phys. stat. sol. (b) **229**, No. 3, R1–R3 (2002)

Rapid Research Note

Absorption and Emission of Hexagonal InN. Evidence of Narrow Fundamental Band Gap

V. Yu. Davydov[1]) (a), A. A. Klochikhin (a), R. P. Seisyan (a), V. V. Emtsev (a), S. V. Ivanov (a), F. Bechstedt (b), J. Furthmüller (b), H. Harima (c), A. V. Mudryi (d), J. Aderhold (e), O. Semchinova (e), and J. Graul (e)

(a) Ioffe Physico-Technical Institute, Russian Academy of Science, Polytekhnicheskaya 26, 194021 St. Petersburg, Russia
(b) Institut für Festkörpertheorie and Theoretische Optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, D-07743 Jena, Germany
(c) Department of Electronics and Information Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
(d) Institute of Solid State and Semiconductor Physics, Belarus Academy of Sciences, Brovki 17, 220072 Minsk, Belarus
(e) LfI, University of Hannover, Schneiderberg 32, D-30167 Hannover, Germany

(Received December 18, 2001; accepted December 20, 2001)

Subject classification: 71.15.–m; 78.40.Fy; 78.55.Cr; S7.14

The physical properties of InN crystals are known rather poorly, since the existing growth techniques have not produced epitaxial layers of good quality [1, 2]. Even a key parameter of InN – the band gap E_g – has not been firmly established so far. E_g values of 1.8 eV to 2.1 eV have usually been estimated from the absorption spectra obtained on polycrystalline and nanocrystalline hexagonal InN [3–6]. No data on the band-to-band photoluminescence (PL) of InN are available in the literature. Recently an improved growth technique has made it possible to obtain single-crystalline InN layers [7]. Optical measurements on these InN layers have shown some strong differences from absorption data reported earlier [8]. In the present work the electronic structure of single-crystalline InN layers was carefully studied by means of optical absorption, PL, and photoluminescence excitation (PLE) spectroscopy as well as by *ab initio* calculations. Our results revealed for hexagonal InN a band gap of about 0.9 eV, which is much smaller than the values of 1.8 eV to 2.1 eV reported previously.

Single-crystalline InN epilayers were grown on (0001) sapphire substrates either by plasma-assisted molecular-beam epitaxy (PAMBE) [7] or metalorganic molecular-beam epitaxy (MOMBE) [9] and were characterized by many techniques. Only hexagonal symmetry, with no traces of other polymorphs, was established by X-ray analysis in all the samples. For characterization the symmetric (0002) and asymmetric $(11\bar{2}4)$ Bragg reflexes were used. From these data the lattice constants in the InN layers were found to be $c = 5.7039$ Å and $a = 3.5365$ Å. The narrow profiles of θ and θ–2θ scans at the (0002) reflex (250–300 arcsec and 50–60 arcsec, respectively) indicate a good crystalline quality. Polarized Raman spectra of InN show agreement with the selection rules for the hexagonal symmetry. The Raman phonon line widths correspond to a well-ordered crystal lattice [9, 10]. Atomic force microscopy measurements did not reveal any columnar structure in the samples studied. According to the Auger data, the oxygen concentration did not exceed 0.1%. The Hall concentration of electrons n ranged from 9×10^{18} to 1.2×10^{19} cm^{-3} in the best samples, and their mobility was found to be as high as $\mu \sim 1900$ cm^2 V^{-1} s^{-1}.

The absorption coefficient $\alpha(\omega)$ for PAMBE- and MOMBE-grown InN samples at 300 K is shown in Fig. 1. The layer thickness was measured by means of scanning electron microscopy. The $\alpha(\omega)$ spectra were calculated from the transmission spectra with corrections for multiple reflections. It can be seen that the edge absorption rapidly reaches values of $\alpha(\omega) > 5 \times 10^4$ cm^{-1}, which is typical of direct band-gap crystals. The inset in Fig. 1 shows that the absorption coefficient can be described by the relation $\alpha(\omega) \sim (\hbar\omega - E_g)^{1/2}$ usually applicable to allowed direct interband transitions. From the measurement of the absorption edges it can be concluded that the E_g

