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Dissociative adsorption of ammonia on the $ZrB_2(0001)$ surface

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ABSTRACT

Zirconium diboride has been proposed as a viable substrate for epitaxial growth of group III nitrides. In many methods of nitride growth on ZrB_2 surfaces, ammonia gas is the nitrogen source. Here we use X-ray photoelectron spectroscopy at a series of fixed temperatures from room temperature to 535 °C and density functional theory to study the dissociative adsorption of ammonia on the $ZrB_2(0001)$ surface. A significant increase is observed between ~250 and ~400 °C for the deposition of nitrogen, which can be desorbed by annealing between 950 and 1150 °C. Two components of the N 1s peak are observed and are associated with bonding of nitrogen to boron or to zirconium. Comparison of spectra obtained at two different emission angles suggests that more N is bonded to B than to Zr at the surface and when boron is bonded to nitrogen, it migrates towards the surface. This may be a factor in limiting group III nitride epitaxial growth on the $ZrB_2(0001)$ surface.

1. Introduction

Group-III nitride semiconductor devices have been widely used for applications in visible and ultraviolet optoelectronics and in high-power and high-frequency electronics. The group-III nitrides are often prepared in the form of thin films grown on various substrates. However, the substrates typically used, sapphire, SiC and Si, have a large mismatch of lattice constant and of thermal expansion coefficient with the heteroepitaxial nitride layers. This causes a high density of threading dislocations [1]. As dislocations are carrier scatterers [2], trap centers [3,4], and leakage current sources [5,6], device performance is often lowered with increased dislocation densities. Furthermore, excess structural strain in the films may lead to the formation of cracks and strong built-in electrostatic fields [7,8]. Therefore a material that closely matches the nitride's lattice constant and thermal expansion coefficient is highly desirable [9]. Recently ZrB_2, a refractory compound with good lattice constant and thermal expansion matches to GaN, has been proposed as a viable substrate for its epitaxial growth [9–11]. Furthermore, ZrB_2 is reflective and metallic, and its use as a substrate in light emitting diodes (LEDs) minimizes loss of light and simplifies the device geometry as ZrB_2 can be used as one of the ohmic contacts [12]. The crystal structure of bulk ZrB_2 is simple hexagonal with alternating layers of boron and zirconium as shown in Fig. 1. Therefore, the (0001) surface of ZrB_2 can be terminated with either a Zr or B layer. Previous studies have indicated that Zr termination is thermodynamically more stable than B termination, in agreement with the predictions for group 4 metals [13–16].

GaN has been grown successfully on the $ZrB_2(0001)$ surface using molecular beam epitaxy (MBE) [10] and pulsed-laser deposition (PLD) [17] techniques. However, it has been reported that a buffer layer grown first at low temperatures is necessary for growing GaN on $ZrB_2(0001)$ by metal organic chemical vapor deposition (MOCVD), the most common method for growing device-quality GaN epitaxial layers [18]. In forming epitaxial layers of group III nitrides on ZrB_2, the growth sequence has been found to be important and the substrates were exposed to the nitrogen sources before the metal sources [10,18,19]. Besides growth sequence, the substrate temperature during nitrogen-source exposure is critical [18]. Wang et al. stated that when the substrate was nitrided at 900 °C, GaN layers would not grow on ZrB_2, which they attributed to formation of an inert hexagonal BN surface [19]. However, no information about the adsorption sites, relative concentration, or temperature effects when ammonia is exposed to a $ZrB_2(0001)$ surface is available.

In this work, the temperature dependent adsorption and reactivity of the $ZrB_2(0001)$ surface towards NH_3 are investigated with X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT). As the initial stages of the MOCVD growth of GaN on $ZrB_2(0001)$ must involve nitrogen deposition through NH_3 dissociation on this surface, the results may prove useful in the development of detailed models to describe the GaN growth mechanism.

2. Experimental methods

The experiments were performed in a stainless steel ultra high vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. The system has been described in detail elsewhere [20]. In brief, the

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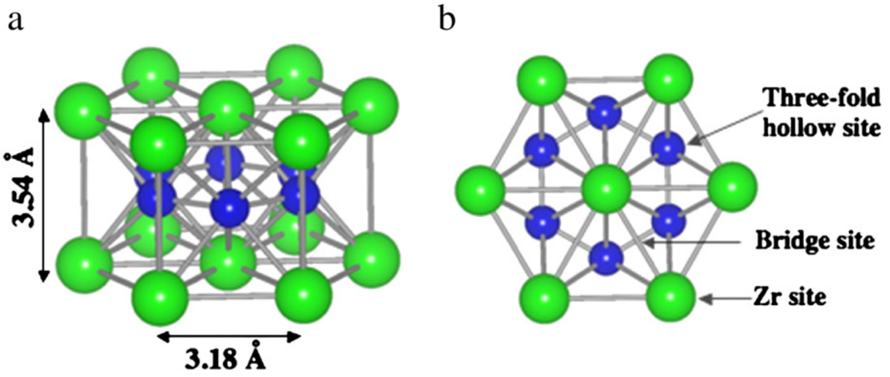

Fig. 1. Side and top views of the $ZrB_2(0001)$ surface with Zr and B atoms represented by large green and small blue spheres, respectively.

chamber is equipped with a hemispherical electron energy analyzer (VG Microtech, Ltd. CLAM2) dual Mg/Al anode X-ray source (VG Microtech), reverse view low energy electron diffraction (LEED) optics (Princeton Research Instruments, RV 8-120SH) and a Fourier transform infrared (FTIR) spectrometer (Mattson, RS-10000).

