ELSEVIER

Photoluminescence of boron carbide

R. Schmechel,[1] H. Werheit,* T.U. Kampen,[2] and W. Mönch

Solid State Physics Laboratory, Gerhard Mercator University, D-47048 Duisburg, Germany

Abstract

The excitation of $B_{4.3}C$ with an Ar-laser ($\hbar\omega = 2.4$ eV) yields a photoluminescence spectrum between about 1.56 and 1.58 eV with its main maximum at 1.563 eV and a weaker maximum at 1.572 eV. It is attributed to the indirect-allowed recombination of free excitons.
© 2003 Elsevier Inc. All rights reserved.

Keywords: Boron carbide; Luminescence; Free exciton recombination

1. Introduction

The electronic properties of boron carbide have been controversially discussed (see Ref. [1]). The optical transition energies determined from optical absorption spectra and starting with 0.47(1) eV [2,3] are much smaller than those theoretically calculated (>2.7 eV) [4–7]. The discrepancy between the theory yielding metallic, and the experiments proving semiconductor character has recently been solved by Schmechel and Werheit [8] showing that the theoretically calculated valence electron deficiency in idealized structures is exactly compensated by structural defects, which generate high-density gap states in the real structures. High-energy critical points were found between 2.5 and 9.5 eV [9]. The excitation of boron carbide with a high-intensity Nd:YAG laser (1.16 eV) yields a broad unstructured emission, which is probably due to thermal effects [10]. Luminescence obtained with higher excitation energy is presented below.

2. Experimental

The sample was coarse-grained polycrystalline boron carbide crystallized from the melt, with a composition close to the carbon-rich limit $B_{4.3}C$ of the homogeneity range (exactly $B_{4.23}C$, for details of properties, see Ref. [11]). Its surface was mechanically polished using diamond spray (Struers) of gradually reduced grain size (final size 1 µm). The luminescence, which was excited with an Ar-Laser (514.5 nm = 2.4 eV), is shown in Fig. 1; it exhibits a distinct maximum at 1.563 and a weaker one at 1.572 eV. There is probably a very weak peak at 1.552 eV.

To show the relation between luminescence and optical properties of boron carbide, some reflectivity-difference spectra are displayed in Fig. 2 [12]. Similar to modulation spectroscopy, which uses the periodical variation of physical parameters like e.g. temperature or electric field to detect weak structures in the optical spectra of solids using lock-in technique, we determined $\Delta R/R$ for small structural changes in semiconductors like boron carbide. ΔR is the small difference of the reflectivity of two boron carbides with slightly changed crystal structures in consequence of different boron isotopes or slighly different chemical compositions. Such structural modifications cause a shift of the energy band structure of the solid, and this is indicated by a corresponding change of the reflectivity spectrum.

3. Discussion

Using $E_0 = 1.56$ eV and an exciton temperature $T_e = 60$ K, the spectral distribution of the main peak of the photoluminescence is well fitted by

$$I(\omega) \propto \sqrt{\hbar\omega - E_0}\, \exp[-(\hbar\omega - E_0)/k_B T_e]$$

*Corresponding author. Solid state Physics Laboratory, Gerhard Mercator University, Bensberger Marktweg 328, D-51069 Cologne Germany. Fax: +49-221-682796.

E-mail address: helmut.werheit@koeln.de (H. Werheit).

[1] Present address: Materials Science Department, Technical University, D 64287 Darmstadt, Germany.