[1]) Corresponding author; e-mail: valery.davydov@pop.ioffe.rssi.ru

 0370-1972/02/22902-00R1 $ 17.50+.50/0

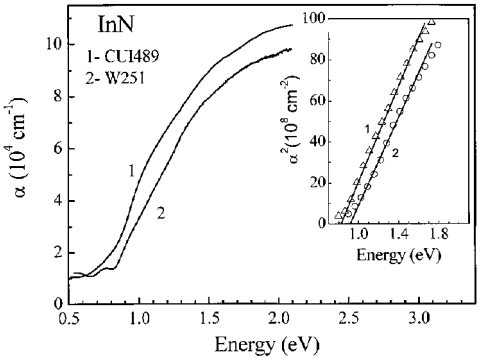

Fig. 1

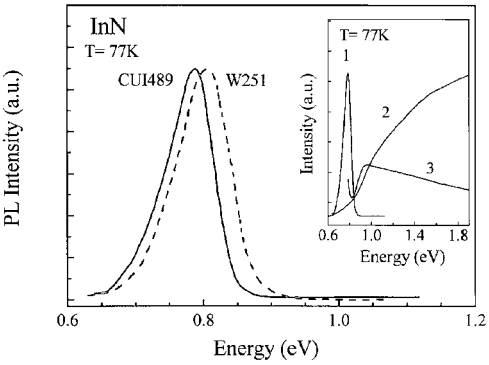

Fig. 2

Fig. 1. Absorption edge of two InN samples with electron concentrations of: $n \sim 9 \times 10^{18}$ cm^{-3} (MOMBE-grown sample CUI489); $n \sim 1.2 \times 10^{19}$ cm^{-3} (PAMBE grown sample W251)

Fig. 2. Photoluminescence spectra of InN samples. The inset shows the PL (curve 1), optical absorption (curve 2), and PLE (curve 3) spectra for one of the samples (CUI489)

value of hexagonal InN is about 0.9 eV. Possible reasons for the difference in E_g observed for the two samples may be the Burstein-Moss shift associated with different doping levels and/or strains in the samples.

In the InN samples studied we succeeded in observing for the first time the near infrared PL (under excitation by an Ar^+ laser) in the region of 0.8 eV to 0.85 eV, which is close to the absorption edge. Figure 2 shows PL spectra at 77 K in the samples discussed above. The spectra display asymmetric bands with a FWHM of 70 meV and 110 meV. The maxima of these bands are shifted to lower energies by 50–60 meV relative to the E_g values estimated from the absorption data. The luminescence band was found to be wider in the sample with larger carrier concentration. Analysis of the PL spectra in the temperature range 300–4.2 K showed that, with decreasing temperature, the PL band is getting narrower, its high-energy edge becomes steeper, and the intensity substantially grows. The observed behaviour of the PL band is typical of radiative interband recombination in heavily doped semiconductors. The PLE spectrum recorded at the PL band maximum in one of the samples is shown in the inset in Fig. 2, together with the PL and absorption spectra. The band gap of a semiconductor can be also estimated with reliable accuracy from the position of the PLE band maximum [11]. The band gap of InN inferred from the PLE data is about 0.9 eV, consistent with the absorption data. Taking into account the good correlation between the absorption, PL, and PLE data, one can conclude that the true value of the fundamental gap of hexagonal InN is about 0.9 eV.

