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Morphology, structural and absorption studies on gallium nitride powder

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A simple method of synthesis of nanocrystalline GaN powders is presented. The morphology and structure of the powders was characterized by XRD and TEM methods. It was observed that the sizes of single grains of gallium nitride depend on parameters of the technological process. Using the Sherrer's rule, the sizes of crystallites were determined to be in the range of 14–33 nm. It was found that *a* and *c* parameters of hexagonal gallium nitride slightly depend on the crystallite size. Changes of the absorption edge and Urbach energies are presented.

Key words: *GaN nanocrystallite; absorption; semiconductor*

1. Introduction

Gallium nitride and related compounds are important materials used in light-emitting devices and lasers operating in the UV spectral region [1, 2]. Recently, nanostructured GaN materials have attracted extensive interest because of their importance in the fundamental physical research but also due to emerging applications in optoelectronics and nanotechnology [3]. As members of the family of III–V group nitrides, AlN, GaN, InN and their alloys are wide-band-gap materials (6.2 eV for AlN, 3.4 eV for GaN and 1.9 for InN at room temperature), and can crystallize in both wurtzite and zinc-blende polytypes [4]. GaN crystallizes in either a thermodynamically stable wurtzite structure having hexagonal symmetry or a meta-stable zinc-blende structure with cubic symmetry [5]. Nitride semiconductors frequently contain large concentrations of impurities, introduced either intentionally or unintentionally. It is well known that the incorporation of impurities can affect the lattice parameters

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of semiconductor [6]. The latter depend on the following factors: (i) free-electron concentration via the deformation potential of a conduction-band minimum occupied by these electrons, (ii) concentration of dopants (or point defects) and the difference of ionic radii of the host and guest ions (size effect), (iii) strains (including those induced by lattice mismatch between a substrate and a layer), and (iv) thermal expansion change by free charges (if the measurements are performed at non-zero temperatures) [7]. The lattice parameters of gallium nitride were reported in a number of papers [8–10]. Song [8] performed the lattice constant refinement for bulk GaN single crystal and obtained the following values: a = 3.1903(3) Å, and c = 5.1864(6) Å. In Refs. [9, 10], the values: a = 3.180 Å, c = 5.180 Å and a = 3.186 Å, c = 5.174 Å, respectively, were reported for GaN powder.

A considerable effort has been put in last years into studies of GaN semiconductor materials exhibiting blue emission: bulk crystals [11], thin films [12] and powders were investigated. In the last few years, the interest has been focused on the GaN nanostructures [13–15] and several methods of their fabrication were put forward. We have recently reported a sol-gel preparation of GaN nanocrystallites embedded in silica glass which demonstrated an intense yellow emission [16]. In the present paper, we report a simple method of the chemical synthesis of pure GaN nanopowders. Their X-ray diffraction patterns and physical properties were studied.

2. Experimental

2.1. Powder preparation and nitridation

Three 0.5 g samples of Ga_2O_3 (99.999%) were used in our experiments. After their solubilization in hot concentrated nitric acid (~115 °C), the solutions were evaporated to dryness. The obtained powders were carefully dried in an oven on gradually increasing the temperature from 70 to 200 °C. Then the powders, put into alumina crucibles, were inserted into a quartz tube (24 mm ID) and calcined at 500 °C for 4 h in air flow (100 cm^3/min) to convert $Ga(NO_3)_3$ into Ga_2O_3. The crushed powder samples were placed at room temperature into a quartz tube in NH_3 flow (120 cm^3/min), and after purging (20 min) the samples were heated (10 °C/min) to the required temperature, i.e., to 700 °C (sample A), 850 °C (sample B) and 1050 °C (sample C) and then were held at the target temperature for 3.5 h. NH_3 used for nitridation (from Messer, Poland, 99.85 vol.%) was additionally purified by passing it over a zeolite trap.

The reaction proceeds according to the scheme:

$$Ga_2O_3 + 2NH_3 \rightarrow 2GaN + 3H_2O \quad (1)$$

One of the gallium nitride samples was prepared according to a slightly modified procedure given in Ref. [18]. This so-called “fluoride method” allows us to obtain GaN nanopowder via the pyrolytic reaction of the ammonium hexafluorogallate, $((NH_4)_3GaF_6)$ with flowing ammonia at 700 °C.

