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1995 J. Phys.: Condens. Matter 7 6035

(http://iopscience.iop.org/0953-8984/7/30/008)

J. Phys.: Condens. Matter 7 (1995) 6035–6044. Printed in the UK

Electronic energy structure of non-stoichiometric cubic boron nitride

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Received 24 January 1994, in final form 10 February 1995

Abstract. In terms of the multiple-scattering theory using the cluster version of the local coherent-potential approximation the electronic energy structures of both stoichiometric and non-stoichiometric cubic boron nitride have been calculated. It was found that vacancies induced in the sublattice of nitrogen in boron nitride resulted in a marked change in the nitrogen p-band, in a noticeable low-energy shift of the total density of electron states of the valence band and in the appearance of additional acceptor energy levels in the region of forbidden energies. The latter explains the twofold increase in the electrical conductivity of non-stoichiometric boron nitride in comparison with stoichiometric boron nitride found experimentally and calculated in the present work. The calculated partial and total densities of electron states of boron nitride have been used to explain the form of its experimental x-ray emission and x-ray photoelectron spectra.

1. Introduction

Until now in spite of abundant publications about the electronic structure of disordered and non-stoichiometric systems, one cannot find works devoted to non-stoichiometric boron nitride. At the same time there is unquestionable experimental evidence for nitrogen deficiency in boron nitride under the usual conditions at room temperature [1, 2]. The concentration of vacancies in the nitrogen sublattice can exceed 23%, which according to [3] must lead to lattice distortions and inevitable changes in the electron structure.

The electronic structure of stoichiometric cubic boron nitride has been studied using various theoretical approaches [4–10]. It was studied first in the 1960s using the orthogonalized-plane-wave (OPW) method [4, 5]. In the work of Zunger and Freeman [6] the electronic structure of cubic boron nitride has been investigated using the so-called numerical-bases-set linear-combination-of-atomic-orbitals (LCAO) scheme. This *ab-initio* self-consistent study also called 'local-density formalism' (LDF) gave the final electronic configuration of B $1s^{2.00}2s^{0.65}2p^{1.75}3s^{0.12}3p^{0.13}$ and N $1s^{2.00}2s^{1.71}2p^{3.52}3s^{0.08}3p^{0.04}$ which indicates the intra-atomic electronic charge transfer (0.35) from boron to nitrogen. Using a similar *ab-initio* approach called the 'efficient minimal-basis orthogonalized LCAO method', Huang and Ching [7] calculated the electronic structure of 32 semiconductors, including some with the zincblende structure (BN and others). Quite a different charge transfer (1.09) from boron to nitrogen was found in this work [7].

In the parallel investigations of Park *et al* [8] and Wentzcovitch *et al* [9] the augmented-plane-wave (APW) method and the pseudopotential method within the local-density approximation, respectively, were applied. The calculations carried out in these investigations were rather laborious as 950 plane waves had to be used. The main results obtained in these studies are shown later in table 1. The last serious study of the electronic

0953-8984/95/306035+10$19.50

structure of cubic boron nitride was carried out by Takahashi *et al* [10] using the self-consistent variational cellular method. Here, as in other work, the valence band widths as well as direct and indirect band gaps were calculated.

Comparison of the results obtained in the work mentioned above and in the present work is made in section 4.

In the present work we calculate the electronic structure of cubic boron nitride in both stoichiometric and non-stoichiometric states using the theoretical scheme [13] to find in a proper way the influence of nitrogen vacancies upon the electronic properties of this compound.

