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RESEARCH PAPER

Generation of InN nanocrystals in organic solution through laser ablation of high pressure chemical vapor deposition-grown InN thin film

Sabri Alkis · Mustafa Alevli · Salamat Burzhuev ·
Hüseyin Avni Vural · Ali Kemal Okyay ·
Bülend Ortaç

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Abstract We report the synthesis of colloidal InN nanocrystals (InN-NCs) in organic solution through nanosecond pulsed laser ablation of high pressure chemical vapor deposition-grown InN thin film on GaN/sapphire template substrate. The size, the structural, the optical, and the chemical characteristics of InN-NCs demonstrate that the colloidal InN crystalline nanostructures in ethanol are synthesized with spherical shape within 5.9–25.3, 5.45–34.8, 3.24–36 nm particle-size distributions, increasing the pulse energy value. The colloidal InN-NCs solutions present strong absorption edge tailoring from NIR region to UV region.

Keywords High pressure chemical vapor deposition · Laser ablation of InN thin film in organic solution · InN nanocrystal synthesis

S. Alkis (✉) · S. Burzhuev · H. A. Vural ·
A. K. Okyay · B. Ortaç (✉)
UNAM Institute of Materials Science and
Nanotechnology, Bilkent University, Bilkent, 06800
Ankara, Turkey
e-mail: alkis@unam.bilkent.edu.tr

B. Ortaç
e-mail: ortac@unam.bilkent.edu.tr

S. Alkis · A. K. Okyay
Department of Electrical and Electronics Engineering,
Bilkent University, Bilkent, 06800 Ankara, Turkey

M. Alevli
Department of Physics, Marmara University, 34722
Istanbul, Turkey

Introduction

In recent years, there has been a lot of interest in indium nitride materials due to their potential applications in optoelectronic devices (Ponce and Bour 1997). Indium nitride presents high mobility and high saturation velocity due to its low effective mass (Mohammad and Morkoc 1996), which makes it applicable in high speed and high frequency electronic devices. It is shown in the literature that it is possible to operate indium nitride-based light emitting diodes at spectral wavelengths ranging from the near-infrared to the ultraviolet region of the electromagnetic spectrum because of its suggested narrow bandgap value of 0.7–0.9 eV (Wu et al. 2002). Furthermore, InN-NCs can find possible applications in biology and medicine due to their non-toxicity and their infrared emissions (Chen et al. 2011).

At present, the growth of high quality indium nitride is generally performed at low pressures by means of different growth techniques such as metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). However, high equilibrium vapor pressure of nitrogen and low decomposition temperature of InN make the synthesis of high quality InN thin films quite challenging at low pressures (Davydov and Klochikhin 2004; Butcher and Tansley 2005). The influence of growth pressure on InN films have been studied by Dietz et al. and they have reported superior quality InN films grown at high temperatures, which are at least 200 °C higher compared to InN films

grown at low pressures (Alevli et al. 2006, 2008; Dietz et al. 2008). They achieved the growth of good quality InN films utilizing a novel high pressure chemical vapor deposition (HPCVD) system which enables the researchers to control the vastly different partial pressures of the constituents involved in the growth process and stabilize the InN films at elevated temperatures (Alevli et al. 2006). Details of the HPCVD reactor and growth process have been reported in the literature (Dietz et al. 2005a, b; Cardelino et al. 2005; Woods and Dietz 2006). The structural and the optical properties of the HPCVD-grown InN thin films on GaN/sapphire templates have been discussed in detail elsewhere (Alevli et al. 2006, 2008; Dietz et al. 2008). Raman spectroscopy and X-ray diffraction (XRD) reciprocal space map analysis indicated high quality and strain-free InN layers and revealed single phase InN (0002). The optical transmission measurement analysis indicates that the optical absorption edge for InN thin film layers grown by HPCVD shifts below 1.1 eV as the free carrier concentration decreases to low 10^{18} cm^{-3} . The infrared reflectance and absorption measurement analysis show that optical bandgap values strongly depend on the carrier concentration (Alevli et al. 2008; Dietz et al. 2008). The InN thin films used in this study were grown on GaN/sapphire templates. Samples were grown with HPCVD at 15 bar reactor pressure and temperatures around 1,150 K, while the NH_3/TMI ratio was 2500. XRD measurements revealed for the sample single phase InN(0002) with hexagonal symmetry (Buegler et al. 2011).