The reaction proceeds according to the scheme:

$$(NH_4)_3GaF_6 + 4NH_3 \rightarrow GaN + 6NH_4F \quad (2)$$

2.2. Sample characterization

Overall phase compositions of the nanopowders were determined by X-ray powder diffraction with a Siemens D5000 diffractometer and $CuK_{\alpha 1}$ radiation, λ = 0.15406 nm. The microstructure of the samples was examined with a Philips CM20 SuperTwin transmission electron microscope (TEM), which provides a resolution of 0.25 nm at 200 kV.

Absorption spectra were recorded in the range of 1.5–4.5 eV at room temperature with a Cary–Varian 5 spectrophotometer.

3. Results and discussion

Figure 1 shows the XRD patterns of GaN powders. All patterns show the diffraction lines which could be ascribed to the formation of hexagonal gallium nitride with a wurtzite-type structure (JCPDS file No. 02-1078).

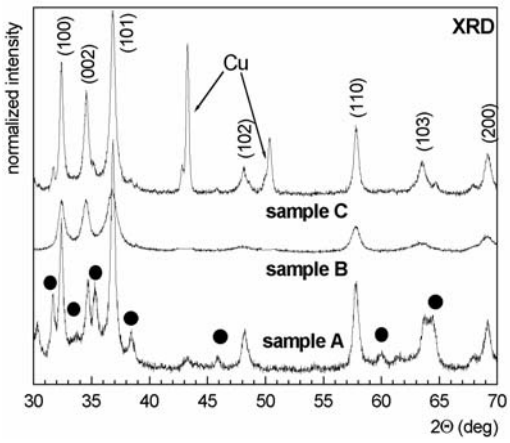

Fig. 1. XRD pattern of GaN nanocrystallite powders. For clarity, the peaks at 2θ = 43.30 and 50.43° due to the copper sample holder (sample B) have been deleted

For the sample A and, to a lower extent, for the sample C we observed additionally the peaks of crystalline gallium oxide (black dots) (JCPDS file No.11-0370) which at temperature of 700 °C was not converted into gallium nitride. The diffraction peaks were broadened indicating that the GaN nanocrystals are very small. The average grain sizes were determined by means of the Scherrer formula [17], and are listed in Table 1, together with the lattice parameters for the hexagonal gallium nitride.

The analysis of TEM micrographs (Fig. 2) clearly indicates that the samples contain aggregated crystallites with the sizes of 20–50 nm (sample C) and 50–110 nm

(sample A), i.e. much larger than those evaluated from XRD (see Table 1). These discrepancies could be due to the fact that the use of the Scherrer formula allows us to determine an average size of the individual crystallites whereas the transmission electron microscopy in certain cases reflects the dimension of the whole agglomerated particle composed of a few nanocrystallites. For the samples nitrided at 850 °C (micrographs not shown here), the average GaN crystallite sizes were 20–100 nm. The spatial distribution of GaN nanocrystals in the samples appears to be rather uniform. The selected area electron diffraction (insets Fig. 2) could be indexed as a hexagonal GaN phase. The lattice plane spacings agree well with those for the hexagonal GaN phase: (100) 2.76Å, (002) 2.59Å and (101) 2.43Å.

Table 1. Lattice parameters of GaN powders

Composite	Crystal mean size[1] $d\pm0.1$ (nm)	Crystal structure	Position (2θ)	*hkl*	Lattice constant[2](Å)	
					$a\pm0.001$	$c\pm0.001$
GaN[3] (700°C) (sample A)	21.5	wurtzite	32.432 34.661 36.863	100 002 101	3.187	5.170
GaN (850°C) (sample B)	14.4	wurtzite	32.394 34.484 36.720	100 002 101	3.194	5.199
GaN (1050°C) (sample C)	33.1	wurtzite	32.381 34.535 36.810	100 002 101	3.191	5.190

[1]Calculated using the Scherrer formula [17].
[2]Calculated using a set of power equation for hexagonal arrangements.
[3]Sample prepared by using the fluoride method [18].

