

Luminescence, vibrational and XANES studies of AlN nanomaterials

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Abstract

The paper reports comparative studies on synthesized aluminium nitride nanotubes, nanoparticles and commercially available micron-sized AlN powder using different spectroscopic techniques: cathodoluminescence measurements (CL), X-ray absorption near edge spectroscopy (XANES) and Fourier-transform infrared spectroscopy (FTIR). Crucial distinctions in CL spectra are observed for nano- and micro-sized aluminium nitride powders; systematic shift of the IR absorption maximum has been detected for nanostructured aluminium nitride as compared to commercial samples. Through XANES experiments on Al K-edge structural differences between nano- and bulk AlN are revealed, intensity of features in absorption spectra has been found to be a function of wurtzite and zincblende phases amount in nanostructured samples. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Aluminium nitride, AlN, is a chemically, thermally and mechanically stable, piezoelectrically active wide band gap semiconductor possessing excellent insulating properties, low dielectric losses and dispersion (Strite and Morkoc, 1992; Ambacher, 1998). These remarkable features of the material open up the possibilities of using AlN in numerous technological applications like LEDs and laser diodes for optical communication, surface acoustic wave devices which can operate under extreme conditions.

In view of the fact that many of the abovementioned advantages of aluminium nitride can be enhanced as one goes to nanoscaled dimensions, various AlN nanosystems (nanotubes, nanocoils, nanorings, etc., Balasubramanian et al., 2004a,b, 2006; Bellucci et al., 2006; Popov et al., 2007; Zhukovskii et al., 2006; Duan et al., 2005) are recently the subject of widespread investigations.

In a huge number of reports on AlN luminescence (Morita et al., 1982; Youngman and Harris, 1990; Lan et al., 1999; Slack et al., 2002; Strassburg et al., 2004; Silveira et al., 2005; Teofilov et al., 2001), attention is basically paid to the analysis of the near band-edge emission (in the case of electron beam excitation) or defect-related bands in the 2.5–4 eV spectral range (revealed both in cathodoluminescence (CL) and photoluminescence (PL) measurements). PL from AlN with crystalline size less than 100 nm within the region of 2–3.1 eV was reported by different workers (Siwec et al., 1998; Xie et al., 2004; Lu et al., 2005; Zhao et al., 2005; Sardar and Rao, 2005). One should notice that these bands were observed for excitation energies ranging from 3.7 to 4.2 eV, i.e. such emission concerns to the direct photoexcitation of the deep defect levels but not to more complicated mechanisms which can be present in case of luminescence under the electron beam irradiation. CL has proven itself to be a powerful tool for characterization of nanowires, especially in case of wide band gap semiconductors such as boron nitride or aluminium nitride (Sekiguchi et al., 2004). However, to our knowledge, CL measurements have not been carried out on undoped nanostructured aluminium nitride samples.

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Herewith we present the results of our comparative study of AlN microcrystalline and nanostructured samples by means of several spectroscopic techniques.

2. Experimental

We investigated nanostructured AlN samples and, for the purpose of comparison, commercially available high purity aluminium nitride powder (from Sigma-Aldrich) with an average grain size of 10 μm . The detailed description of nanocrystalline samples preparation is given elsewhere (Balasubramanian et al., 2004b). AlN nanosamples on 80% consist of 0.3–0.5 μm long nanotubes with a diameter of about 20–30 nm and on 20% of the spherical nanoparticles.

X-ray absorption near edge spectroscopy (XANES) and Fourier-transform infrared spectroscopy (FTIR) experiments were done at the Synchrotron Radiation facility of the Laboratori Nazionali di Frascati (soft X-ray DRX-1 beamline and synchrotron infrared SINBAD beamline, respectively). XANES measurements were done in 10 min runs on about 70 eV energy range near Al K-edge (1.56 keV) with the energy step not less than 0.4 eV. FTIR spectra were recorded in mid-infrared range (600–4000 cm^{-1}) as well as in far-infrared region (200–400 cm^{-1}) using a Bruker Equinox interferometer modified for low vacuum operation which provides a resolution of 4 cm^{-1} . A liquid helium cryostat was utilized for low-temperature measurements.

