Home   Search   Collections   Journals   About   Contact us   My IOPscience

Characterization of aluminium nitride nanostructures by XANES and FTIR spectroscopies with synchrotron radiation

Characterization of aluminium nitride nanostructures by XANES and FTIR spectroscopies with synchrotron radiation

C Balasubramanian[1,2]**, S Bellucci**[1]**, G Cinque**[1]**, A Marcelli**[1]**,
M Cestelli Guidi**[1]**, M Piccinini**[1,3]**, A Popov**[4]**, A Soldatov**[5] **and
P Onorato**[1,3]

[1] INFN-Laboratori Nazionali di Frascati, Via E Fermi 40, 00044 Frascati (RM), Italy
[2] Department of Environmental, Occupational and Social Medicine, University of Rome Tor Vergata, 00133 Rome, Italy
[3] Department of Geological Science, University of Roma Tre, Via della Vasca Navale 84, 00146 Rome, Italy
[4] Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble, France
[5] Faculty of Physics, Rostov State University, 344090 Rostov-on-Don, Russia

Abstract
We investigated different AlN nano-systems using spectroscopic methods. Experiments were performed at the Synchrotron Radiation Facility of the Laboratori Nazionali di Frascati using both XANES (x-ray absorption near edge spectroscopy) and FTIR (Fourier transform infrared spectroscopy) techniques in order to investigate materials with both interesting tribological and electronic properties. Comparisons have been performed between measurements by standard x-ray diffraction (XRD) and x-ray absorption (XRS) at the K-edge of Al, a spectroscopy method sensitive to the local order and correlated to the local and empty density of states of this wide band-gap semiconductor. Preliminary XAS simulations at the Al K edge are also presented. Correlations between XRD and XAS have been drawn, since x-ray absorption reveals structural information complementary to that addressed by x-ray diffraction. Moreover, a comparison has been performed by infrared (IR) absorption both in the mid- and in the far-IR ranges between different AlN forms: namely, powders, nanoparticles and nanotubes. Data clearly show changes connected with the electronic properties and the optical phonon modes of AlN nano-systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Aluminium nitride is a wide band-gap semiconductor and has peculiar mechanical properties, such as hardness with a typical value of 11.8 GPa. In modern technology, this material is

commonly used in thin film devices due to its high thermal conductivity and small thermal expansion coefficient [1, 2]. At room temperature, AlN crystallizes in the wurtzite phase [3], even though thin films of zincblende polytypes [4] have also been grown under high nitrogen ion bombardment. One-dimensional nanostructures have numerous applications in science and technology due to their fascinating electrical, optical and thermal properties. The atomic structure of nanotubes or particles is normally different to that in the bulk or in thin films due to the reduced symmetry and/or highly non-equilibrium synthesis routes. Both hexagonal (wurtzite-AlN) and cubic phases (zincblende-AlN) of aluminium nitride have found applications in a variety of technologies, ranging from cutting/grinding to corrosion or in exotic devices such as electro-acoustic systems [5, 6] etc. While the synthesis of highly textured and/or crystalline thin films with wurtzite can be carried out rather easily using various methods [5, 7], the synthesis of a cubic AlN in the form of thin films is much more difficult. To our knowledge, there are no reports of zincblende AlN in bulk form. Some studies have revealed that techniques, such as pulsed-laser deposition (PLD), magnetron sputtering etc, could be meaningfully used to synthesize thin films of AlN with zincblende or cubic structure [8]. The specific characterization of these nanosystem has been performed by XANES [9], which is a spectroscopic technique that is sensitive both to the electronic properties and to the local geometrical structure and symmetry. A preliminary comparison with theoretical calculations in the framework of multiple scattering theory is also presented.