2. Method of calculation

The electron energy distribution $N(E)$, i.e. the electron density-of-states (DOS) function, which determines the electronic properties of a substance, was calculated using the so-called local coherent-potential method of multiple scattering, introduced by Gyorffy [11, 12] for alloys and developed for other substances [13, 14]. The electronic DOS for boron nitride can be written using the retarded Green function

$$N(E) = -\frac{1}{\pi}\,\mathrm{Im}\{\mathrm{Tr}[G^{+}(E)]\} \tag{1}$$

which can be expressed explicitly as has been described [11, 12] in terms of the scattering path operator

$$T = \sum T_{LL'}^{nn'}$$

which satisfies the equation

$$T_{LL'}^{nn'} = \mathbf{t}_l^n \delta_{LL'}^{nn'} + \sum_{n_1,L} \mathbf{t}_l^n g_{LL_1}^{nn_1} T_{L_1L'}^{n_1n'} \tag{2}$$

where n is the site number, L is both the azimuthal and the polar quantum number, $g_{LL'}^{nn'}$ is the energy-dependent lattice function and $\mathbf{t}_l^n$ is the single-site **t**-matrix given by

$$\mathbf{t}_l^n(E) = -\frac{1}{\sqrt{E}} \exp(\mathrm{i}\delta_l^{\mathrm{A}}) \sin\delta_l^{\mathrm{A}} \tag{3}$$

where $\delta_l^{\mathrm{A}}(E)$ is the energy-dependent scattering phase shift and A denotes the sort of atom in the nth site, i.e. boron, nitrogen or vacancy.To calculate the phase shift as a function of energy, one has to know the potential for an electron moving around the atom scatterer. The muffin-tin approach [15] was used to calculate the crystal potential as the sum of the Coulomb contribution $V_{\mathrm{C}}(r)$, Madelung contribution $V_{\mathrm{M}}(r)$ and exchange contribution $V_{\mathrm{E}}(r)$:

$$V(r) = V_{\mathrm{C}}(r) + V_{\mathrm{M}}(r) + V_{\mathrm{E}}(r) \tag{4}$$

utilizing tabulated Herman–Skillman electron radial wavefunctions for the atoms boron and nitrogen. First the crystalline charge electron density functions $f(r)$ for boron nitride were determined, taking into account the contributions from the neighbouring atoms of 16

coordination shells. The functions $f(r)$ found enabled us to calculate the Coulomb potential and the exchange potential. The latter was calculated according to Slater with a variable parameter α from $\frac{2}{3}$ to 1.

The Madelung potential for a zincblende lattice was calculated using the well known Ewald method, taking into account the electrostatic contributions of two different sublattices: one sublattice consists of atoms of the same type (for instance boron atoms). The potential created by one sublattice at the site occupied by an atom of the same kind was found to be $\varphi_{11} = \varphi_{22} = -4.849q/a$, where q is the charge of an ion and a is the lattice constant. The Madelung potential created by a sublattice at site where an atom of another sublattice exists is equal to $\varphi_{12} = \varphi_{21} = -0.801\,94q/a$. The very important parameters for the muffin-tin potential are radii of muffin-tin spheres which were taken to be equal for boron and nitrogen atoms and touching one another: $r_{mt} = 1.4787$ au. In this case the density of electron charge outside muffin-tin spheres appeared to be $0.056\,57e$ and the charges on a B sphere and a N sphere were found to be $3.36e$ and $5.66e$, respectively.

The calculated crystal potential in each of the three different possible muffin-tin sphere was used in calculations of the energy-dependent single-site matrices $\mathbf{t}_l^N(E)$, $\mathbf{t}_l^B(E)$ and $\mathbf{t}_l^{vac}(E)$. The latter were used to compute the elements of the crystal matrix of the multiple scattering for every type of cluster, centred at a B atom, a N atom and a N vacancy.The local partial electron DOS was calculated according to the formula

$$n_l^A(E) = -\frac{\sqrt{E}}{\pi}\int_0^{rws}[rR_l^A(E,r)]^2\,dr\,\frac{\mathrm{Im}(T_r T^A_{lm,l'm'})}{\mathrm{Im}[t_l^A(E)]} \tag{5}$$

where A denotes the type of cluster (B, N or vacancy), l is the orbital quantum number, $R_l^A(E,r)$ are the radial wavefunctions, T is a matrix element of the scattering operator and the index 0 shows the centre at which the atom of A type is situated.The phase shifts δ_l^A were determined by solving the radial Schrödinger equation with Numerov's method for angular momenta $l = 0, 1$ in the energy range 0.02–3.0 Ryd in steps of 0.02 Ryd, the energy being counted from the muffin-tin zero. The radial wavefunctions were adjusted to the asymptotic solution for the constant potential beyond the muffin-tin sphere:

$$R_l^A(r) = j_l(r\sqrt{E})\cos[\delta_l^n(E)] - n_l(r\sqrt{E})\sin\delta_l^A \tag{6}$$

at its boundary r_{mt}^A. Here n_l and j_l are the spherical Neumann and Bessel functions, respectively. If γ_l is the value of the logarithmic derivative of the radial function at $r = r_{mt}^A$, then the phase shifts are

$$\delta_l^A(E) = \tan^{-1}\left(\frac{\sqrt{E}j_l'(r_{mt}^A\sqrt{E}) - \gamma_l^A(E)j_l(r_{mt}^A\sqrt{E})}{\sqrt{E}n_l'(r_{mt}^A\sqrt{E}) - \gamma_l^A(E)n_l(r_{mt}^A\sqrt{E})}\right). \tag{7}$$

The single-site scattering matrix $\mathbf{t}_l^n(E)$ (equation (3)) calculated for every sort of atom, was used to determine the crystal scattering matrix for two types of cluster in the centre of which boron or nitrogen atoms were placed in the case of boron nitride. This enabled us to calculate the local partial DOS $n_l^A(E)$ for every kind A of BN atoms and the total electron DOS

$$N^{BN}(E) = \sum n_l^B(E) + \sum n_l^N(E). \tag{8}$$

3. The calculations of the electronic structure of stoichiometric and non-stoichiometric boron nitrides

The calculations of the electronic DOS of boron nitride performed earlier [16] with clusters containing five, 17, 29 and 35 atoms showed that the last number of atoms in clusters is sufficient to obtain reliable results. The same type of clusters is used therefore in the present work. This means that in such clusters four coordination shells with the distribution of scatterers 1–4–12–12–6 were taken into consideration. The results of the calculations of the partial local and total electron DOSs of stoichiometric BN are presented in figure 1. It is seen that the upper part of the valence band is determined by nitrogen electron states whereas, in the conduction band, boron and nitrogen participate equally.

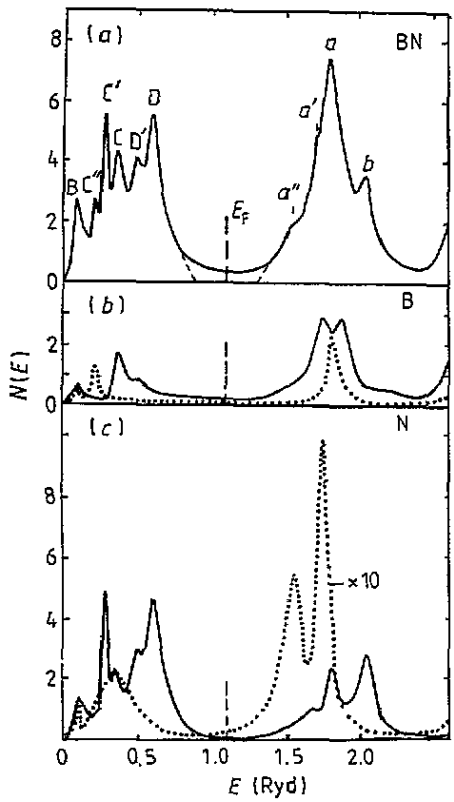

Figure 1. (*a*) The total electron DOS of stoichiometric cubic boron nitride (BN), (*b*) the local electron DOS of boron in stoichiometric cubic boron nitride (BN) and (*c*) the local electron DOS of nitrogen in stoichiometric cubic boron nitride (BN): ·····, s states; ——, p states.