Researchers have also been interested in the synthesis of InN nanostructures because of the great potential they offer for studying the dependence of various electronic and optoelectronic properties on dimensionality and size (Hu et al. 2006). There has been a lot of attention on group III-nitride nanostructures for nanoscale electronic and optoelectronic device applications (Briot et al. 2003; Tan et al. 2007). InN nanostructures have been obtained by means of the vapor–liquid–solid process at high temperatures in the presence of ammonia (Zhang et al. 2002). Sardar et al. synthesized InN nanocrystals in chloroform with an average diameter of 15 nm through a solvothermal reaction (Sardar et al. 2005). It is also possible to grow InN nanoparticles through solvothermal autoclave methods (Wu et al. 2005; Xiao et al. 2003), ammonolysis (Schwenzer et al. 2005), solid-state metathesis reactions (Cumberland et al.

2001), halide precursor, and nitric acid post-treatment process (Hsieh et al. 2009). Recent work of Chen et al. showed that it is possible to obtain uniform-sized InN-NCs by means of a combined method of solution and vapor-phase methods under silica shell confinement. This method provides a fast nucleation and a slow growth process (Chen et al. 2011). However, all these syntheses are complex chemical procedures involving the use of various precursor chemicals that are critical especially for applications of nanocrystals in biological systems.

Another promising method for nanoparticle generation is the laser ablation method (Mafune et al. 2000a, b, 2001; Niu et al. 2010; Hong et al. 2003). The use of unique scientific facilities of laser-matter interaction properties opens the door to the generation of a wide variety of noble nanoparticles (Amendola and Meneghetti 2009; Deniz et al. 2011; Sylvestre et al. 2004), semiconductor nanocrystals (Švrček et al. 2006; Yang et al. 2008; Kuzmin et al. 2010, Liu et al. 2008a; Intartaglia et al. 2011), nitride, metal and metal oxide nanocrystals (Liu et al. 2008b; Nishi et al. 2010; He et al. 2007). Compared to other nanostructure synthesis methods, laser ablation, especially in liquids, is a versatile method of generating colloidal, highly pure, and agent-free nanocrystals. In this paper, we report a chemical-free synthesis of InN-NCs in ethanol solution through nanosecond laser ablation of HPCVD-grown InN thin film on GaN/sapphire template substrate with varying pulse energies. The formation of InN-NCs is confirmed using transmission electron microscopy (TEM) images, and the structural, the optical, and the chemical properties of InN-NCs were studied by ultraviolet and visible absorption spectroscopy (UV/VIS), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy techniques. We demonstrate an effective way of synthesizing crystalline InN nanostructures in organic solution by means of laser ablation of thin film structures with varying pulse energies.

Materials and experimental methods

The generation of colloidal InN-NCs was carried out using a commercial nanosecond pulsed ND:YLF laser (Empower Q-Switched Laser, Spectra Physics) operated at 527 nm with pulse duration of 100 ns and a pulse repetition rate of 1 kHz. Three different experiments were done by varying laser output power