2. Characterization tools

For this study, both aluminium nitride nanoparticles (NP) and nanotubes (NT) were synthesized separately by DC arc plasma, as described in a previous communication [10]. Standard characterization has been performed using an x-ray diffractometer (Phillips model PW1840 and Pan Analytical X'Pert PRO) using Cu Kα radiation and a transmission electron microscope (TEM, JEOL JEM 2010 and JEOL 1200EX). For XRD experiments, the diffraction pattern was recorded directly from powder (bulk) samples. For TEM imaging, the samples were suspended in iso-propylic alcohol and ultrasonicated for a sufficient period of time. Then a micro drop of the sample was placed on a carbon-coated copper 400 mesh grid. The tubes analysed by TEM and SEM and were found to form in typically two size ranges: (a) larger tubes of diameter 25–30 nm and lengths of ∼700 nm, and (b) smaller tubes of 2–3 nm with length scales of ∼700 nm. X-ray diffraction analysis of these samples revealed material possessing a rare metastable cubic phase (zincblende structure). The smaller tubes have helicoidal structure and the bigger ones have hollow tubular structure [11, 12].

A more accurate characterization was performed at Frascati using synchrotron radiation emission from DAΦNE, the storage ring operational at the Laboratori Nazionali of Frascati of the Istituto Nazionale di Fisica Nucleare (INFN). The synchrotron infrared beamline (SINBAD) was used for FTIR spectroscopy, while the soft x-ray beamline (DRX-1) was used for x-ray absorption experiments on a set of AlN samples described in section 3. At the DAΦNE-Light laboratory, the IR radiation is extracted from a bending magnet of the electron ring and transmitted to an interferometer at a distance of about 25 m using a beam line kept under ultra-high vacuum up to a diamond window placed at the entrance of the spectrometer. The instrument is a BRUKER Equinox 55, modified to work in a low-vacuum regime in the whole IR range down to the far-IR domain [13]. Experiments were performed in a vacuum of about 10^{-2} mbar in transmission mode at room temperature and versus temperature down to liquid nitrogen (LN$_2$) temperature. All the samples used for FTIR analyses were prepared in the form of pellets after mixing with a commercial CsI powder of 99.995% purity.
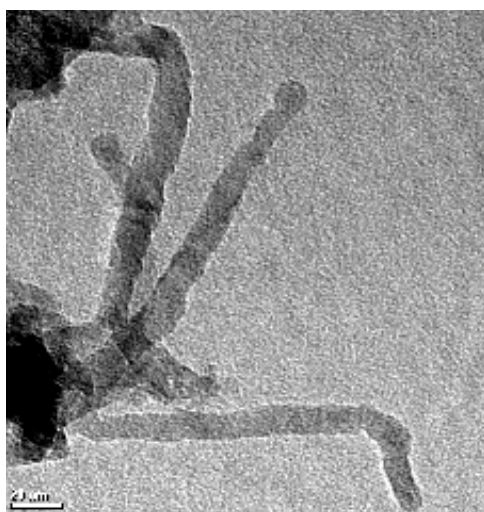
Figure 1. TEM image of the sample NT3 e.g., an AlN nanotube system.

The same set of samples was characterized by the XAS technique in transmission at the soft x-ray beamline. The transfer line collects and transmits the radiation originated by one of the DAΦNE 6-pole equivalent wiggler sources endowed with a critical energy of around 300 eV. For the XANES study, samples of extremely low thickness were prepared. This was done by manually grinding the powders and fixing them onto both sides of 8 μm thick paper supports.

3. AlN samples

Mainly, three different samples were analyzed using the above-mentioned techniques. The first sample (NT3) consists of AlN nanotubes with an average diameter of 25–30 nm and an estimated length of 700 nm. The ratio of nanotubes in this sample is about 85%; the remainder is composed of spherical-shaped nanoparticles of diameter 25 nm. Figure 1 is a TEM image of the NT3 sample. This sample and all the others presented in the manuscript were also characterized by x-ray diffraction. The XRD spectrum shown in figure 3 (top curve) refers to the NT3 sample and indicates the presence of an almost pure cubic (zincblende) structure. With XANES, two additional nanotube samples, previously characterized by XRD and showing similar diffraction patterns but with different intensities (e.g., different cubic versus hexagonal phase compositions, NT2 and NT4), have been measured.

The second AlN nano-system (NP) consists of nanoparticles with an average size of 100 nm. In the samples analyzed, we were not able to detect one-dimensional (1D) structures and the TEM images show the prevailing presence of particles with hexagonal symmetry. The TEM image in figure 2 shows the typical shape of the nanoparticles present in the sample. The XRD data of this sample confirm that it is a mixture of both cubic (zincblende) and hexagonal (wurtzite) phases (figure 3—bottom curve).