CL was studied using an automated set-up on the basis of MDR grating monochromator. Samples were placed in a vacuum chamber and excited by an electron gun which produced periodic microsecond pulses assuring an electron beam energy of about 9 keV and an emission current of 150 μA . The dispersed light from the output slit of the monochromator was focused on the FEU-106 photomultiplier (PMT). For calibration purposes the conventional procedure using standard light source was employed.

3. Results and discussion

Obtained XANES data for AlN powder are generally consistent with previous experimental reports and first principles calculations (Mizoguchi et al., 2004; Suga et al., 2005). From our experiments it was revealed that Al K-edge in nanostructured aluminium nitride is slightly (about 0.1 eV) shifted down to lower energies as compared to the reference material. This shift is due to an additional feature near the edge observed for AlN nanosystems only and not present in the absorption spectrum of the commercial powder. The intensity of noticed feature has been found to depend on the ratio of wurzite and zincblende phases in the investigated samples.

This band indicates the existence of localized density of states in the band gap concerned to defects or possible Al–N hybridization.

In order to analyze the vibrational modes of Al–N bonds FTIR measurements were performed. The IR spectrum of the bulk aluminium nitride exhibits two sharp features in the 200–1800 cm^{-1} wavenumber range: a peak at 698 cm^{-1} and

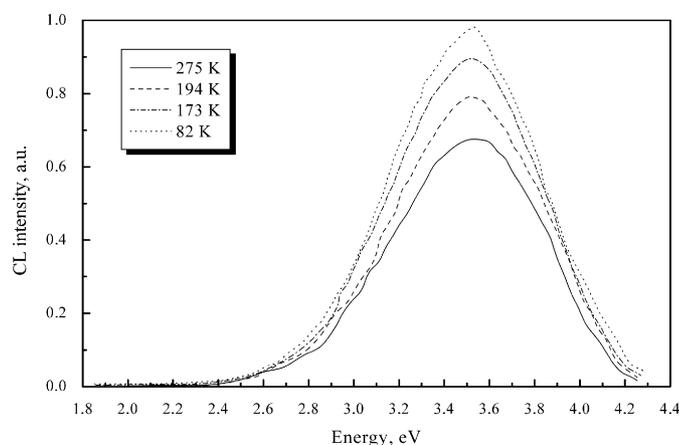


Fig. 1. Cathodoluminescence spectra of commercial grade AlN powder at different temperatures.

another one at 605 cm^{-1} . The latter frequency is fairly close to that of $A_1(\text{TO})$ phonon while the first one differs slightly from reported values of $E_1(\text{TO})$ phonon frequency both being Raman and infrared active (for example, see Sanz-Hervas et al., 2003; Prokofyeva et al., 2001 and references, included therein). Maximum at 698 cm^{-1} in the FTIR spectrum of the sample, consisting mostly of nanotubes shifts to 755 cm^{-1} . This peak probably represents the main phonon band of nanostructured AlN. Similar behavior (taking into account the additional small temperature shifts) was observed for both samples at 80 K. In the mid-infrared domain spectra of nanostructured samples show a number of temperature dependent features which are the subject of further study.

Detailed analysis of the XANES and FTIR spectra has been recently done and published (Balasubramanian et al., 2006).

CL spectra of AlN powder is shown in Fig. 1 for different temperatures. As it is clear from Fig. 1 neither temperature shift nor broadening of the single emission band at approximately 3.5 eV is observed.

This emission in AlN material has been extensively studied in the past four decades. In particular, usually observed broad emission bands in the range from 2.8 to 4.2 eV have been attributed to the presence of oxygen, which is a commonly encountered impurity in the AlN crystals. The peak position of this band has been associated with the oxygen concentration (Pacesova and Jastrabik, 1979; Youngman and Harris, 1990; Slack et al., 2002).

For example, the peak position of this band is 3.8 eV, when oxygen concentration is $1.2 \times 10^{21} \text{ cm}^{-3}$, and it is at 3.3 eV, when oxygen concentration is $5 \times 10^{19} \text{ cm}^{-3}$ (Slack et al., 2002). An appropriate mechanism of donor–acceptor pair recombination has been proposed by Youngman and Harris (1990). Structure of this donor–acceptor pair has been recently established by electron paramagnetic resonance (EPR), electron nuclear double resonance (ENDOR) and optically detected EPR (Schweizer et al., 2000). In particular, the donor is an electron trapped on an oxygen impurity which substitutes for a nitrogen on a regular lattice, while the acceptor was estab-

