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## Fabrication and structural studies of “opal–III nitrides” nanocomposites

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**Abstract.** Three-dimensional system of GaN and InN nanoclusters have been synthesized for the first time in a void sublattice of artificial opal. Structural studies of the samples by X-ray diffraction phase analysis and Raman spectroscopy were carried out.

### Introduction

It was recently [1] proposed to use synthetic opals as matrices for obtaining three-dimensional (3D) arrays of electronic nanodevices. In [2–4] 3D regular systems of Si and Si-Pt nanostructures have been fabricated in a void sublattice of synthetic opal. The results obtained demonstrated an ability of creating 3D multilayer p-n junctions and Schottky barriers on the inner surface of opal voids. This approach is expected to yield a higher (by six orders of magnitude, up to  $10^{14} \text{ cm}^{-3}$ ) density of active elements as compared to that produced by state-of-the-art planar technology.

In this work the synthetic opals were infiltrated by GaN and InN for the first time. Group-III nitrides based structures are highly attractive materials because of their great potential for development of optoelectronic devices [5]. Use of opal matrices enable to reach the working area of the junctions per unit volume in III nitride-based LED as high as  $10 \text{ m}^2/\text{cm}^3$ . This will allow reducing the current density in such nanodevices by 3–4 orders of magnitude as compared with the conventional planar systems. It is also to be expected that the photonic-crystal electromagnetic structures of the opal matrices, characterized by the presence of an stop band, will lead to novel photonic effects in these nanodevices [6, 7].

### 1. Experimental

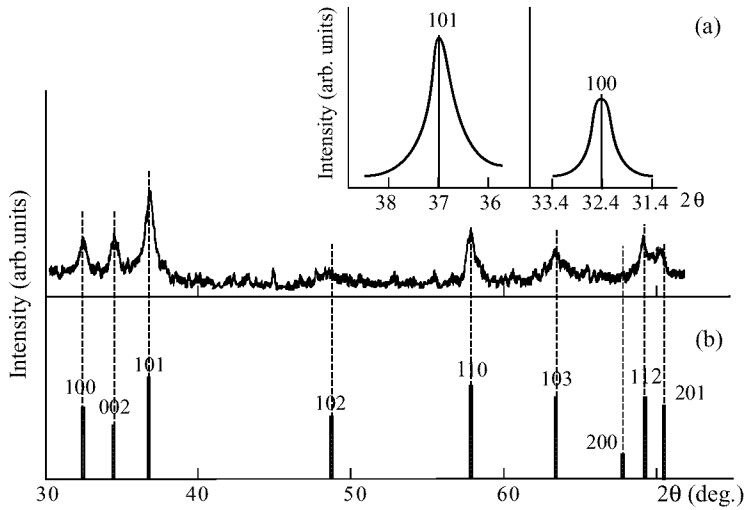
The perfect “monocrystals” of synthetic opals consist of 230 nm diameter close packed amorphous silica spheres and have a regular sublattice of voids (45–90 nm) up to 26% accessible to filling by other substances [1].

To incorporate III nitrides into opal voids we used chemical heterogeneous reaction of solid precursors containing group III elements preliminary embedded inside opal voids with gaseous nitrogen hydrides.

The microstructure of substances was determined by X-ray diffraction (XRD) and Raman measurements. The XRD patterns were obtained by using  $\text{CuK}\alpha$  radiation (Ni filter). Polycrystalline germanium was used as a standard. The Raman spectra were measured at room temperature under  $\text{Ar}^+$  laser (488 nm) excitation.

### 2. Results and discussion

Figure 1 shows XRD patterns of an “opal-GaN” nanocomposite (a) and a hexagonal bulk GaN (b). As evident from these diffractograms the material synthesized in the opal is the