The reference sample is a commercial, high-purity (99.9%) aluminium nitride powder from *Sigma-Aldrich*. The average particle size is 10 μm and, as shown in figure 4, XRD analysis confirms that its crystal symmetry is hexagonal (wurtzite phase).

Resistivity measurements have also been performed on sample pellets using a Keithley 6485 Picoammeter. Electrical contacts on the pellets were made with silver paint on the surface and the resistivity was measured at an applied voltage of 500 V. The data of the investigated
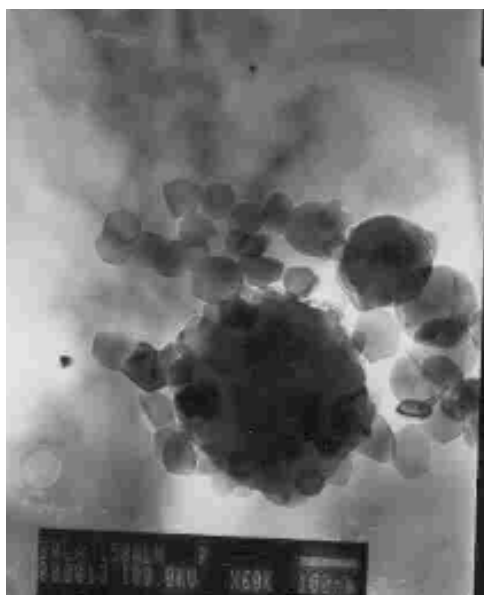
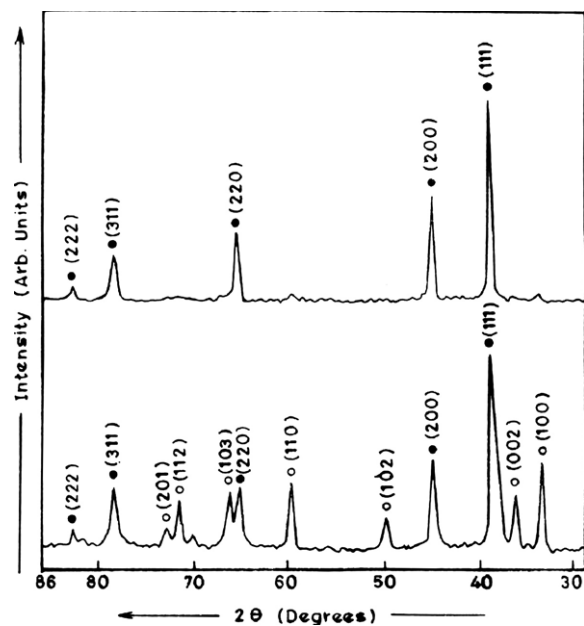**Figure 2.** TEM image of the sample NPs, e.g., AlN nanoparticles.

Figure 3. Comparison of the XRD spectra of two samples: the AlN nanotubes NT3 (top curve) and the AlN nanoparticles NP (bottom curve).

samples are listed in table 1), together with the results of the standard XRD characterization. The phase compositions, estimated by XRD and summarized in table 1, are given within 1–2%.

4. Experiments

X-ray absorption experiments were performed on powders in transmission mode. Actually, the transmission signals were acquired using ion chambers filled with N_2 gas in order to absorb, respectively, ~15% of the x-ray beam in the first one and over 90% in the second one. In this
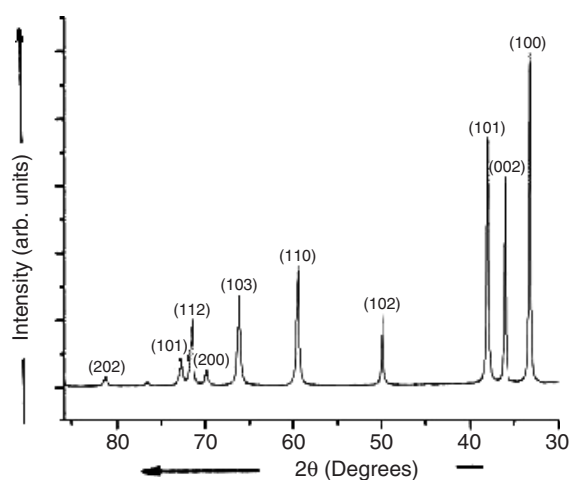
Figure 4. XRD spectrum of the commercial-grade AlN powders.