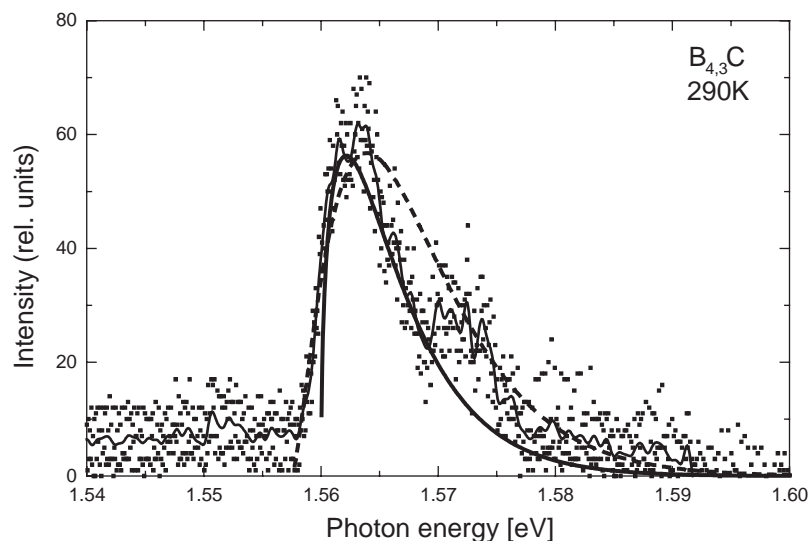[2] Present address: Institute of Physics, Technical University, D 09107 Chemnitz, Germany.

Fig. 1. Photoluminescence spectrum of $B_{4.23}C$ at 290 K. Excitation with the 514.5 nm (2.4 eV) line of an Ar laser; intensity 280 mW/mm2. Squares, experimental results, thin solid line, averaged experimental results, bold solid line, recombination model of free excitons; bold dashed line, model for the transition of electrons between energy band and defect level.
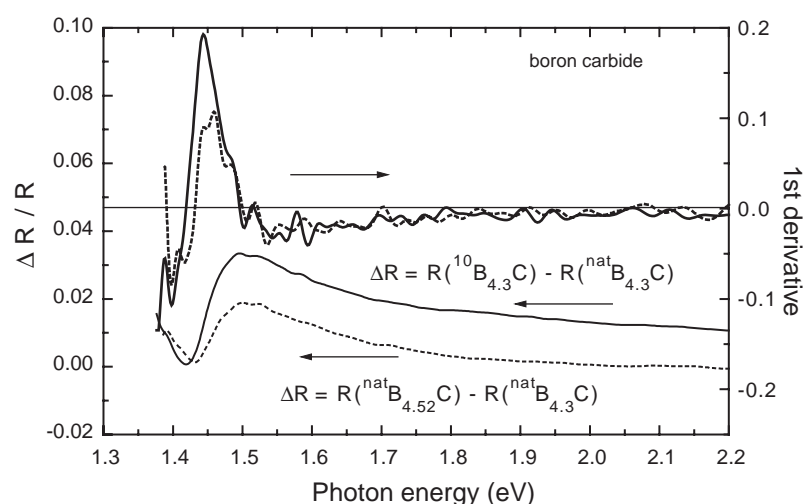

Fig. 2. Reflectivity-difference spectra $\Delta R/R$ and their calculated first derivatives for boron carbide with chemical composition close to the carbon-rich limit of the homogeneity range. Solid line, $\Delta R = R(^{10}B_{4.3}C) - R(^{nat}B_{4.3}C)$; dashed line $\Delta R = R(^{nat}B_{4.52}C) - R(^{nat}B_{4.3}C)$ [12].

which is expected for direct-allowed band-band recombination or for the indirect-allowed recombination of free excitons [13]. According to the evaluation of the absorption edge spectrum [3], direct interband transitions can be excluded.

Based on the experimentally determined indirect interband transition of 2.1 eV [3], the luminescence yields an exciton bond energy of about 500 meV. For a Wannier–Mott exciton the bond energy is described by

$$E = -m_n m_p [13.6 \text{ eV}/(\varepsilon_r^2(m_n + m_p))].$$

Using the dielectric constant $\varepsilon_r \approx 10$ [1], this leads to a carrier effective mass in the order of $10m_0$ which quite well agrees with the evaluation of the dynamical conductivity of boron carbide [14,15]. A corresponding value for the effective mass was estimated from IR optical investigations [16], and was obtained from the curvature of the theoretically calculated energy bands [17].

The bond energy of 500 meV is also compatible with the theoretically calculated ionization energies of some hundred meV for polarons [18].

