of AlN/VN, AlN/TiN and VN/TiN systems. In agreement with previous studies we predict that the VN/TiN exhibits interface induced toughening of VN as compared to bulk values, and a similar effect is predicted also to occur in the VN/AlN system. However, a more detailed insight reveals, that the theoretical critical stress for brittle cleavage largely oscillates (even below the critical stress for bulk) with the distance from the interface inside the VN layer, a phenomenon not present (or hugely reduced) in TiN and AlN layers. The oscillating values for critical stress well correlate with the same behavior of interplanar distances and charge density. The origin of these unexpected properties was pinpointed to structural instabilities of cubic VN.

1. Introduction

The ever more demanding application conditions call for new systems with properties over-performing current materials. In addition to alloying and self-organization, a multilayer architecture is a perspective concept to reach these goals. For example, it has been shown that TiN/VN superlattices with bi-layer period in a range of several nanometers yield hardness values higher than either of the constituent materials [1]. Similarly, AlN/CrN system has been reported to exhibit increased hardness [2] with respect to the AlN or CrN alone. Recently, Hahn et al. [3] reported on a peak in hardness and toughness as functions of the bi-layer period of TiN/CrN superlattice.

No doubt, *ab initio* calculations are nowadays not only capable of reproducing experimental data, and hence helping with their interpretation, but also have predictive power, and can be effectively used for predicting trends of various material properties. Particularly in the field of nitride-based protective coatings, the symbiosis between experiment and quantum mechanical modeling has proven extremely successful in the past years, providing rich information about phase stability, elasticity, or electronic properties (e.g., Refs. [4–7] and references therein). With the increasing available computational power, it becomes feasible to treat larger system such as superlattices also on the *ab initio* level [8–13]. There is, however, only a limited number of theoretical works investigating the effect of the superlattice design on their ideal strength. One such example was the pioneering study by Lazar et al. [14].

The questions which ultimately motivated the present work were: What is the weakest link in a perfect superlattice? Is it the material with smaller toughness, the interface, or is the answer yet more complicated? With this paper we aim on a detailed exploration of the interface impact on the ideal strength of nitride superlattices.

We focus on a rocksalt structure (B1, NaCl prototype, space group #225, $Fm\bar{3}m$), which is a stable configuration of TiN, a prototype hard coating material [15]. Industrially important is the metastable supersaturated solid solution $Ti_{1-x}Al_xN$ [16], nevertheless TiN/AlN, TiN/CrN, and CrN/AlN multilayers have also attracted significant attention due to their extraordinary properties [2,3,17-20]. To avoid struggling with magnetism of CrN [13,21-25], we choose AlN as the second system for the present study. AlN crystallizes in a wurtzite B4 structure (ZnS prototype, space group #186, $P6_3mc$), but can be stabilized in the rocksalt structure by coherency stresses present in the superlattices [2,3,17-19,26-28]. In contrast to metallic TiN, AlN (in both, wurtzite and cubic phases) is a wide band gap semiconductor with a strong covalent bonding character. Finally, a third system,

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VN, was chosen as a benchmark to compare our results with the literature [14] as well as to provide an insight into the impact of the lattice mismatch, since the lattice constant of cubic B1 VN lies between the values of TiN and AlN. Surface and formation energies of various combinations of these three nitrides were studied by Stampfl and Freeman [20] who, however, did not address their cleavage properties.

2. Methods

Epitaxial superlattices consisting of various combinations of cubic AlN, TiN, and VN having a common (001) plane as the interface, were loaded along the [001] direction. Brittle cleavage along (001) planes was simulated by splitting a particular system into two rigid blocks. The cleavage energy, E_c, was obtained by fitting the thus obtained total energy of the system, E, as a function of the separation, x, with the universal binding energy relation [29]

$$E(x) = E_c[1 - \left(1 + \frac{x}{l}\right)\exp\left(-\frac{x}{l}\right)]. \quad (1)$$

The above fit also provides the critical length, l, i.e., the separation at which the stress σ perpendicular to the cleavage plane (causing the separation) reaches its maximum, σ_c. This cohesive stress is given as

$$\sigma_c = \left.\frac{dE}{dx}\right|_{x=l} = \frac{E_c}{el} \quad . \quad (2)$$

The total energy, E, was computed from first principles using the Density Functional Theory as implemented in the Vienna Ab initio Simulation Package (VASP) [30,31] employing a plane wave basis set. Electron-ion interaction was described with pseudopotentials supplied with VASP [32] which are compatible with the projector augmented waves method. The plane-wave cut-off energy was set to 600 eV which together with a 15 × 15 × 1 Monkhorst-Pack mesh sampling the first Brillouin zone guarantee accurate total energies and forces. The solution was considered sufficiently converged when the total energy values computed in two consecutive steps of the self-consistent cycle differed less than 10^{-6} eV. Whenever we optimized the structure, forces acting on atoms were relaxed below $5{\cdot}10^{-4}$ eV/Å. The exchange-correlation energy was evaluated within the generalized gradient approximation (GGA) parametrized by Perdew and Wang [33].