Table 1. Experimental data of the investigated AlN samples. (Note: data are taken from standard resistance values available for commercial AlN powders.)

Sample	Cubic (zincblende)	Hexagonal (wurtzite)	Resistivity
AlN powder (C)	—	$\sim$100%	$2\text{--}3 \times 10^5$ GΩ cm^{-2}
AlN nano-particles NP (B)	46%	50%	60 ± 4 MΩ cm^{-2}
AlN nanotube NT4	75%	20%	1200 ± 70 GΩ cm^{-2}
AlN nanotube NT3 (A)	91%	7%	4100 ± 150 GΩ cm^{-2}
AlN nanotube NT2	66%	31%	120 ± 15 MΩ cm^{-2}

configuration, the two thin windows made by 300 nm thick polyethylene film supported on 0.4 mm Si mesh (vertical ribs) allow an overall 76% transmission at the Al K edge energy. A fixed-exit 'boomerang' monochromator from Toyama is used to perform photon energy selection using two crystals of KTP(011). At this energy, the energy resolution is mostly dominated by the intrinsic crystal properties since, geometrically, resolution slits and Bragg's angle of work are equivalent to a resolving power of 10^3.

The XANES measurements were performed in single runs of typically 10 min at an energy range of 60–70 eV around the Al K-edge. The constant energy step used is between 0.2 eV and 0.4 eV and the acquisition time is either 1 s or 2 s per point. Pure Al metal foil was used as reference material for energy calibration, as well as Al_2O_3 powder deposited on thin paper, as for previous samples, for oxidation state comparison and cross-control of measurements.

IR spectroscopy gives an insight into the molecular structure through the specific vibrational frequencies, so experiments were performed first in the range 600–4000 cm^{-1} with the interferometer working in vacuum and with a resolution of 4 cm^{-1}. For these measurements, a mercury, cadmium, telluride (MCT) detector (1 mm^2 in size) cooled to liquid nitrogen temperature and a KBr beam splitter were used. Data have been also collected down to low wavenumbers in the far-IR domain to probe the phonon modes and, consequently, the long-range periodicity of the crystalline structure of these nanosystems. FTIR characterization in the far-IR domain (200–600 cm^{-1}) has been performed in vacuum both at room temperature (RT) and at low temperature (about 80 K) using a bolometer working at 4.2 K and a BRUKER T222 mylar beamsplitter.
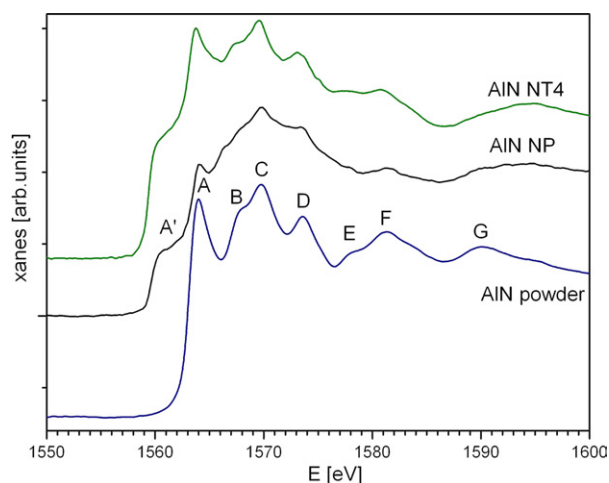
Figure 5. Soft x-ray absorption data at the Al K-edge in aluminium nitride (AlN) powder, nanoparticles (NP), and nanotube sample 4 (NT4).