**Fig. 1.** X-ray diffraction patterns. (a)—“opal-GaN” nanocomposite, (b)—hexagonal bulk GaN.

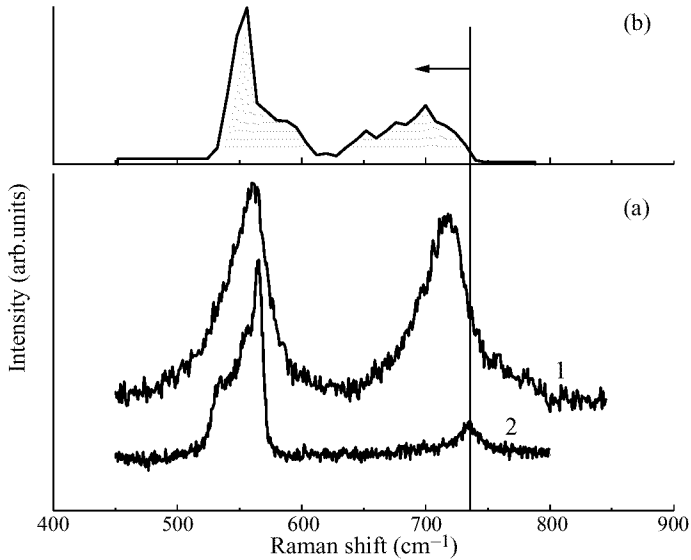
hexagonal GaN. The lattice parameters were found to be  $3.18(1) \text{ \AA}$  and  $5.19(1) \text{ \AA}$ , which are in good agreement with data available for bulk GaN [8]. The average size of GaN crystallites were determined by the approximation method. It was found from the angular dependence of the “half-width” of reflections that the physical broadening of the diffraction lines is only caused by a small size of the crystallites. The crystallite average size calculated from the measurements of the “half-width” of 101 and 100 GaN reflections is  $180(20) \text{ \AA}$ .

Figure 2(a) shows the Raman spectra of a “opal-GaN” composite (1) and a hexagonal polycrystalline GaN (2). Experimental data are compared with the one-phonon density-of-states (DOS) function of the hexagonal GaN crystal (Fig. 2(b)) [9]. There are the two features in Raman spectrum of the polycrystalline sample: the high-frequency line centered at  $740 \text{ cm}^{-1}$  results from the longitudinal optical phonons, the low-frequency feature ranging in  $530\text{--}570 \text{ cm}^{-1}$  is attributed to the transverse optical phonons. The phonon modes of the opal-GaN sample are shifted and broadened with respect to the lines of the polycrystalline GaN. Such behavior is due to a spatial confinement of optical phonons when the crystal has a finite dimension. As a result phonons with the wave vector  $q \neq 0$  add a contribution to the first-order Raman-scattering spectrum at energies  $\hbar\omega$  that are determined by the dispersion relations  $w(q)$ . Based on the above reasoning the Raman spectra of nanocrystalline materials are to reflect a phonon DOS which is similar to the one-phonon DOS in a bulk crystal. Thus, the observed low-frequency shift of the LO phonon line towards the phonon DOS maximum and broadening of this mode in the opal-GaN sample as well as the transformation of TO mode correspond to a nanocrystalline structure of GaN formed in the opal voids.

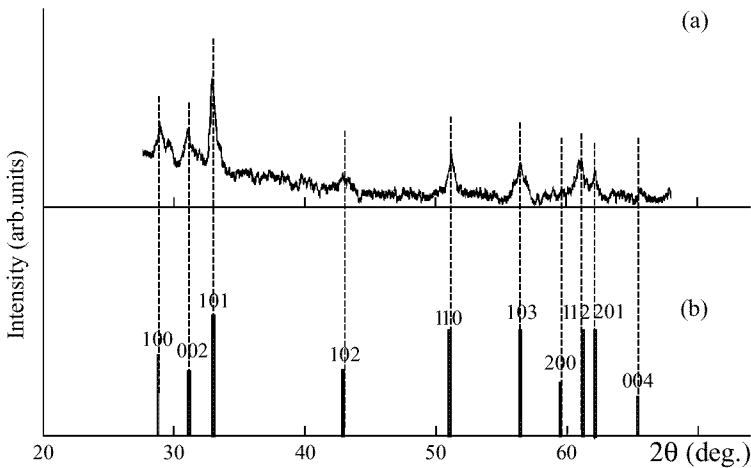
Figure 3(a) shows a XRD pattern of hexagonal InN in opal voids. The determined lattice constants of InN ( $a = 3.54(1) \text{ \AA}$ ,  $c = 5.68(3) \text{ \AA}$ ) are in agreement with those of bulk InN [8]. The Raman spectra of the “opal-InN” sample is not detected because Raman-scattering cross-section of InN is essentially (at least on one order of magnitude) less than that of GaN.

### 3. Conclusion

It has been shown that hexagonal nanocrystalline GaN and InN can be synthesized by chemical methods directly within a 3D regular void sublattice of artificial opals. We hope



**Fig. 2.** (a) 1—Raman spectrum of a “opal-GaN” nanocomposite, 2—Raman spectrum of polycrystalline GaN, (b) 1—hexagonal GaN one-phonon density-of-states.



**Fig. 3.** X-ray diffraction patterns. (a)—“opal-InN” nanocomposite, (b)—bulk hexagonal InN.

that this work is the first step to create 3D systems of efficient optoelectronic nanodevices with a high density of elements and a large working area per unit volume based on artificial opal matrices.

#### Acknowledgements

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