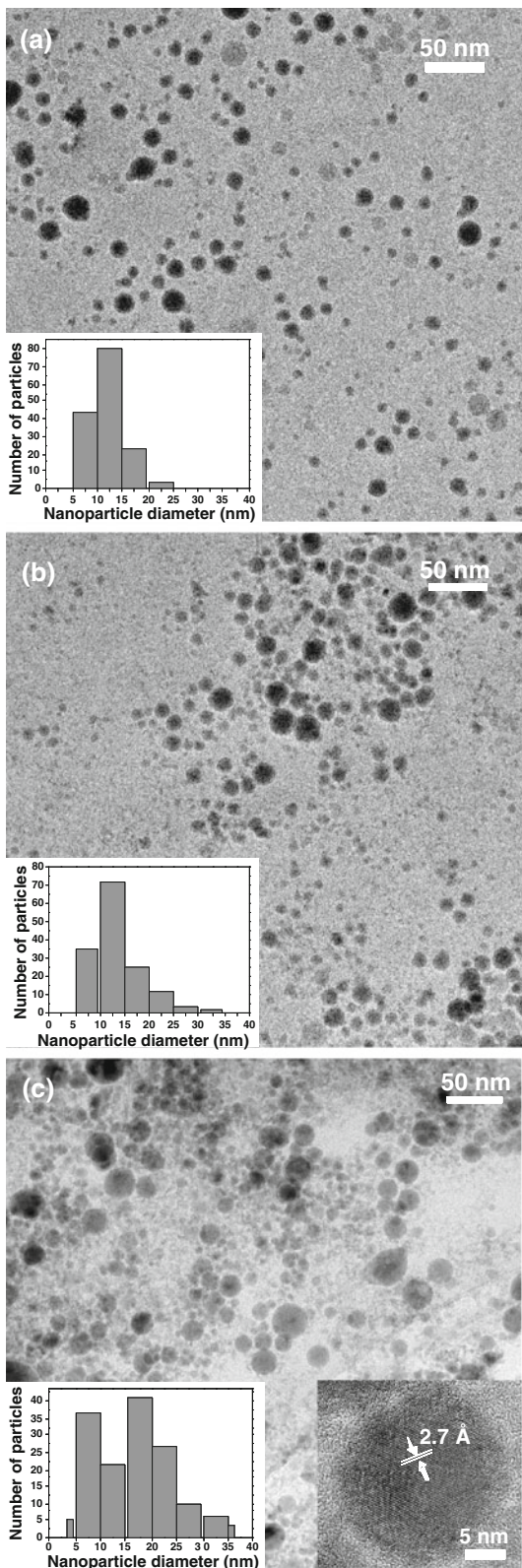


Fig. 1 TEM images of the laser-generated InN-NCs under laser pulse energy values of 8 mJ (a), 12 mJ (b), and 16 mJ (c) with corresponding particle size distributions (insets), 20 nm size InN nanocrystal generated by laser pulse energy of 16 mJ showing crystal spacing of 2.7 Å (c, inset)

parameters from 8 to 12 W and then 16 W. The pulse energies were 8, 12, and 16 mJ, respectively. The laser beam was focused on InN sample target placed in a glass vial containing 20 mL of pure ethanol using a plano-convex lens with a focal length of 50 mm. The height of liquid layer over the InN target is about 5 mm. The laser ablation was carried out for 5 min.

The high-resolution transmission electron microscope (HR-TEM) imaging of the InN-NCs was carried out using a FEI-Tecnai G²F30 type TEM instrument at an operating voltage of 300 kV. InN-NC TEM samples of all three final products were prepared by drop-casting solutions onto separate carbon-coated TEM grids for TEM imaging. Raman spectroscopy studies of the In-NCs solutions obtained from the last ablation process were performed using a Witec Alpha 300S Micro Raman spectrometer with a Nd:YAG laser at an excitation wavelength of 532 nm (laser power: 10 mW) and a Nikon 100x (N.A. = 0.9) air objective. The optical absorption spectra of the final colloidal nanoparticles' solutions containing InN-NCs were obtained using a Varian Cary 5000 UV/Vis/NIR spectrophotometer. The elemental composition and the chemical state of the InN-NCs were studied by XPS. The XPS data were recorded with InN-NCs samples placed on quartz substrates. XPS measurements were performed on a monochromatic K-Alpha instrument (Thermo) operating at 12 kV and 2.5 mA. XPS spectra were collected with a photoelectron take off angle of 90° from a 200 μm diameter circular spot on the sample surface plane, energy steps of 0.1 eV, and a pass energy of 30 eV. The control of the flow of the electrons to the surface is achieved by means of a well-controlled flood gun technique. The sample surface was first sputtered by an Ar ion beam at 2 keV for 30 min to remove surface contamination and native oxidation by carbon-containing or water molecules absorbed from the environment.