The $ZrB_2(0001)$ single crystal was grown as described elsewhere [21] and was cut and polished to a mirror finish at the National Institute for Materials Science in Tsukuba, Japan, by methods similar to those described by Aizawa et al. [22]. Details on the crystal mounting, heating, and cleaning procedures are given elsewhere [23]. The purity and quality of the surface were confirmed using a combination of LEED and XPS. The clean $ZrB_2(0001)$ surface gave a sharp (1 × 1) LEED pattern. Oxygen was the principal contaminant observed and the surface was considered clean when no O 1s signal was detected with XPS. The measured Zr $3d_{5/2}$ and $3d_{3/2}$ peaks at binding energies of 179.2 and 181.6 eV, respectively, matched those reported previously for clean ZrB_2 [17,19,24]. For the clean surface, a B:Zr ratio of ~1.5 was determined from the areas of the Zr 3d and B 1s peaks and the appropriate atomic sensitivity factors and is similar to that found earlier [24]. The X-ray source was operated at a power of 221 W (13 kV bias, 17 mA emission current). The XPS system was calibrated based on the Au $4f_{7/2}$ binding energy of 84.0 eV of a piece of gold foil that was cleaned in UHV by argon ion sputtering. All XPS spectra were acquired using Mg Kα radiation and a constant analyzer pass energy of 50 eV corresponding to a nominal resolution of 1.32 eV. All XPS spectra were taken at a 15° angle between the analyzer and the surface normal, except for the grazing angle spectra, which were taken at 70°. The ammonia (experimental grade) was purchased from Matheson and used without further purification. Gas exposures are given in units of Langmuir (L), where 1 L is 1×10^{-6} Torr-s. For ammonia exposures above room temperature (RT), the surface was first heated to the desired temperature and allowed to equilibrate for about 2 min prior to exposure. For the annealing experiments, the sample was heated to the desired temperature and held there for ~2 min.

3. Theoretical methods

The calculations were performed using density functional theory (DFT) with the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (GGA) and the projector augmented wave method in the VASP implementation [25,26]. We used an energy cutoff of 400 eV, the Gaussian smearing method with a 0.1 eV smearing width, and a (4 × 4 × 1) Monkhorst-Pack grid for k-point sampling, which we checked to provide convergence to within 0.01 eV. The calculated lattice parameters a and c of ZrB_2 are 3.179 Å and 3.548 Å, respectively, which are in good agreement with experimental values. The surface calculations were performed with the optimized lattice parameters using a slab consisting of seven and eleven atomic layers of ZrB_2 to model the Zr-terminated and B-terminated surfaces, respectively. To eliminate spurious dipole effects, we worked with symmetric (non-stoichiometric) slabs, using both sides for adatom adsorption. The vacuum region size was ~17 Å in the direction normal to the surface. The surface unit cell was (2 × 2), which we checked to be large enough to eliminate interaction with the neighboring cells. Fig. 1 shows the different surface sites and in the (2 × 2) surface unit cell there are four Zr sites and eight three-fold hollow sites. With the N adsorbates favoring the threefold hollow sites, the choice of the (2 × 2) unit cell size allowed us to study N coverages (Θ_N) from 1/8 monolayer (ML) to a full ML, where 1 ML is defined as one adsorbate per (1 × 1) unit cell. To obtain accurate total energies, single point calculations with the tetrahedron method and a (5 × 5 × 1) Monkhorst-Pack mesh were performed on the optimized N/ZrB_2 structures. For density of states calculations, a (11 × 11 × 1) k-point sampling was adopted. Diffusion barriers were computed with the climbing image nudged elastic band method [27] using only one side of the slab.

4. Relative concentration estimate

The relative concentration (RC) of element x is estimated using the equation [28]

$$C_x = \frac{I_x/S_x}{\sum_i I_i/S_i} \tag{1}$$

where I_x is the integrated area of an XPS peak of element x, and S_x is the peak sensitivity factor. This expression gives only semiquantitative results with accuracies of 10-20% [28]. Its use for estimating the RC of constituents assumes a homogeneous sample, which is not the case here. The measured signal is weighted over the photoelectron escape depth, λ_e, which is calculated in terms of the inelastic mean free path λ_T. λ_e is related to λ_T by $\lambda_e = \lambda_T \cos\theta$, where θ is the angle between the analyzer and the crystal normal, which is ~15° and 70° for the normal emission and grazing angle experiments in this study, respectively. Penn [29] describes a procedure for calculating λ_T as a function of electron kinetic energy ε. For the B 1s and Zr 3d photoelectrons with binding energies of 188 and 180 eV, respectively, excited with Mg K_α radiation (1253.6 eV), $\varepsilon_B = 1065$ eV and $\varepsilon_{Zr} = 1073$ eV, which give $\lambda_T \sim 17.5$ Å for ZrB_2, so the calculated values of λ_e are 16.9 and 6.0 Å, respectively, for normal and grazing angle experiments. The reported lattice constant of $ZrB_2(0001)$ in the normal direction is 3.53 Å [30] (see Fig. 1), so the XPS probe depth is ~5 and 2 atomic layers, respectively, for θ = 15° and 70°.