LETTER TO THE EDITOR

Fabrication and structure of an opal–gallium nitride nanocomposite

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Abstract
A three-dimensional gallium nitride lattice has been synthesized within the
void sublattice of an artificial opal. The composite structure has been
characterized using X-ray diffraction, Raman spectroscopy and transmission
electron microscopy.

1. Introduction

It has been suggested recently that synthetic opals can be used as matrices for fabrication of three-dimensional (3D) electronic nanodevices [1]. The results obtained for 3D regular arrays of Si and Si–Pt nanostructures show that p-n junctions and Schottky barriers can be formed on expanded inner surfaces of opal voids [2–5]. The density of the active elements in such a structure may be as high as 10^{14} cm^{-3}, which exceeds by six orders of magnitude the value achieved by the state-of-the-art planar technology.

GaN-based structures are very promising materials for numerous electronic and optoelectronic devices [6, 7]. The thermal stability of GaN enables the electronic devices to operate at high temperature in hostile environment. The wide-band-gap GaN-based structures are especially attractive because of their great potential for development of stable and efficient light-emitting diodes and lasers for the blue-to-ultraviolet spectral region.

In the present work, synthetic opals were impregnated with GaN. Fabrication of junctions in GaN-based light-emitting diodes, using such an opal matrix, would provide a working area per unit volume of 10 m^2 cm^{-3}. The photonic-crystal behaviour of the 3D opal matrix characterized by the presence of a stop band may also lead to novel photonic effects [8, 9]. Namely, 3D-ordered opal-GaN composites can enable control of the spontaneous emission from GaN-based nanodevices fabricated within the opal voids.

2. Experimental

Perfect 'single crystals' of synthetic opal, composed of 230 nm diameter close-packed amorphous silica spheres, contain $\sim$90 nm octahedral voids and $\sim$45 nm tetrahedral voids, which allows up to 26% of the crystal volume to be filled with guest materials [1]. The typical linear dimensions of the samples were $5\times5\times1$ mm. GaN was synthesized directly within such voids. First, solid precursors (metal Ga or its oxide) were introduced into the voids. Metal gallium was introduced from its melt under pressure of about 100 MPa. Gallium oxide was obtained inside the voids from soluble gallium salts, e.g., gallium formate Ga(HCOO)$_3$. To synthesize GaN, both types of the samples were annealed in the presence of nitrogen hydrides (ammonia or hydrazine) at temperatures lower than 1100 °C for $\sim$50 h on introducing solid precursors (metal Ga or its oxide) into an opal sample.

The resulting structure was characterized using x-ray diffraction (XRD), transmission electron microscopy (TEM) and Raman spectroscopy. XRD patterns were taken using CuK$_\alpha$ radiation, with Ni filter and polycrystalline germanium as a standard. Raman spectra were taken at room temperature using a 488 nm Ar$^+$ laser. TEM images and energy-dispersive x-ray (EDX) spectra were obtained using JEOL JEM-4000EXII and JEM-3000F electron microscopes. Samples were prepared for TEM examination by mechanical polishing to a thickness of 40–60 μm and Ar ion milling at 5 kV until perforation.

3. Results and discussion

Figure 1 shows XRD patterns taken from (*a*) opal–GaN nanocomposite and (*b*) hexagonal GaN. The unit cell parameters of the material synthesized in the opal were found to be $a = 0.318(1)$ nm and $c = 0.519(1)$ nm, which is in good agreement with data available for bulk hexagonal GaN [10]. The average size of the GaN crystallites was determined to be 18(2) nm from the angular dependence of the full width at half-maximum of the 101 and 100 GaN reflections, on the assumption that the broadening is only caused by the small size of the crystallites.
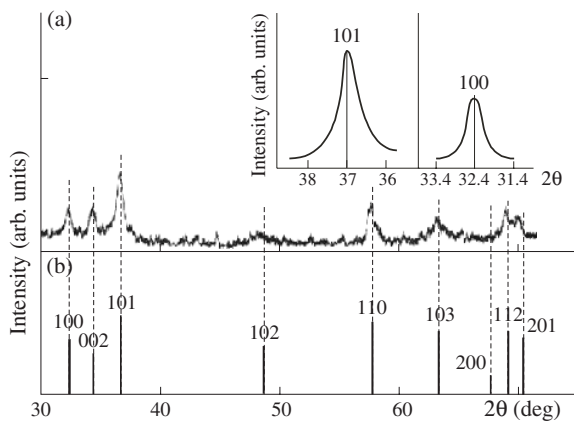

Figure 1. X-ray diffraction patterns obtained from (*a*) opal–GaN nanocomposite and (*b*) bulk hexagonal GaN.
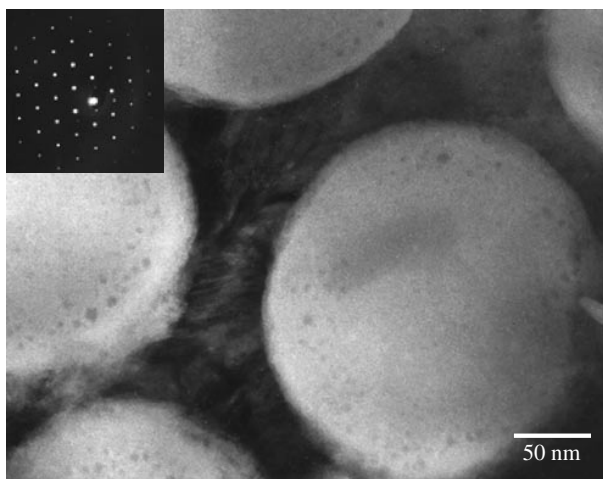
Figure 2. Representative TEM image of opal–GaN demonstrating complete filling of voids between silica spheres with GaN. Inset: (1120) microdiffraction pattern.