The form of the upper part of the valence band determined in the present calculations has a fine structure: the maxima C′, C″ and D′, which are absent in the calculations made by the OPW [5], APW [8] and pseudopotential method [9, 10], appear distinctly. The bottom of the conduction band also has noticeable peculiarities. Table 1 contains the results of calculations such as the full width of the valence band, the widths of its lower and upper parts and the energy gap estimation. The latter value of 5.7 eV cannot be found with a

high accuracy because the DOS within the gap is not equal to zero owing to the limited number (35) of atoms in the clusters in our calculations. In the table the values of the same quantities obtained in other work are given. They will be discussed and compared in section 4.

To calculate the local partial and total electron DOS distributions of cubic boron nitride with 25% nitrogen deficiency we assumed that the vacancies were distributed in the crystal in such a way that, in every coordination sphere consisting of nitrogen atoms and centred at a boron or nitrogen atom or vacancy, there were just 75% of nitrogen atoms and 25% vacancies. For the cluster centred at a boron atom the first coordination sphere consisted of three nitrogen atoms and one vacancy, and in the third coordination sphere there were nine nitrogen atoms and three vacancies. For the clusters centred at a nitrogen atom or nitrogen vacancy in the sites of all even coordination spheres (excepting the centre) an effective scatterer was used with the single-site scattering matrix

$$\mathbf{t}_l^{\mathrm{eff}}(E) = 0.75\mathbf{t}_l^{\mathrm{N}}(E) + 0.25\mathbf{t}_l^{\mathrm{vac}}(E). \tag{9}$$

The total electron DOS, in which one projection of the electron spin was taken into account, was calculated as the sum of all the local partial DOS:

$$N(E) = \sum_{l=0}^{1} n_l^{\mathrm{B}}(E) + 0.75 \sum_{l=0}^{1} n_l^{\mathrm{N}}(E) + 0.25 \sum_{l=0}^{1} n_l^{\mathrm{vac}}(E). \tag{10}$$

In figure 2 the partial local and total DOSs of non-stoichiometric metric $BN_{0.75}$ are presented.

The upper part of the valence band of the non-stoichiometric boron nitride investigated is formed from p states of nitrogen atoms mainly and s–p-hybridized states of boron. They form the most intensive maximum B. Peak C consists of the electron p states of both boron and nitrogen. Peak D contains p states of nitrogen only. These peaks C and D form the so-called p-like band of $BN_{0.75}$. The width of this part of the valence band is equal to about 14 eV. The s-like band of the boron nitride is formed by electron states of nitrogen. This band is located below the muffin-tin zero in both stoichiometric and non-stoichiometric boron nitride and it is not shown in the figure.

4. Discussion

In table 1 a comparison of valence-band widths and band gaps found in various experiments (XES, XPS and AES) and theoretical calculations is given. The results obtained in the present work are straightforward for the 'upper' part of the valence band and for the energy gap of stoichiometric and non-stoichiometric (indicated by an asterisk) boron nitride in the zincblende structure. The widths of the 'lower' part and full valence band were obtained using XES and XPS data; so these values are semiempirical. The results of the width calculations of stoichiometric and non-stoichiometric boron nitride differ from each other less than from the results of the calculations following other theoretical models. At the same time our values are very near to the experimental estimations. The latter are not easy to obtain with high accuracy because of the inherent and instrumental smearing of the experimental curves. In figure 3 the spectroscopic experimental curves of the nitrogen DOS are presented as determined by the XPS, XES and AES methods. To simplify the comparison of the theory and experiment the partial (s- and p-)electron DOSs of nitrogen multiplied by the

Table 1. Comparison of valence band widths and minimum band gaps of BN and $BN_{0.75}$ (indicated by asterisks) from the present calculations with experimental results and other theoretical calculations.

