

Thickness-dependent structural transformation in the AlN film

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Abstract

We report the nature of the thickness-dependent structural transformation in AlN film. The non-equilibrium cubic AlN, which normally exists under high pressures of more than 22.9 GPa, can be epitaxially stabilized in ambient atmosphere in the form of thin films grown on TiN substrate. A critical thickness, ≈ 1.95 nm, at which the pseudomorphic growth cannot be preserved and after which the cubic phase transforms into its hexagonal counterpart, has been quantified. Details of the structural transformation were simulated. The present studies, by means of crystal-chemical atomic dynamics based on the first-principles calculations, provide in situ physical details on an atomic scale of the thickness-dependent structural transformation, which are hardly observed in experiments.

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1. Introduction

Structure and properties, and the relationships between them, have been the major concerns in materials. In addition, it has become known that the physical properties of a material in the form of thin film may oscillate with thickness [1–5]. Recently, such an oscillation due to the quantum size effect was demonstrated quantitatively by Guo et al. [6] who investigated the thickness-dependent modulation of superconductivity in a Pb film. In terms of structural issues, it has long been understood that a non-equilibrium phase, whether metal or ceramic, could be epitaxially stabilized in thin films grown on a substrate whose lattice parameter was close to that of the film. Such a pseudomorphic growth could be preserved up to a certain thickness. For example, as early as the 1960s, researchers recog-

nized that films of face-centered cubic cobalt with several nanometers could be obtained if the metal was deposited on a copper substrate [7]. In recent years, non-equilibrium cubic B1-AlN [8], a potential candidate for application in microelectronics, was stabilized in the form of thin film epitaxially grown on TiN substrate and a structural transformation from cubic to hexagonal AlN was observed when the film was over a critical thickness of several nanometers [9–12]. For example, Madan et al. [9] applied ultrahigh vacuum direct current magnetron sputtering and stabilized the cubic AlN in epitaxial AlN/TiN superlattices with AlN layer thickness ≤ 2.0 nm. Kim et al. [10] used reactive sputtering and produced a 2.0–2.5 nm cubic AlN layer. And Pankov et al. [11] obtained a 1.0 nm cubic AlN layer using room temperature pulsed laser deposition. Despite some experimentally accumulated data in the past decades, a quantitative description on an atomic scale on this thickness-dependent phenomenon has been lacking. In this paper, we provide physical details on the pseudomorphic growth and the thickness-dependent structural

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transformation of cubic AlN grown on TiN substrate by means of crystal-chemical atomic dynamics (AD) simulations based on first-principles calculations. Since the size-effect in a thin film with a constant structure may modulate physical properties, a structural transformation in the film is believed to result in a new spectrum of oscillating properties. The present study is expected to provide some fundamental information on establishing relationships between structure, property, and size-effect of the low-dimensional nano-materials.

2. Computational method and model

Cross-sectional high-resolution transmission electron microscopy (HRTEM) studies confirmed that the non-equilibrium cubic AlN, structurally isotypic with TiN, could be epitaxially grown on TiN(001) substrate. Details of the film growth were reported in our previous publication [13]. The multilayer samples for cross-sectional HRTEM observation were prepared by the conventional method, i.e., by slicing, grinding, dimpling, and finally ion-milling. A JEOL 2010 high-resolution electron microscope operated at 200 kV was used for lattice imaging. Fig. 1 shows an HRTEM image taken at the B1-AlN/TiN interface along [010] direction, from which a pseudomorphic growth is clearly seen. The two nitrides, whose interface is marked with a pair of white arrows, have parallel orientation relationships. Such an experimental image provides a geometrical configuration for which chemical bonding across the interface is to be established.