The brittle cleavage of the cubic nitrides was modeled using a tetragonal (periodically repeated) cell consisting of either two slabs of nitrides (hereafter referred to as "superlattice") to simulate a bulk region of a multilayer, or two slabs separated by 20 Å of vacuum (hereafter labeled as "bi-layer") both illustrated in Fig. 1. In the latter case, the positions of the surface atoms were fixed (in the (001) plane by the crystal symmetry) in order to simulate bulk region of a stable material in which any interface-induced displacements shall vanish. The reason for using the bi-layer configuration instead of a full superlattice one is to keep the overall simulation box dimensions constant in all calculations, and hence to minimize any numerical errors. The impact of this assumption will be discussed later. Each (001) plane contains 1 metal and 1 N atom, i.e., the supercell vectors are along the [1$\bar{1}$0], [110], and [001] directions (with respect to a reference conventional cubic coordination frame). According to tests we made, twelve atomic planes, i.e. 24 atoms, (as illustrated in Fig. 1) are sufficient to build a representative model of the nitride multilayers. Unless stated otherwise, we used the same number of atoms for all the presented calculations.

Nitrides for protective coating applications are typically synthesized by physical vapor deposition techniques. In order to obtain superlattices with a well defined epitaxial relationship between individual layers, the deposition process has to be adjusted with a special care. One of the important parameters is the substrate selection, acting as a seed for well orientated growth. Experimental experience shows that an MgO(001) substrate is particularly suitable to trigger the growth of (001) orientated TiN [34]. Consequently, in all our simulations we fixed the interface in-plane lattice parameter (in the (001) plane) to the experimental value of the MgO lattice parameter (4.22 Å), while the structures were relaxed in the perpendicular [001] direction.

3. Results and discussion

3.1. Bulk VN, TiN, AlN phases

In order to check the accuracy of our calculations, we have computed the equilibrium lattice constant, a_0, and the single crystal elastic constants, C_{11}, C_{12} and C_{44}, of studied cubic nitrides (see Table 1). The values are in good agreement with other theoretical [14,35,36] as well as experimental [37,38] data. Experimental values for cubic AlN are missing since its stable bulk form is the hexagonal wurtzite structure. The largest difference with respect to experimental data is 24% obtained for C_{12} of VN. On the other hand, the technologically more important tetragonal shear modulus, $C' = (C_{11} - C_{12})/2$, reaches the difference of only 11% between our and the experimental value.

For predicting cleavage properties of each of the considered material systems, supercells consisting of twelve (001) layers were constructed within the periodic boundary conditions to form a bulk crystal. To stay consistent with later reported results for two-phase systems, also in this case of single-phase systems we fixed their in-plane lattice parameter to that of MgO(001), while the lattice

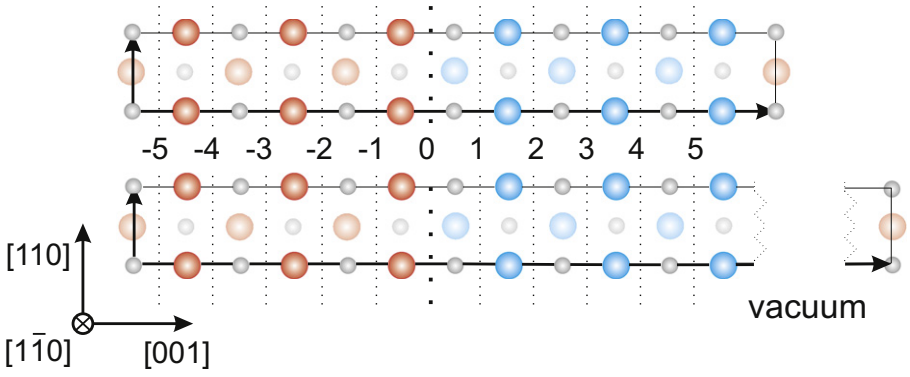

Fig. 1. Two types of cells used in our calculations. The upper one called "superlattice" consists only of stacks of (001) planes. Cell referred to as "bi-layer" contains also vacuum slab (on the right). The numbered vertical dotted lines mark considered positions of cleavage planes.