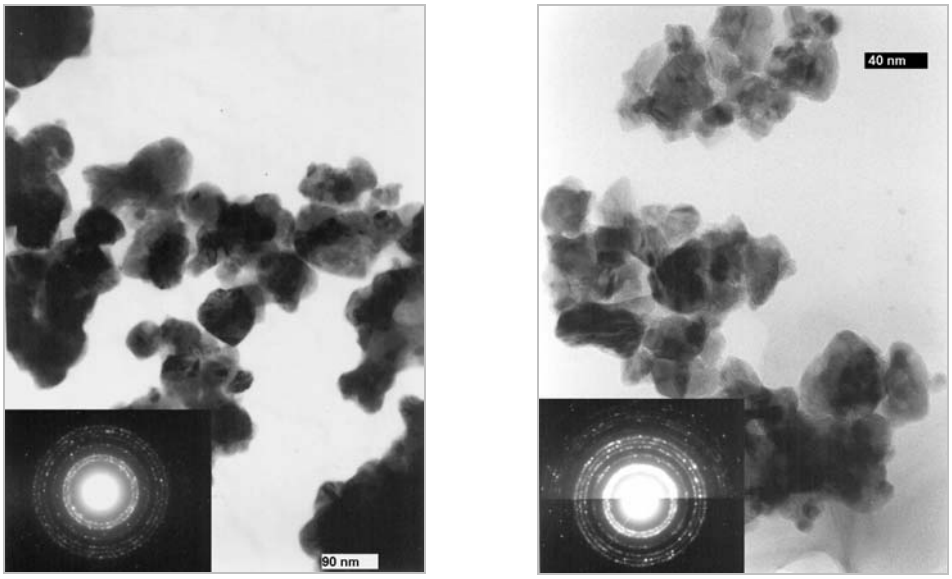

Fig. 2. TEM image and SAED pattern of a GaN nanoparticle nitrided at: a) 700 °C, b) 1050 °C

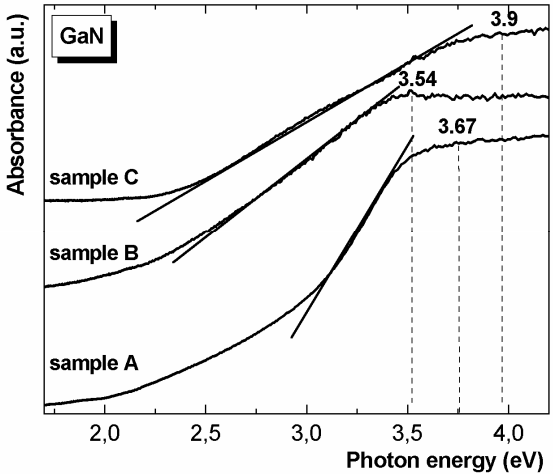

Fig. 3. Absorption coefficient as a function of energy for the sample A nitrided at 700 °C, sample B at 850 °C and sample C at 1050 °C

In Figure 3, the band gap absorption at 300 K, measured in the range of 1.5–4.5 eV, is shown for three samples differing in average sizes of GaN grains. We found that the energy of the absorption edge (E_g) depends on the annealing temperature and hence on the size of grains: E_g = 3.67 eV (sample A), E_g = 3.54 eV (sample B) and E_g = 3.9 eV (sample C) [19, 20]. The regions of the so-called Urbach spectral tail can be found in the spectra of the samples A, B and C. The absorbance (α) in this spectral region can be approximated by a linear function and, consequently, for 3.0 eV < $h\nu$ < 3.5 eV

$$\alpha(h\nu) \approx b + \frac{h\nu - E_g}{U} \tag{3}$$

where b is a constant, and U is the so-called Urbach energy.
In the low energy region the spectral dependence of the absorption coefficient is characterized by a small slope and hence, by an extremely large Urbach energy, U = 0.7 eV for sample A, U = 1.4 eV for sample B and U = 2 eV for sample C. This parameter was found to be dependent on the crystal size and annealing temperature. Jacobson et al. reported [21] for GaN films that the Urbach tails are combined of two linear functions characterized by two energies: U_1 = 400–470 meV and U_2 = 10–20 meV. We believe that the first part with a large Urbach energy U_1 is associated with the presence of a strongly disordered material.

3. Conclusions

GaN nanocrystalline powders have been prepared using a simple synthetic method, the so-called combustion method. The size of GaN particles was found to

depend on the nitridation temperature and ranged from 14 up to 33 nm as found by the Scherrer method. The sizes of agglomerated particles, however, estimated from TEM were found much larger, attaining 110 nm. The phase composition, morphology and absorption properties of GaN nanocrystalline powders have been also determined. Changes of the edge of absorption and Urbach energies are presented. The Urbach energy was found to increase with increasing temperature of nitridation.

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