5. Results and discussion

AlN nano-systems have been characterized by XANES spectroscopy, which is a technique that is sensitive to both the electronic and structural properties. Recently, several investigations have been devoted to the investigation of the Al K edge in AlN systems [14–16] and, in the case of thin films that appear amorphous by XRD, XANES allows recognition of the symmetry around the Al site and the related phase. Data clearly show that AlN systems mainly grow in the hexagonal wurtzite phase.

In figure 5, we compare the Al K edge spectra of our AlN systems. In particular, the bottom curve is the spectrum of the AlN powder which, comparing the zero of the first derivative, shows a shift towards higher energy of about 3.5 eV with respect to the edge of the Al metal placed at 1559.6 eV, and is in agreement with the Al K edge spectra published previously in the literature. As shown in figure 6, the XANES spectrum of AlN is well reproduced by a multiple scattering (MS) theoretical simulation for clusters of AlN containing about 200 atoms using the hexagonal (wurtzite type) lattice with the following cell parameters: $a = 3.110$ Å, $c = 4.980$ Å, and $u = 0.3821$ [17]. The theoretical analysis of the Al K-edge of x-ray absorption in AlN has been carried out on the basis of the self-consistent full multiple-scattering method [18] implemented in FEFF8.4 code. Actually, spectra have been calculated starting from the band structure density functional theory (DFT) approach (WIEN2k) combined with the real-space self-consistent full multiple scattering theory (FEFF8.4) and full potential finite difference method (FDMNES2005). Within the real-space multiple scattering approach, spectra were calculated for different types of exchange potentials: a non-local Dirac–Fock potential, the Hedin–Lundqvist potential, and the Dirac–Hara potential. The spectra dependence on relaxation of electrons in the presence of a core–hole has been studied as well. The dependence of the XANES spectra on the cluster size around the absorbing atom has also been investigated and the partial projected density of states (DOS) for both bulk AlN and AlN nanoparticles has been calculated and found to be different between the bulk and nanoparticles. The best agreement with experiment has been achieved for the spectra calculated using the Hedin–Lundqvist potential. Data show that a large cluster of atoms (of at least about 200 atoms) around the photoabsorbing Al must be taken into account. More details of the calculations are the subject of a forthcoming manuscript.

Figure 5 clearly also addresses the presence of the different phases in the samples investigated. Indeed, the spectrum of AlN nanoparticles is the superposition of a hexagonal
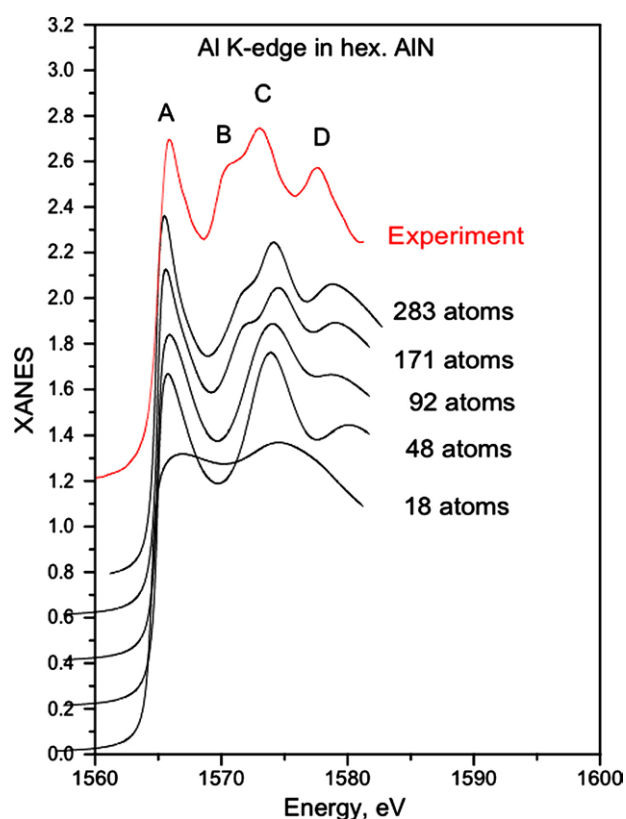
Figure 6. Comparison between Al K edge MS simulations with increasing clusters of the AlN system with hexagonal symmetry and experimental data of the AlN powder.