TEM studies (figure 2) and EDX spectra confirmed that the opal voids were filled with a material that has higher mass absorption coefficient than the silica spheres and contains only Ga and N. Microdiffraction patterns (such as that shown in the inset of figure 2) from perfect areas of GaN contained reflections exactly corresponding to those of hexagonal GaN. Stripes of defects, parallel to the basal plane of hexagonal GaN, were observed in regions having the c-axis in the image plane.

Figure 3(*a*) shows a Raman spectrum of an opal–GaN sample. The low-frequency feature in the range 530–570 cm^{-1} is due to transverse phonons of A_1(TO) and E_1(TO) symmetry and a nonpolar phonon of E_2 (high) symmetry in hexagonal GaN. The higher-frequency band which peaked at around 725 cm^{-1} arises from the longitudinal components of polar phonons. The band positions for opal–GaN differ from those for hexagonal GaN (arrowed in the same figure). The differences are pronounced in the region associated with longitudinal phonons, where the peak at 717 cm^{-1} is shifted to lower frequencies by $\sim$20 cm^{-1} from the zone-centre phonon position. The differences can be explained by the spatial confinement of optical phonons in a crystal with finite dimensions. Phonons with non-zero wavevector q contribute to the first-order Raman-scattering spectrum at energies $h\omega$ determined by the dispersion relations $\omega(q)$. The shift of the Raman line in the region corresponding to LO phonons in the opal–GaN sample is in good agreement with the fact that zone-centre LO phonons have maximum energies and their dispersion branches throughout the Brillouin zone are directed towards lower energies (figure 3(*c*)). At the same time, the dispersion branches of the transverse components of polar phonons and of the nonpolar E_2 phonon are directed from the Γ point towards higher energies (figure 3(*c*)). Therefore, a small high-frequency shift of the low-frequency feature in the spectrum of the opal–GaN sample, compared with the spectrum of single crystal GaN, is also consistent with the spatial confinement of transverse optical phonons.
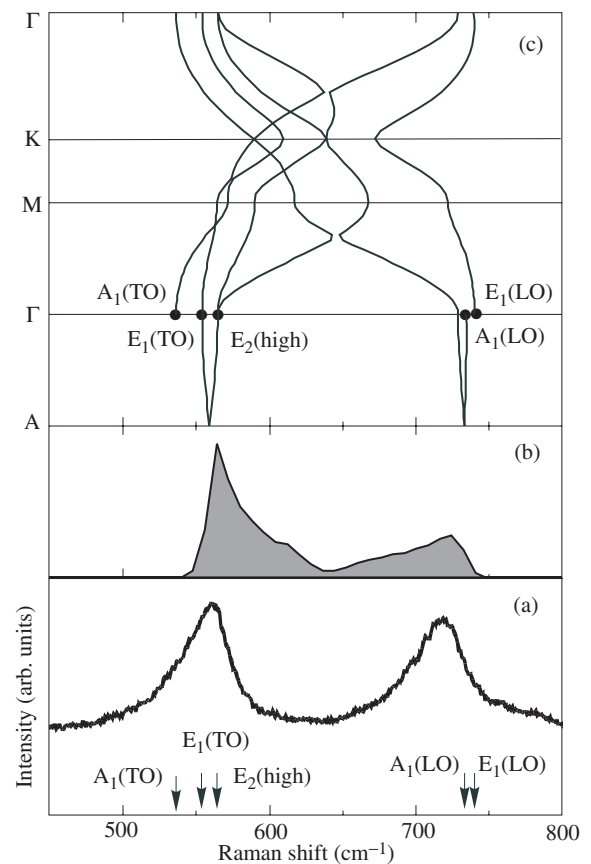
Figure 3. (*a*) Raman spectrum of nanocomposite opal–GaN; (*b*) calculated single-phonon DOS of GaN; (*c*) phonon dispersion curves for bulk GaN.

Raman spectra of nanocrystalline materials reflect the vibrational density of phonon states, which is similar to the one-phonon density of states of a single crystal [11]. In addition to the phonon dispersion curves, figure 3(*b*) shows the single-phonon density of states (DOS) [12]. The calculated DOS is in good agreement with recent neutron data [13]. The major features observed in the Raman spectrum of the opal–GaN sample and the calculated DOS are consistent in the regions of both TO and LO phonons, thus confirming the nanocrystalline nature of GaN introduced into the opal.

4. Conclusion

Hexagonal nanocrystalline GaN has been synthesized directly within the 3D regular void sublattice of an artificial opal. Such composite structures can serve as a basis for fabrication of 3D systems of Group-III nitride-based optoelectronic nanodevices with high density of elements and large working area per unit volume.

Acknowledgments

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