DFT studies of hydrogen retention in beryllium nitride

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ABSTRACT

The valence band density of states of bulk beryllium nitride (alpha-Be_3N_2) and the solvation energy of hydrogen atoms in this nitride is herein studied using the generalized gradient approximation density functional theory. The DOS is compared to photoelectron spectroscopy investigations of nitrogen-implanted beryllium. The presence of defects (atomic vacancies) was taken into consideration in the calculations on the trapping of deuterium. The barriers of activation for hydrogen atom diffusion in the bulk and from the defect were calculated and compared to their values in pure beryllium metal and in beryllium oxide. Some consequences regarding the effects of nitrogenation of beryllium as a plasma-facing material in nuclear fusion devices are eventually proposed.

Introduction

Beryllium is planned to be used as a plasma-facing material for the international nuclear fusion experiment ITER and hence will be subjected to hydrogen isotopes deuterium and tritium escaping from the magnetically confined plasma. Therefore, hydrogen atom implantation and release in beryllium are vital issues that have been the focus of many investigations [1]. On the other hand seeding of impurities in the plasma is often used in tokamak experiments for various purposes. In particular, the absence of carbon in modern divertor concepts makes radiative cooling by nitrogen seeding mandatory to reduce the power flux. Thus, puffing of nitrogen reduces the divertor temperature [2,3].

Hence, understanding the interaction of nitrogen with beryllium is of great importance [4]. It has been shown that some part of the injected N_2 will be transported to the main chamber wall and deposited on the beryllium cladding to form a stable nitride layer. Furthermore, N can also be co-deposited with Be eroded from the main wall. The first potential problem is that the insulating nature of the nitride layer could increase detrimental arcing. The next problem is that nitration influences the retention of hydrogen isotopes in the material in a way and amplitude that are not well understood [5] Experiments on hydrogen release from this material have been conducted by various groups and notably at the PISCES-B facility [6]. It was observed that beryllium bombardment with energetic deuterium and nitrogen brought about the formation of mixed Be_xN_y compounds. Comparison between

nitrided and un-nitrided samples is lead through thermal desorption measurement of deuterium retention.

The understanding of desorption implies understanding the fundamental processes of diffusion and trapping in the material. Elevated temperatures lead to diffusion of deuterium atoms in the bulk as interstitial atoms to reach the crystal surface where they can recombine and desorb. During diffusion they can be trapped into crystal defects, especially atomic vacancies produced by atom displacements (Frenkel pairs).

Wide band-gap semiconductors such as metal nitrides have also attracted considerable interest in recent years because of their wide-ranging technological applications in blue to UV light-emitting diodes and laser diodes [7]. Only a small number of papers has been devoted to ab initio calculation of the electronic structure and properties of beryllium nitride; they all detail the electronic structure of the perfect crystal [8–13] except Lange et al. [14] who deal with the similar problem of hydrogen-containing point defects in Mg_3N_2.

The paper is organized as follows: Section "Computational details and electronic structures" provides details on the DFT method and the results it yields on the geometry and electronic structure of Be_3N_2, as well as a comparison to X-ray photoelectron spectroscopy (XPS) measurements in the valence band. Section "Trapping and diffusion of an interstitial hydrogen atom" relates to the interstitial hydrogen diffusion. Section "Hydrogen in atomic vacancies" deals with atomic vacancy reactivity toward hydrogen and Section "Surface structures and reactivity" with the crystal surface structure and reactivity. Discussion and conclusions are proposed in Section "Discussion and conclusions".

Computational details and electronic structures

The calculations are performed within the framework of the spin-polarized gradient-corrected density functional theory (DFT) using the Perdew-Burke-Ernzerhof functionals (PBE [15]) and including a semi-empirical pairwise London damped dispersion correction (PBE-D2 [16,17]). A plane-wave basis set was used with an energy cutoff of 32 Rydberg (435 eV); the ionic core potential was modeled using Vanderbilt ultrasoft pseudopotentials. The pseudopotentials were taken from the Quantum-Espresso library [18], and they were discussed in detail in a previous paper [19]. Integration in the first Brillouin zone was performed using the $6 \times 6 \times 6$ k-points Monkhorst-Pack sampling for the bulk and $6 \times 6 \times 1$ points for the surfaces.