spectrum plus the contribution associated with the nanoparticles having cubic symmetry. From XRD data in table 1, we know that this sample is indeed composed of almost the same amount of the two phases. From this spectrum, we may also see that Al K edge in this system is shifted to lower energy by only about 0.1 eV, because an intense structure, A′, associated with an empty localized density of states appears just before the main peak A. The same A′ feature, but even more intense, is present in the spectrum of the AlN nanotube (NT4), which also shows the characteristic features of the wurtzite phase (h-AlN). The feature A′ should be associated with the content of the zincblende phase (c-AlN) which, in the NT4 sample, is about 75%, e.g., higher than the content of the AlN nanopowder. In contrast, as we will show next, the feature A′ in nano-systems can only be associated with the different electronic properties of these systems. Actually, in these high wide-band gap semiconductors, we noticed the presence of many defect sites in the band gap (see figure 6 in [19]), which are confirmed by the XANES behaviour at the edge. These defects may strongly affect the electron localization and the conductivity behaviour.

To understand the origin of the feature A′ and to explain the shape of spectrum of sample NT4, in figure 7 we compare the XANES of the three nanotube samples characterized by different concentrations of both wurtzite and zincblende phases (see table 1). All spectra are characterized by the same features, whose intensity scales proportionally with the content of the hexagonal AlN phase. As a consequence, the feature A′ is smaller in the NT3 sample that contains only 8% of the wurtzite phase, as returned by the XRD data. Although there is a strong similarity between the spectra of the AlN powder and those of AlN nanotubes characterized by a significant wurtzite phase, the presence of the feature A′ near the metallic edge addresses a
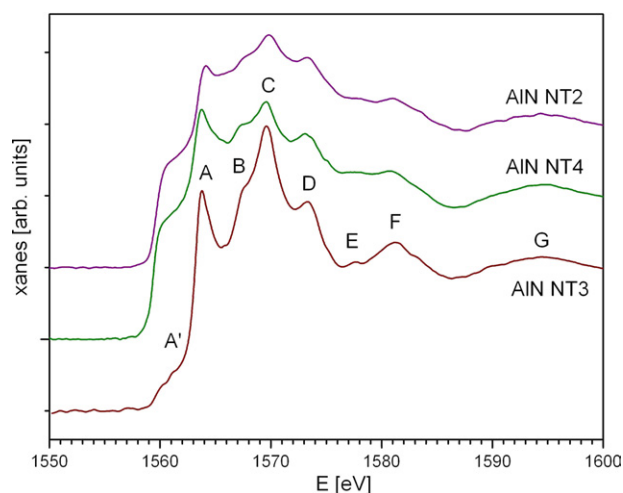
Figure 7. Comparison of XANES spectra at the Al K-edge for three samples of AlN nanotubes containing different concentrations of the two crystalline phases.

specific behaviour of these nano-systems. The strong A′ feature, which is also present in the spectrum of nanopowders, is a clear marker of the presence of a density of states in the gap probably due to defects and/or the hybridization between Al and nitrogen atoms. The intensity of the A′ structure increases as the hexagonal phase increases and a clear correlation, as shown in table 1, also exists with the resistivity data. In nanotubes, the resistivity decreases with the increase in the content of the wurtzite phase and reaches a minimum in the NT2 samples, where it is more than four orders of magnitude smaller compared with the almost cubic sample (NT3).

To improve the characterization of these nano-systems, we also performed Fourier transform infrared (FTIR) spectroscopy experiments. Because mid-IR spectroscopy gives an insight into the molecular structure through the specific vibrational frequencies, in the last four decades the phonon structure of AlN has been the subject of numerous investigations with these techniques [20, 21]. In figure 8, we show the IR spectra of the three AlN samples (e.g., bulk, nanopowders, and nanotubes) extended from the mid-to the far-IR domain. Indeed, the far-IR domain probes the lower phonon modes and, consequently, the long-range periodicity of the crystalline structure of these systems. The main infrared active phonons of the Al–N bonds occur in the domain 200–1000 cm^{-1} [22]. Looking at figure 8, the spectra recorded for the three samples showed definite and systematic shifts in the absorption values for both nanotubes and nano-particles compared with the bulk spectra and the values reported in the literature [23]. Moreover, no significant shifts in the main peaks of the corresponding samples between the low temperature (LT) and room temperature (RT) spectra have been observed.