Results and discussion

During the laser ablation, colloidal solutions with dispersed InN-NCs in liquid media were observed, and

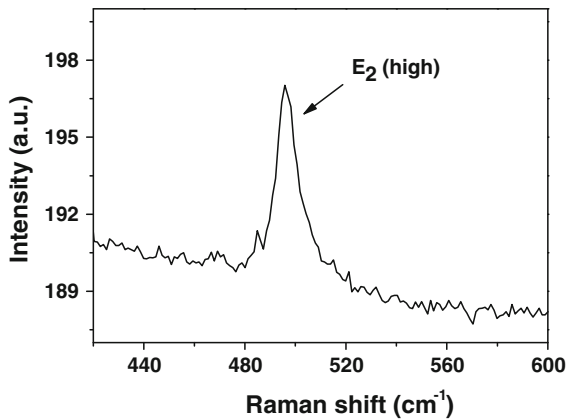


Fig. 2 Raman spectrum for InN-NCs generated by laser pulse energy of 16 mJ, peak at 496.76 cm^{-1} represents the E_2 (high) phonon mode of the InN wurtzite structure

after laser irradiation, the color of the colloidal solutions became light orange for all three experiments. A representative TEM image of the colloidal InN-NCs obtained by laser ablation is shown in Fig. 1. The TEM images clearly show that InN-NCs exhibit spherical-like geometries without any aggregation in all organic solutions. To obtain accurate information about the size distribution of InN-NCs, we have counted the sizes of 150 particles seen in TEM images. The sizes of InN-NCs obtained with a laser pulse energy of 8 mJ range from 5.9 to 25.3 nm (inset, Fig. 1a), the sizes of InN-NCs obtained with a laser pulse energy of 12 mJ range from 5.4 to 34.8 nm (inset, Fig. 1b), and the sizes of InN-NCs obtained

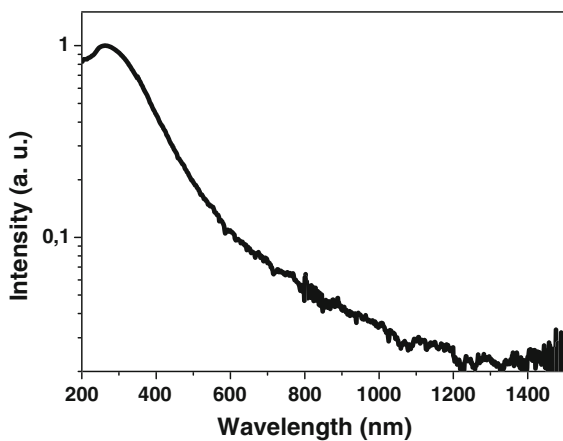


Fig. 3 Normalized UV-Vis-NIR absorption spectrum of InN-NCs generated by laser pulse energy of 16 mJ at the room temperature

with a pulse energy of 16 mJ range from 3.24 to 36 nm (inset, Fig. 1c). It should be noted that particles with sizes larger than 36 nm are not observed in this study. Figure 1c presents the HRTEM image of a crystalline 20 nm InN nanoparticle. HRTEM image of a single isolated InN-NC shows the crystalline lattice fringes with lattice spacing of 0.27 nm corresponding to the (0002) planes of the wurtzite structure which also confirms InN-NCs generation by nanosecond pulsed laser ablation technique in liquid environment (see Fig. 1c). The TEM analysis clearly shows that nanosecond laser ablation of InN sample targets in ethanol produced broadening size distributions, increasing pulse energy value.

Raman spectroscopy is a widely applicable technique to study the optical properties of nanomaterials (Hu et al. 2006). The InN-NCs solution obtained from the highest pulse energy laser ablation experiment was drop-casted onto a quartz substrate and the Raman spectrum was recorded at room temperature. The