	Value (eV)									
	Experiment				Theory					
	XES [17]	XPS [20]	AES [21]	Empirical [22]	OPW [4]	APW [24]	Pseudopotential [25]	LDF [6]	Semiempirical [26]	Our work
Full	20.2 22.0 [18]	17.1	21.1		23.2 23.4 [5]	17.8 20.7 [8]	17.9 19.7 [10] 20.3 [9]	19.1	27.5	23.3 21.4*
Lower			6.0		5.0 6.1 [5]	4.5 6.5 [8]	5.6 5.3 [10] 5.9 [9]	5.1	6.8	8.6 6.6*
Upper	16.1		11.8		12.7 11.8 [5]	8.0 11.6 [8]	3.5 10.1 [10] 10.8 [9]	9.0	16.5	12.0 15.2*
Indirect gap	4.6 6.0 [18] 6.4 [19]			5.0 7. 0 [23]	3.4 [5]		5.0 [10] 4.2 [9] 7.0 [7]			5.7 5.7*

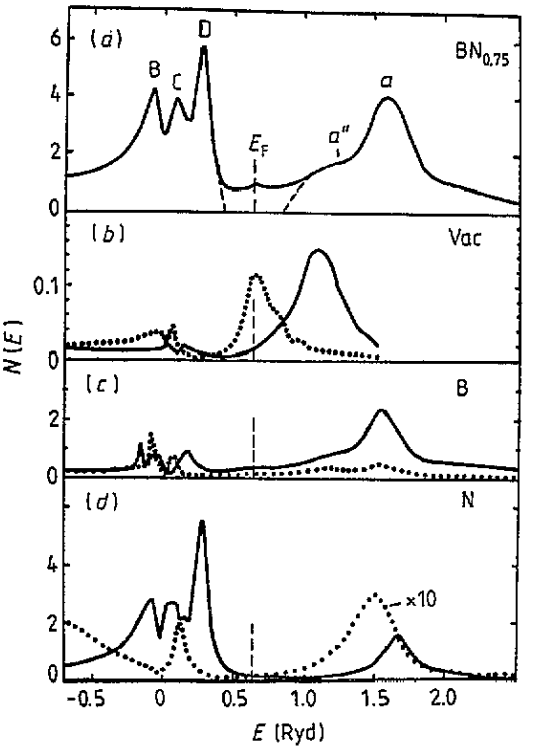

Figure 2. (*a*) The total electron DOS of non-stoichiometric cubic boron nitride ($BN_{0.75}$); (*b*) the local electron DOS of vacancies in non-stoichiometric cubic boron nitride ($BN_{0.75}$), (*c*) the local electron DOS of boron in non-stoichiometric cubic boron nitride ($BN_{0.75}$), and (*d*) the local electron DOS of nitrogen in non-stoichiometric cubic boron nitride ($BN_{0.75}$): ·····, s states; ——, p states.

corresponding cross section values were summarized to 'synthesize' the experimental XPS and AES curves (figure 3(*c*)). The partial $n_p(E)$ of nitrogen is compared (figure 3(*a*)) with the XES emission band. One can see good agreement between energy difference between maxima C′ and D for the theoretical curve and the experimental C'_4–D_4 (figure 3(*a*)) and C'_2–D_2 (figure 3(*b*)). The general form of the upper part of the 'spectroscopic' DOS of nitrogen calculated in the present work nearly coincides with the analogous curve (figure 3(*c*)) determined from APW calculations [8], but our curve reveals a richer fine structure.

Our calculations of spectra are made for stoichiometric boron nitride because there are no spectra for non-stoichiometric boron nitride. However, comparison of the experimental XES data for nitrogen with the p-partial nitrogen DOS of non-stoichiometric boron nitride (figure 2(d)) shows a remarkable correspondence. One may assume that the experiments were carried out with non-stoichiometric boron nitride. This is very probable because boron nitride loses nitrogen quite easily at under the usual conditions and also under irradiation.