The most prominent and broad absorption band for commercial-grade AlN powder was observed at 698 cm^{-1}, while the nanoparticle spectrum showed multiple peaks at 741 cm^{-1} and 755 cm^{-1}, and that of nanotubes exhibited a maximum in absorption at 748 cm^{-1}. The mid-IR spectra of both nanoparticles and nanotubes are rich in broad features in the range 1200–1700 cm^{-1} that shift versus temperature.

In figure 8, we observe a systematic shift of the peak towards higher wavenumbers as one moves from bulk (698 cm^{-1}) to nanoparticles ($\sim$750 cm^{-1}) and then to nanotubes (755 cm^{-1}). The increase in energy can be associated with the lower dimensionality of the system. Indeed, the difference in the crystal structure is not expected to give such a large change
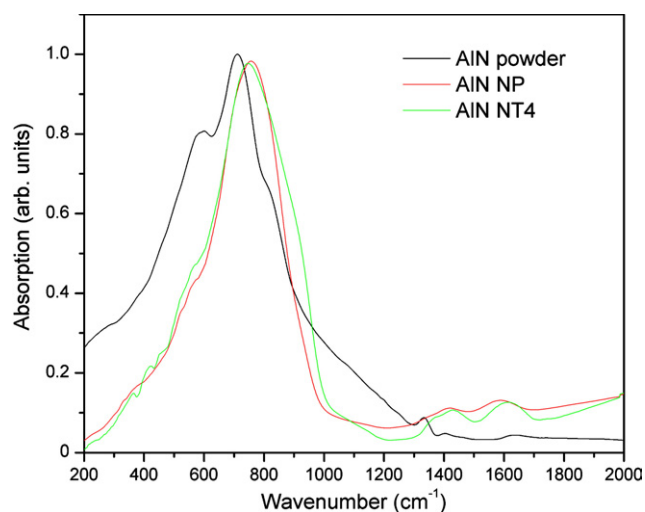
Figure 8. Normalised FTIR spectra of various AlN samples at LT (LN$_2$) temperature as well as RT (room temperature); AlN powder represents commercial-grade micron-sized powder (nanoparticles = NP) (nanotubes = NT4).

in the vibrational energy of the spectra, as the lattice parameter for zincblende and wurtzite is fairly close. The frequency behaviour of the molecular vibration supports the hypothesis of the formation of stronger bonding in the nanotube compared to its bulk counterparts. Low-temperature spectra show a similar trend, but with an additional shift of 4–5 cm^{-1} towards higher wavenumber in all the investigated samples. Although this is in agreement with the XANES behaviour shown in figure 5, where the single scattering feature at about 1590 eV slightly expands, when moving from bulk to nanoparticle and nanotube systems further FTIR experiments are necessary. A more accurate and systematic analysis of the data on these samples is in progress and will be the subject of a dedicated FTIR investigation. However, the significant hardening observed in this system should be explained also by an almost continuous evolution of the local structure, e.g., a local distortion of the AlN structural unit that can also be correlated to the observed changes in the AlN transport properties (see table 1). Quite similar behaviour has recently been detected by Raman spectroscopy in manganite thin films. With this vibrational spectroscopy, which is extremely sensitive to subtle structural modifications that are barely detectable by XRD, Dore *et al* [24] demonstrated the occurrence of a strong hardening of the bending and stretching phonons on decreasing the film thickness *d* below 100 Å. Moreover, while the spectra do not change in the range 1000–100 Å, for ultra-thin films of manganite, the observed hardening clearly demonstrates the correlation between vibrational modes and local structure, a correlation that becomes critical in the nanometre range.

6. Conclusions

Nanostructured aluminium nitride systems were synthesized and characterized by XRD. Morphological studies have also been performed using TEM imaging. Accurate spectroscopic investigations have been performed on a selected set of AlN systems by both x-ray absorption and FTIR spectroscopies. A comparison between the local structure of AlN nanosystems and XRD data has been performed and the results applied to a limited set of nanotube samples with different compositions of wurtzite and zincblende phases.