As a further possibility, based on the present knowledge of the energy band scheme, the photoluminescence could be attributed to the transition between an energy band and a defect level in the band gap. However, the spectral distribution based on the Roosbroeck–Shockley equation [19]

$$I(\omega) \propto \alpha(\omega)\omega^2 \exp[(E_0 - \hbar\omega)/k_B T_e]$$

using for $\alpha(\omega)$ the Lucovsky theory [20] describing transitions between deep levels and parabolic bands fits much less well to the experimental luminescence spectrum (see Fig. 1).

Based on these estimations and considering numerous other results, which are available for boron carbide (see Ref. [1]), we prefer to attribute the photoluminescence of boron carbide to the indirect-allowed recombination of free excitons. However, further investigation, in particular of the temperature dependence of the luminescence are required to confirm this assumption.

It can be excluded that the weak peak at 1.552 eV is a phonon replica of the main peak at 1.563 eV. The energy difference of 11 meV ($\tilde{v} \sim 88$ cm^{-1}) is by far too small, as after calculations by Shirai [21] even the acoustic modes at the zone boundary of boron carbide exceed 200 cm^{-1}.

4. Conclusion

The photoluminescence spectrum of $B_{4.3}C$ between about 1.56 and 1.58 eV with its main maximum at 1.563 eV and a weaker maximum at 1.572 eV is attributed to the indirect-allowed recombination of free excitons.

Acknowledgments

References

[1] H. Werheit, Boron compounds, in: O. Madelung (Ed.), Landolt-Börnstein, New Series Group III, Vol. 41D, Springer, Berlin, 2000, pp. 1–492.

[2] H. Werheit, H. Binnenbruck, A. Hausen, Phys. Stat. Sol. (b) 47 (1971) 163.

[3] H. Werheit, M. Laux, U. Kuhlmann, R. Telle, Phys. Stat. Sol. (b) 172 (1992) K81.

[4] D.M. Bylander, L. Kleinman, Phys. Rev. B 42 (1990) 1394.

[5] D.M. Bylander, L. Kleinman, Phys. Rev. B 43 (1991) 1487.

[6] L. Kleinman, AIP Conf. Proc. 231 (1991) 13.

[7] D. Li, W.Y. Ching, Phys. Rev. 52 (1995) 17073.

[8] R. Schmechel, H. Werheit, J. Phys.: Condens. Matter 11 (1999) 6803.

[9] H. Werheit, C. Janowitz, R. Schmechel, T. Tanaka, Y. Ishizawa, J. Solid State Chem. 133 (1997) 132.

[10] U. Kuhlmann, H. Werheit, J. Alloys Compd. 205 (1994) 87.

[11] U. Kuhlmann, H. Werheit, K.A. Schwetz, J. Alloys Compd. 189 (1992) 249.

[12] H. Werheit, R. Schmechel, T. Lundström, T. Tanaka, Y. Ishizawa, Structure-modulated reflectivity spectra of icosahedral boron-rich solids, presented at the 12th International Symposium on Boron, Borides and Related Compounds, Baden, Austria, 1996.

[13] H.B. Bebb, E.W. Williams, Photoluminescernce I: Theory, in: R.K. Williardson, A.C. Beer (Eds.), Semiconductors and Semimetals, Vol. 8, Transport and Optical Phenomena, Academic Press, London, 1972, p. 182.

[14] R. Schmechel, H. Werheit, J. Solid State Chem. 133 (1997) 335.

[15] R. Schmechel, H. Werheit, J. Mater Process. Manufact. Sci. 6 (1998) 329.

[16] H. Binnenbruck, H. Werheit, Z. Naturforsch. 34a (1979) 787.

[17] R. Armstrong, J. Bolland, P.G. Perkins, G. Will, A. Kirfel, Acta Crystallogr. B 39 (1983) 324.

[18] D. Emin, Phys. Rev. B 48 (1993) 13691.

[19] W. van Roosbroeck, W. Shockley, Phys. Rev. 94 (1954) 1558.

[20] G. Lucovsky, Solid State Commun. 3 (1965) 299.

[21] K. Shirai, Personal communication, 1999.