The interaction energy (or dissolution energy) of a hydrogen atom with the beryllium nitride bulk (clean or defective) is defined as:

$$\Delta E_H = [E(Be_nN_m + H) - E(Be_nN_m) - 1/2E(H_2)] \quad (1)$$

where $E(Be_nN_m + H)$ represents the total system (clean or defective) energy and $E(H_2)$ the energy of the hydrogen molecule calculated in the same unit cell.

The temperature correction applied to the DFT energies is evaluated through calculation of the Helmholtz free energy, which is also the Gibbs free enthalpy of the system, when the pressure and volume variations are neglected [25]:

$$G(T) = E^{el} + E^{vib} - TS^{vib} + PV \quad (2)$$

E^{el} is the DFT electronic contribution, E^{vib} and S^{vib} are vibrational contributions to the total energy and entropy, respectively; and T, P and V are temperature, pressure and volume. When the P and V variations are neglected and $T = 0$ K $G(0) = E^{el} + E^{vib}$ is known as the Zero Point Energy; hereafter, the energies given without any other specification must be understood as ZPE-corrected PBE-D2 free energies, no further temperature adjustment will be proposed. Due to the large dimension of the working super-cell the phonon dispersions needed for evaluation of Eq. (2) are performed at the (0,0,0) point of the reciprocal crystal lattice within Density Functional Perturbation Theory [20], taking into account all degrees of freedom of the entire supercell when calculating trapping energies. The diffusive energies are corrected using only the diffusive atom modes with their coupling to the substrate's phonon modes.

The stationary state structures were optimized using the damped molecular dynamics algorithm implemented in the Quantum-Espresso package. All the atoms were included in the optimization procedure, without any geometry or symmetry constraint. The activation energies for trapping, detrapping and diffusion are evaluated using the Nudged Elastic Band (NEB) algorithm [21–23]. The NEB calculations provide the three PBE-D2 energies (ΔE_{PBE}) for the initial and final configurations as well as for the transition state. ZPE correction is further added using Eq. (2).

Under normal pressure the beryllium nitride has two phases, alpha and beta. The α-phase (anti-bixbyite type) is stable between 20 and 1200 °C, it is a cubic structure with symmetry space group Ia-3 (206), and lattice parameter of 8.145 Å [8]. The unit cell includes 80 atoms. It is constituted as an A-B-A-C stacking (Fig. 1). Layer A is only constituted of beryllium (12 atoms). Two types of nitrogen atoms are
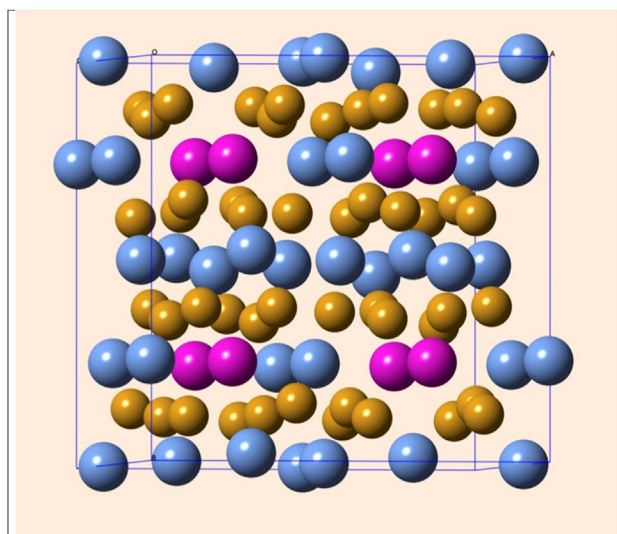

Fig. 1 – Unit cell of α-Be_3N_2: The beryllium atoms are in yellow color, two types of nitrogen atoms can be identified: N^α in purple and N^β in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)