XANES data clearly shows the presence of relevant structural differences in these nano-systems and the possibility of probing electronic properties in agreement with both XRD and resistivity experiments. The main result obtained from the analysis of the XANES data in the samples investigated, and independently from the order, is the high sensitivity to the presence of both symmetries: hexagonal and cubic. Indeed, all spectra are characterized by the same features whose intensity scales proportionally with the content of the wurtzite AlN phase. Moreover, the presence of a specific feature near the edge addresses the specific behaviour of nano-systems, e.g., the occurrence of a density of states in the gap probably due to defects and/or to the hybridization between Al and nitrogen atoms that appears correlated to the resistivity data.

For the same systems, we performed FTIR experiments at both RT and LN$_2$ temperatures. The nano-structured materials showed prominent peaks in the wavenumber region at about 750 cm^{-1}, with a shift of the order of 50 cm^{-1} towards higher wavenumber. These peaks could be treated as the signature of the main phonon bands for nanostructured and 1D AlN systems.

Acknowledgments

References

[1] Virkar A V, Jackson T B and Cutler R A 1989 *J. Am. Ceram. Soc.* **72** 2031
[2] Strite S and Morkoc H 1992 *J. Vac. Sci. Technol.* B **10** 1237
[3] Meng W J 1994 *Group III Nitrides* ed J H Edgar (London: INSPEC) pp 22–9
[4] Ren Z-M *et al* 2000 *Japan. J. Appl. Phys.* 2 **39** L423
[5] Pierson H O 1996 *Handbook of Refractory Carbides and Nitrides, Properties, Characterisation, Processing and Applications* (Westwood, NJ: Noyes Publications)
[6] Dimitrova V, Manova D and Valcheva E 1999 *Mater. Sci. Eng.* B **68** 1
[7] Godbole V P *et al* 1999 *Mater. Sci. Eng.* B **68** 85
[8] Madan A, Kim I W, Cheng S C, Yashar P, Dravid V P and Barnett S A 1997 *Phys. Rev. Lett.* **78** 1743
[9] Bianconi A 1988 XANES spectroscopy *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* ed D C Konigsberger and R Prins (New York: Wiley) p 573
[10] Balasubramanian C *et al* 2004 *Nanotechnology* **15** 370–3
[11] Balasubramanian C, Bellucci S, Castrucci P, De Crescenzi M and Bhoraskar S V 2004 *Chem. Phys. Lett.* **383** 188
[12] Bellucci S 2004 *CANEUS 2004-Conf. on Micro–Nano-Technologies (Monterey, CA, Nov. 2004)* AIAA paper 2004-6752
[13] Cestelli Guidi M, Piccinini M, Marcelli A, Nucara A, Calvani P and Burattini E 2005 *J. Opt. Soc. Am.* **22** 2810
[14] Katsikini M *et al* 1997 *J. Appl. Phys.* **82** 1166
[15] Suga T *et al* 2005 *Appl. Phys. Lett.* **86** 163113
[16] Guo Q *et al* 2005 *Appl. Phys. Lett.* **86** 111911
[17] Schulz H and Thiemann K H 1977 *Solid State Commun.* **23** 815
[18] Ankudinov A L, Bouldin C E, Rehr J J, Sims J and Hung H 2002 *Phys. Rev.* B **65** 104107
[19] Bellucci S 2005 *Phys. Status Solidi* c **2** 34
[20] Collins A T, Lightowlers E C and Dean P J 1967 *Phys. Rev.* **158** 833
[21] Loretz J C, Despax B, Marti P and Mazel A 1995 *Thin Solid Films* **265** 15
[22] Nyquist R A and Hagel R O 1971 *Infrared Spectra of Inorganic Compounds* (New York: Academic)
[23] Ruiz E, Alvarez S and Alemany P 1994 *Phys. Rev.* B **49** 7115
[24] Dore P, Postorino P, Sacchetti A, Baldini M, Giambelluca R, Angeloni M and Balestrino G 2005 *Eur. Phys. J.* B **48** 255