In addition, the fundamental gap of hexagonal InN at the Γ point was calculated using the density-functional theory (DFT) in the local density approximation (LDA). Details of the calculations based on a pseudopotential-plane-wave code can be found in Ref. [12]. Quasiparticle corrections of 0.93 eV [13] were added to account for the excitation aspect. The calculations were performed at the theoretical lattice constants and by using electronic dielectric constants computed also within DFT-LDA. One problem of the calculation is related to the In 4d electrons. In DFT-LDA they are too shallow, and their levels occur in the valence bands. As a consequence, the pd-repulsion is overestimated, and the resulting fundamental gap $E_g = 0.74$ eV becomes too small. To estimate the repulsion effect we present a second set of data calculated for the In 4d electrons being frozen in the core, but taking into account a self-interaction correction. In the latter case the pd-repulsion practically vanishes, and the gap $E_g = 1.50$ eV is overestimated. The difference of 0.76 eV between 0.74 and 1.5 eV represents the total pd-repulsion. Because of the electronic relaxation effects, the In 4d levels are by 8 eV deeper in energy than those estimated within DFT-LDA. Therefore, the true pd-repulsion should be about 50% of the total value. This results in a theoretical band gap value of about 1.1 eV. Taking the uncertainties of the calculations due to the pd-repulsion, the self-energy calculation and the use of the theoretical lattice constants into account, reasonable agreement with the measured values can be stated.

In the present work the band gap of hexagonal InN close to 0.9 eV was found to be much smaller than the E_g values reported in the literature. Several reasons for findings of E_g higher than 0.9 eV can be suggested. One of them could be the formation of oxynitrides or alloys of the InN–In_2O_3 type due to a low efficiency of the nitrogen source during the layer growth ($E_g = 3.1$ eV in In_2O_3). Another possible reason can be the spontaneous formation of needle-like nanocrystals during heteroepitaxial growth of InN, which is accompanied by a blue shift of the absorption edge due to quantum-size effects. No doubt, the problem of the overestimated E_g values reported earlier requires further investigations.

In summary, some convincing experimental and theoretical arguments have been discussed, which show that the true value of E_g in hexagonal InN is about 0.9 eV, much smaller than E_g of 1.8 eV to 2.1 eV reported previously. The experimental data correlate well with our calculations. Our conclusions are also confirmed by the data on optical spectra of $In_xGa_{1-x}N$ alloys ($0.4 < x < 1$) to be presented in a separate paper.

Acknowledgements The authors are grateful to Prof. R.A. Suris, Prof. S.A. Permogorov, Prof. T. Inushima, and Prof. E.E. Haller for fruitful discussions. We thank A.V. Sakharov, A.N. Smirnov, M.P. Scheglov, V.A. Kapitonov, V.V. Mamutin, and V.A. Vekshin for their assistance in measurements and MBE growth. This work is partly supported by RFBR (No. 99-02-18318 and No. 99-02-17103), the Program "Nanostructures", CRDF (grant No. RP1-2258), and the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm "Gruppe-III-Nitride", Project Be 1346/8-5).

References

[1] T. L. Tansley, in: Properties of Group III Nitrides, Ed. J. H. Edgar, INSPEC, London 1994 (p. 39).
[2] A. Tabata, A. P. Lima, L. K. Teles et al., Appl. Phys. Lett. **74**, 362 (1999).
[3] K. Osamura, K. Nakajima, and Y. Murakami, Solid State Commun. **11**, 617 (1972).
[4] T. L. Tansley and C. P. Foley, J. Appl. Phys. **59**, 3241 (1986).
[5] K. L. Westra, R. P. W. Lawson, and M. J. Brett, J. Vac. Sci. Technol. A **6**, 1730 (1988).
[6] K. Ikuta, Y. Inoue, and O. Takai, Thin Solid Films **334**, 49 (1998).
[7] V. V. Mamutin, V. A. Vekshin, V. Yu. Davydov et al., phys. stat. sol. (a) **176**, 247 (1999).
[8] T. Inushima, V. V. Mamutin, V. A. Vekshin, S. V. Ivanov et al., J. Cryst. Growth **227**, 481 (2001).
[9] J. Aderhold, V. Yu. Davydov, F. Fedler, H. Klausing et al., J. Cryst. Growth **222**, 701 (2001).
[10] V. Yu. Davydov, V. V. Emtsev, I. N. Goncharuk et al., Appl. Phys. Lett. **75**, 3297 (1999).
[11] B. Monemar, Phys. Rev. B **10**, 676 (1974).
[12] F. Bechstedt, U. Grossner, and J. Furthmüller, Phys. Rev. B **62**, 8003 (2000).
[13] B. Wenzien, G. Cappellini, and F. Bechstedt, Phys. Rev. B **51**, 14701 (1995).