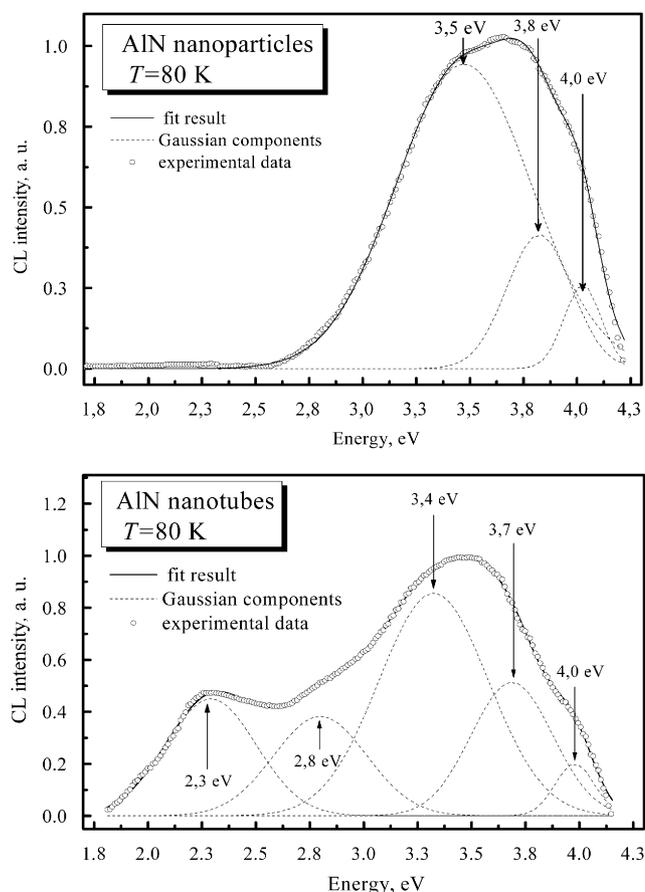


Fig. 2. Cathodoluminescence spectra of AlN nanoparticles and nanotubes at 80 K. Gaussian components shown as dotted lines.

lished by ENDOR to be a hole trapped on an O_N - v_{Al} complex (O_N oxygen on a regular N site, v_{Al} Al vacancy) and X-ray luminescence is due to recombination between such distant donor–acceptor pairs.

Thus in our case, CL of commercial AlN at 3.5 eV is due to the recombination of such donor–acceptor pairs. Its temperature behavior can be explained by thermal ionization of such pairs. Since the spectra of AlN nanomaterials shown in Fig. 2 are normalized ones it should be mentioned that, in fact, luminescence intensity is significantly diminished in comparison with the reference powder. Components at 3.5 and 3.4 eV have, probably, the same nature as in the bulk AlN (small shift may be due to different oxygen contamination in the samples), namely oxygen-related donor–acceptor recombination in hexagonal nanoparticles and nanotubes, while 3.8 and 3.7 eV could be due to the same recombinations in cubic structure case.

Two relatively broad bands, peaked around 2.3 and 2.8 eV, found in CL spectrum of nanotubes can be suggested to originate from smaller nanotubes of diameter 2–3 nm (Balasubramanian et al., 2006). It is theoretically shown that in the case of smaller tubes there should be an effect of band gap decrease of up to 1 eV (Zhao et al., 2003, Zhukovskii et al., 2006). Then similar decrease of luminescence energies of the abovementioned donor–acceptor transition for both hexagonal and cubic structures could be expected. We have to note that in

this case the quantum-sized effect on distant donor–acceptor pair is also possible, but more efforts should be devoted to prove it. Nevertheless, it is interesting to mention that Siwiec et al. (1998) have observed very similar emission bands at 2.3 and 2.7 eV in nanocrystalline AlN with a diameter of 4–8 nm (48%) that is confirming the abovementioned preliminary analysis. More detailed discussion will be given in a forthcoming paper.

4. Conclusions

Principal differences in the physical properties of micron sized commercially available aluminium nitride powder and AlN nanomaterial synthesized by DC arc plasma method have been shown by means of various spectroscopic techniques. XANES measurements revealed distinctions in electronic structure of the investigated samples. From infrared studies a significant shift of phonon modes was detected. Cathodoluminescence spectra of AlN nanotubes and nanoparticles exhibit features not peculiar to the bulk material.

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