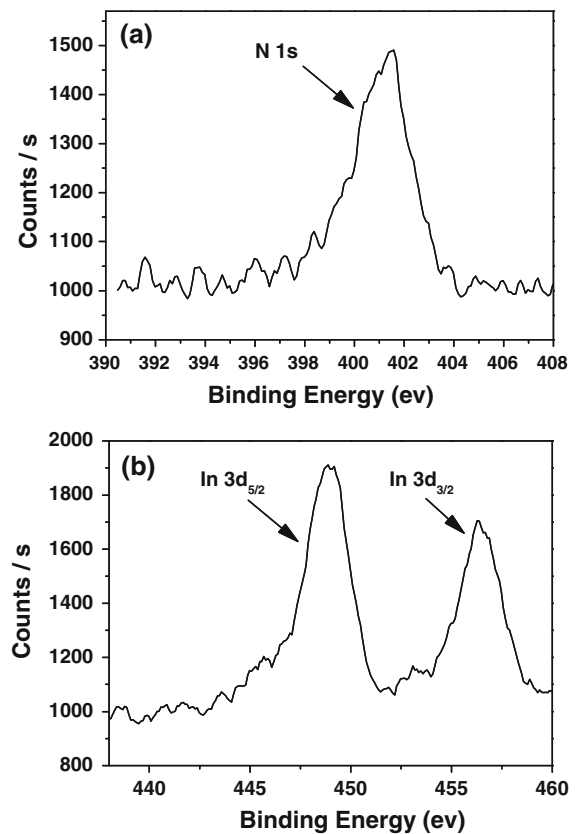


Fig. 4 **a** Core-level XPS spectrum of N1 s and **b** core-level XPS spectrum of In3d for InN-NCs, InN-NCs generated by laser pulse energy of 16 mJ

Raman spectrum of laser-prepared InN-NCs is given in Fig. 2. The sharp peak at 496.76 cm^{-1} represents the strain-sensitive E_2 (high) phonon mode of the obtained InN-NCs (Alevli et al. 2006). It should be mentioned that the full width half maximum of the E_2 (high) mode is 5.36 cm^{-1} . This value is similar when compared to HPCVD-grown InN thin film, and this indicates that InN thin film was not affected when it was exposed to laser beam and the InN thin film turned into InN-NCs inside organic solution (Alevli et al. 2006).

The optical properties of InN-NC materials are highly important for various photonics and optoelectronics applications (Chen et al. 2011; Woods and Dietz 2006; Tan et al. 2007). Figure 3 shows the normalized, room temperature UV–Vis–NIR absorption spectrum of InN-NCs obtained from the highest pulse energy laser ablation experiment, in ethanol solution. The optical absorption spectrum of colloidal InN-NCs show a minimum optical absorption feature tailored down to 1,200 nm, prominent shoulders at 260 nm, and the onset of absorption edge starting around 500 nm. Figure 4a, b shows the XPS elementary analysis spectrum of InN-NCs obtained from the highest pulse energy laser ablation experiment. Peaks with binding energies of 448.89 and 456.42 eV correspond to $\text{In}3d_{5/2}$ and $\text{In}3d_{3/2}$ states of trivalent indium (see Fig. 4a) (Kurimoto et al. 2004). On the other hand, N 1s peak shows up at 401 eV, which also agrees with the literature (Kurimoto et al. 2004). XPS data also confirm the formation of InN nanostructures in solution form by laser ablation method.

Conclusion

In conclusion, spherical InN nanocrystals within size ranges of 5.9–25.3, 5.4–34.8, and 3.24–36 nm have been successfully synthesized in organic liquid through nanosecond laser ablation of HPCVD-grown InN thin film on GaN/sapphire template substrate using laser pulse energy values of 8, 12, and 16 mJ. The formation of InN nanocrystals is confirmed by TEM, Raman Spectroscopy, and XPS analysis. A sharp peak at 496.76 cm^{-1} corresponding to the strain-sensitive E_2 (high) phonon mode of InN was observed. The XPS study also confirmed InN nanostructure synthesis. The UV/VIS/NIR spectrum analysis shows the strong absorption edge tailoring from

NIR region to UV region. Due to their promising optical properties, these semiconductor InN-based nanomaterials could be prime candidates for photonics, optoelectronics, and biological applications (Chen et al. 2011). We believe that this method could be an alternative route to synthesize InN-NCs in solution form without the presence of precursor chemicals. It could be possible to synthesize other nanostructures with low decomposition temperatures by means of laser ablation method. In addition, ultra-short pulsed laser ablation method could offer new advantages in nanomaterial synthesis due to a minimum Joule heating effect for smaller nanocrystal generation with reduced mean sizes (Intartaglia et al. 2011).

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