

Electronic structure of neutral vacancies in cubic, wurtzite and hexagonal boron nitride

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The important properties of boron nitride (BN) for basic science and technology have motivated a large number of theoretical and experimental investigations in the last years. Among the several polymorphic modifications of BN, the diamond-like zincblende (c-BN) and wurtzite (w-BN) structures arise as very important materials due to their interesting mechanical, thermal, electronic and optical properties. The polytype c-BN is even more promising for electronic and optoelectronic applications because, unlike diamond, it can be doped both p- and n-type. On the other hand the graphite-like hexagonal (h-BN) modification is an important quasi-two-dimensional insulating comprising properties similar to those of semimetallic graphite. In recent years, the successful preparation of BN thin films achieved by low pressure and low-temperature deposition methods has given motivation for further research work on the BN polytypes [1]. Since most applications, mainly those related to the electronic and optoelectronic device technology, require a good control of the sample quality and doping conditions, the study of native defects and impurities in BN is highly desirable. Particularly, there is an experimental indication accumulated since long time that the nitrogen vacancy plays an important role on the electrical, optical and magnetic properties of these materials.

In this work a systematic study of the electronic properties of neutral B and N vacancies in c-BN w-BN and h-BN is performed. Selfconsistent one-electron state calculations are carried out for these native defects by using the full potential linear augmented plane wave (FLAPW) method within the local density (LDA) and large unit cell approximations. We have shown that the FLAPW is an accurate method to study point defects and impurities in nitride semiconductors [2]. The aim of this work is to access the common features and trends in the structural and electronic properties of the vacancies in these three BN polytypes. Moreover, we use the calculations to interpret experimental results which have been currently ascribed to native defects in BN. We start by first performing FLAPW-LDA electronic structures calculations for the bulk c-BN, w-BN and h-BN. Results for band structure, lattice parameter, cohesive energy, bulk modulus, electron and hole effective masses, TO phonon frequency at Γ and structural stability are obtained for each polytype. The results of our study of BN structural stability are shown in Fig. 1. We found that at low temperature, the c-BN modification is the most stable polytype.

Fig. 2 depicts the defect levels induced by the isolated neutral unrelaxed vacancies of B and N in the three modifications of BN. The vacancy of B is found to be a deep acceptor center in all three structures. Nondegenerate s-like resonancies are found deep in the valence bands. Linear V-I characteristics as a function of temperature, observed for undoped c-BN monocrystals, show the presence of an acceptor level with an activation energy of 1.1 eV. We believe that this energy is related to the B vacancy in c-BN and that analogous transitions should be observed in the other polytypes. Fig. 2 shows that the creation of a N vacancy in c-BN leads to a shallow donor level or even to a donor state in the conduction band. This finding is consistent with the high n-type activity found in nominally undoped grown material. This donor level is found to be deeper in the w- and h-BN than in c-BN modification. The stability of these centers and the effects of relaxations on their electronic structure will be discussed.

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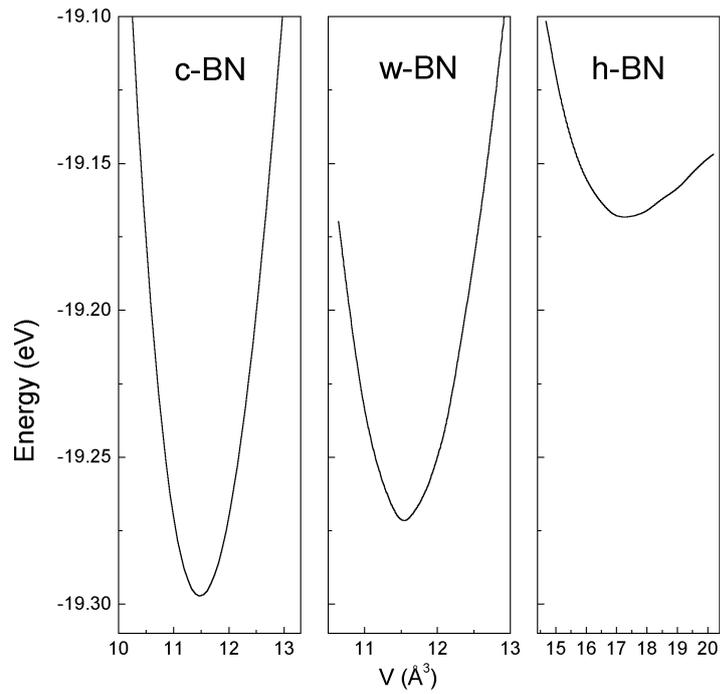


FIG. 1: LDA total energy per BN pair relative to the energy of the separated B and N atoms. For each structure, the minimum energy gives the cohesive energy of the corresponding crystal.

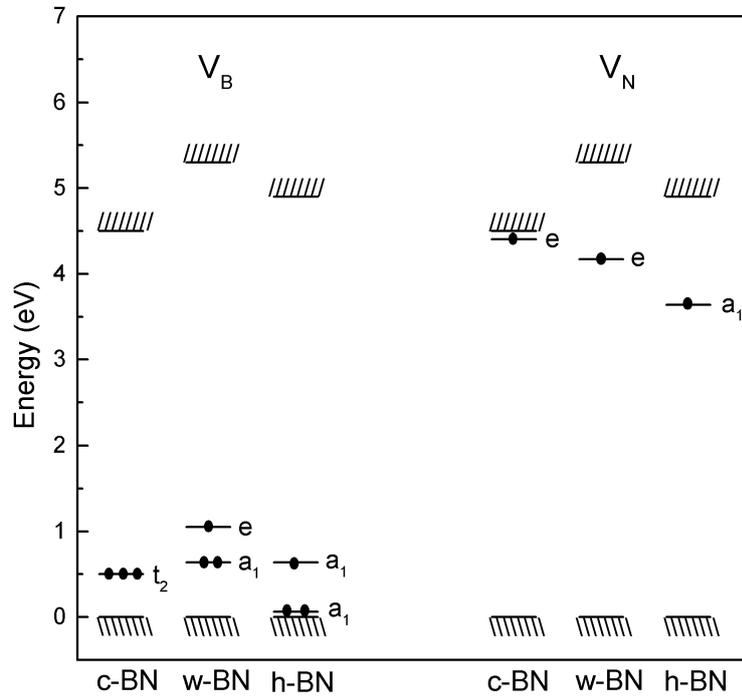


FIG. 2: Defect levels for B and N vacancies (respectively V_B and V_N) in the cubic (c-), wurtzite (w-) and hexagonal (h-) phases of BN. The zero of energy is taken as the top of the valence band. The symmetry of each level and its occupancy by electrons are shown.