The first-principles calculations in the present study, based on the plane wave pseudopotential (PWPP) method [14], clarified that the atomistic bonding of Al to N and N to Ti across the interface is energetically favorable, which is the same as in the case of the TiN/MgO system [15]. Based on the PWPP calculations, we construct an initial B1-AlN/TiN(001) superlattice cell, as shown in Fig. 2, to simulate the pseudomorphic growth and structural transformation by using the total energy minimization criterion in AD relaxation. The supercell is composed of

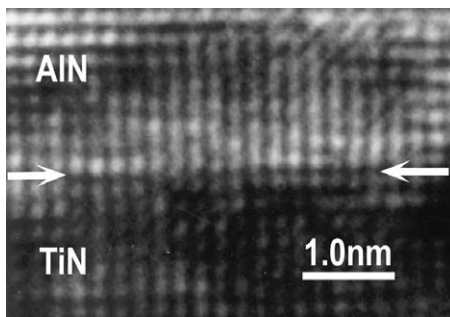


Fig. 1. [010] HRTEM image taken at the interface of B1-AlN/TiN showing a pseudomorphic growth of AlN on TiN(001).

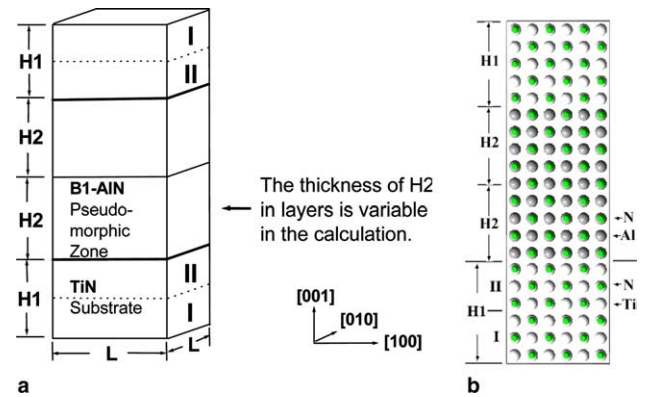


Fig. 2. (a) Scheme of the B1-AlN/TiN(001) superlattice cell used in the present calculations. (b) A structural projection showing atomic configurations in the initial supercell before relaxation. Here, H2 is designated as 5 MLs and N, Al, and Ti atoms near the interface are labeled.

two H1 zones: each of them has 6-monolayer (6-ML) TiN, in which 3-ML is designated bulk-like (H1 I) for TiN substrate and all atoms in it are fixed; another 3 MLs are close to the interface (H1 II) in which the atoms can be relaxed. The H2 + H2 zone of B1-AlN with a variable number of layers is confined by the two H1, forming two coherent interfaces with interfacial spacing of 2.0 Å [9]. The size of the initial supercell is $L \times L \times (2H1 + 2H2)$ Å³, the length L in the horizontal [100] and [010] directions is 12.72 Å but H2 in [001] direction is chosen as 3, 5, 7, 9, 11 or 15 MLs in the present calculations. Periodic boundary conditions are applied in the [100] and [010] directions but there is a fixed boundary condition in the [001] direction. The relaxation of atomic positions is allowed only for the atoms in the H2 and H1 II zones.

For ionic crystals, long-range interaction can be described in terms of the Coulomb interaction potential, while the short-range interaction is expressed by the Pauli repulsive potential. The potential function is given in [16–18]. Based on the bond valence concept [16], we simulated the dynamic behaviors in the B1-AlN/TiN(001) supercell, in which the simulation was implemented with the Aix-la-Chapelle's crystal chemical atomic dynamics computer (aixCCAD) code [17–19]. All simulations were performed for the case of an NVT ensemble, whereby the number of particles N , the volume V and the temperature T can be set to desired values. The simulating temperature was chosen as 300 K. The interatomic forces for determining the relaxed atomic positions were calculated by the velocity Verlet algorithm [20]. The summation over the Coulomb interactions was done using the Ewald summation technique [21]. A cut-off radius 6.0 Å turned out to be appropriate with respect to both speed and accuracy. To ensure a full relaxation of each mode with the H2 regions of 3, 5, 7, 9, 11 and 15 MLs, the time step chosen was 0.001 ps and the total simulation time was up to 300,000 time steps.

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