From the comparison of the DOS curves for non-stoichiometric boron nitride with that for stoichiometric boron nitride it is possible to conclude that the generation of nitrogen vacancies results in

(1) a low-energy shift in the valence and conduction bands,
(2) smearing of the peaks of the DOS in the conduction band;
(3) the appearance of a small maximum in the forbidden part of the energy range and

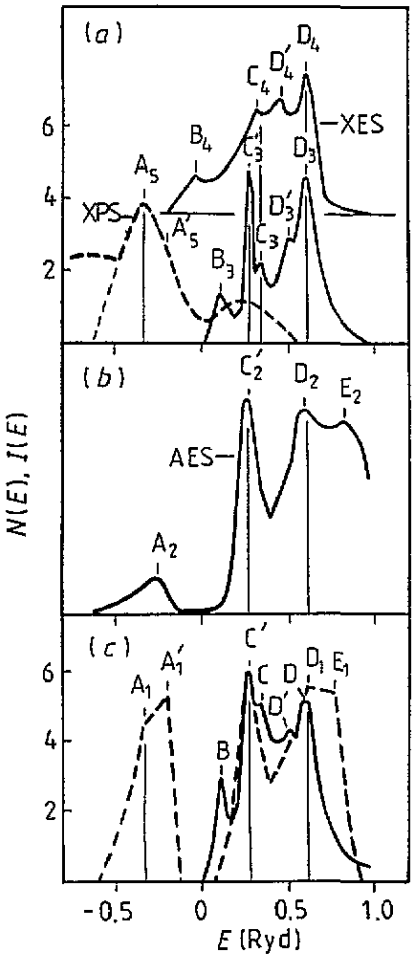

Figure 3. Comparison of calculated DOSS of boron nitride with the experimental XES, XPS and AES data: (*a*) nitrogen electron p-state energy distribution (——) compared with x-ray emission K band of nitrogen (XES) and x-ray photoelectron spectrum of boron nitride (XPS); (*b*) Auger electron spectrum of nitrogen in boron nitride; (*c*) the local nitrogen electron DOS with cross sections of excitation taken into account (——) and the theoretical spectrum calculated [8] by the APW method (- - - -).

(4) a decrease in the number of peaks and a change in the valence band.

The shift of the energy levels in non-stoichiometric boron nitride compared with stoichiometric boron nitride can be explained in the following way: the absence of nitrogen atoms at some lattice sites results in an uncompensated positive charge at boron atoms and an additional attractive potential that leads to deepening of the potential pits and a decrease in the average value of the crystal potential in the out-of-muffin-tin-spheres region, this value being taken as the zero level for both cases in our calculations.

The smearing of the conduction band peaks can be attributed to a reduction in the degree of order in non-stoichiometric boron nitride. The small maximum of the DOS in the energy gap is due to the vacancy states. The intensity of this maximum is proportional to the nitrogen vacancy concentration.

The nitrogen deficiency results in a serious change in the valence band form. This is inevitable because for this kind of compound a decrease in the number of valence electrons per atom cannot provoke a simple shift in the Fermi level similar to that in alloys.The present work supports the conclusions of [27] that the creation of non-metal vacancies in nitrides and carbides of d metals results in

(1) the origin of localized states in the vicinity of the Fermi level which influences the physical properties of these compounds,

(2) broadening of the valence band of another component (metal) and

(3) depletion of the s–p band which leads to weakening of the metal–metal bonding.

The conductivity σ of boron nitride estimated in the framework of the simple model in [28] showed that σ increased with increasing temperature; this is characteristic of semiconductors as also is the increase of a factor of 2.3 when going from stoichiometric boron nitride (BN) to non-stoichiometric boron nitride ($BN_{0.75}$). The latter is easy to explain if we take into account the appearance of the acceptor levels due to vacancies in the energy gap. At room temperature (300 K) the calculated value of the conductivity of the non-stoichiometric $BN_{0.75}$ is found to be 7.5×10^{-3} S m^{-1}.

5. Conclusions

The general form of the features of the upper part of the valence band of non-stoichiometric boron nitride is similar to that of stoichiometric boron nitride. This shows that inducing vacancies in the nitrogen sublattice does not change the character of the chemical bonding in non-stoichiometric boron nitride but it nevertheless results in

(1) a significant distortion of the nitrogen p-band form,

(2) a low-energy shift in the total DOS distribution and

(3) the appearance of additional acceptor levels within the energy gap which leads to an increase in conductivity.

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