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Structural characterization and X-ray analysis by Williamson–Hall method for Erbium doped Aluminum Nitride nanoparticles, synthesized using inert gas condensation technique

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HIGHLIGHTS

- Structural characterization of AlN:Er NPs using XRD, Debye–Scherrer and Williamson–Hall analysis.
- Calculation of crystallite size, stress, strain and energy density for AlN:Er NPs.
- Optical characterization of AlN:Er NPs to study nanoscale thermal sensing capabilities of these NPs.

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ABSTRACT

We have synthesized AlN nanoparticles (NPs) doped in-situ with Er (AlN:Er) using inert gas condensation technique. Using x-ray diffraction (XRD) peak broadening analysis with the Williamson–Hall (W–H) Uniform Deformation Model (UDM) the crystallite size of the NPs and the strain in NPs were found to be 80 ± 38 nm and $3.07 \times 10^{-3} \pm 0.9 \times 10^{-3}$ respectively. In comparison, using the Debye–Scherrer's (DS) formula, we have inferred that the crystallite size of the NPs was 23 ± 6 nm and the average strain was $4.3 \times 10^{-3} \pm 0.4 \times 10^{-3}$. The scanning electron microscopy images show that the NPs are spherical and have an average diameter of ~300 nm. The crystallite size is smaller than the size of the NPs revealing their polycrystalline behavior. In addition, the NPs strain, stress and energy density were also calculated using W–H analysis combined with the Uniform Deformation Stress Model (UDSM) and the Uniform Deformation Energy Density Model (UDEDM). Suggested by the spherical geometry and polycrystalline nature of the AlN NPs, the strain computed from UDM, UDSM and UDEDM were in agreement confirming an isotropic mechanical nature of the particle. Luminescence measurements revealed the temperature dependence of the optical emission of the Er^{3+} ions, confirming the use of AlN:Er NPs for nano-scale temperature sensing.

1. Introduction

The progress in semiconductor device scaling has approached the nanoscale size regime due to which controlling the real device temperature has become a challenging task and this in turn calls for developing sensitive nanoscale thermal sensors. Similarly, temperature measurement of biological tissues or single molecules in cancer treatment also requires precisely localized nanoscale temperature measurement. Thus nanoparticles (NPs) exhibiting temperature-sensing capacity have been recognized as having potential for practical applications [1–4].

It is well known that Erbium (Er) ion has unique electronic and optical properties due to its incompletely filled 4f inner shell and two closed outer shells. Currently, Er is widely used in many specific material systems, including semiconductor NPs, as a local probe of morphology (e.g. by monitoring crystal field modified by point defects, impurities, etc.) and their effect on host material's optical and electrical properties [5]. Specifically, Er doped III nitride semiconductor thin films have been studied in the past for temperature sensing purpose [6–8]; however NPs of the same systems have not been studied so far. Recently we have reported on synthesis and characterization of Aluminum Nitride doped in-situ with Erbium (AlN:Er) NPs [9]. Wide band gap materials have proven to be efficient hosts for Er-doping due to their physical and chemical properties resulting in reduced thermal quenching of optically active rare-earth ions luminescence [10–16]. AlN has the highest band gap of ~6.2 eV among III-nitrides and its properties

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such as radiation hardness, high mechanical strength and stability, high thermal conductivity and high melting point render it capable of high power and high temperature operations [13–15].

It is known that optical properties of NPs are remarkably affected by their size, morphology and structure. Moreover, in the case of the Er^{3+} ion, optical properties resulting from intra-configurational 4f–4f transitions vary depending on the position of the Er ion in the crystal lattice and resulting crystal field environment [10–16]. Thus study of structural and mechanical properties of these NPs is of significance for use in intended applications. It is known that crystal structure irregularities in NPs cause strain in the particle resulting in broadening of diffraction peaks. Thus analyzing diffraction peaks from XRD spectra one can obtain the crystallite size and lattice strain of the NPs [17,18]. Due to the presence of polycrystalline aggregates, most of the time, the crystallite size of NPs differs from the geometric size of the NP [19]. Lattice strain can be caused due to various factors including lattice dislocations, grain boundary, different types of stresses, stacking faults, etc. [20]. Apart from these factors mechanical alloying is known to cause large amounts of lattice strain in NPs. In AlN:Er the Er^{3+} ion replaces an Al^{3+} atom in the crystal and the comparatively larger radius of Er induces strain in the AlN host. Theoretically, from thermodynamic modeling the mechanical response of a spherical nanoparticle depends on the lattice strain, compressive and thermal stresses, and well as quantum trapping from size [21]. Using Debye–Scherrer's (DS) method and Williamson–Hall (W–H) analysis combined with the Uniform Deformation Model (UDM), Uniform Deformation Stress Model (UDSM) and Uniform Deformation Energy Density Model (UDEDM) one can obtain NPs crystallite size, strain, stress and energy density [22,23].

In this paper, we study AlN:Er NPs synthesized using inert gas condensation (IGC) technique. These NPs have optical properties that make them good candidates for nano-scale thermal probing in mechanically harsh environments. The NPs structural analysis was carried out using XRD peak broadening analysis. We have calculated crystallite size and lattice strain for hexagonal (h-) AlN NPs using DS and W–H analysis. Furthermore, stress and energy density for h-AlN:Er NPs were calculated using W–H UDSM and UDEDM, respectively.

2. Experimental

AlN:Er NPs were synthesized using inert gas condensation, a vapor phase synthesis technique; the experimental details are described elsewhere [9,24]. In short, a 99.99% pure 37 mm diameter Al target with an additional 6 mm diameter Er pellet (99.99%) was sputtered in presence of 99.99% pure Ar and N_2 gases (1:1) using the R. F. magnetron sputtering process. The base pressure of the system was maintained at 10^{-7} Torr. A sputtering power of 40 W was used with condensation chamber pressure of 1 Torr. The pressure difference between the condensation and the deposition chamber was maintained at 1000 Torr. Sputtering was carried out for 30 min with an aggregation length of 6 cm while the substrate was fixed at a distance of 1 cm from the nozzle. NPs were deposited on glass for XRD and SEM analysis. Characterization of AlN:Er NPs was carried out ex-situ using Rigaku MiniFlex-II X-Ray Diffractometer and Hitachi S-4500 Field Emission SEM. Additional ex situ cathode and photo-luminescence measurements were performed under variable temperature conditions. Cathode-luminesce measurements carried out with a 5 KeV electron gun with samples mounted on a cold finger. A charge coupled device (CCD) camera, by Princeton Instruments, recorded the spectra in the 300–1100 nm wavelength range. Photo-luminescence measurements were performed using a WITec scanning near-field optical microscope with an adjustable power 532 nm wavelength-heating laser.

3. Results and discussions

3.1. Structure

Fig. 1 shows the XRD spectrum for AlN:Er NPs synthesized using IGC technique. The diffraction peaks 100, 002, 110 and 200 correspond to a P63mc h-AlN phase with corresponding lattice constants $a=b=3.18\pm0.02$ Å and $c=4.68\pm0.02$ Å. Compared to reported bulk values of $a=b=3.113\pm0.001$ Å and $c=4.981\pm0.001$ Å [25], the NPs crystal structure is expanded in the basal plane of the hexagon, while contracting along the c-axis, however the unit cell volume of the nanoparticle remains constant as compared to the unit cell volume of the bulk. From the shifts in the 2θ XRD peaks position from the bulk 2θ positions it is seen the NPs experience a uniform distortion in addition to further distortions attributing to strain in the AlN:Er system as discussed below. In addition to this, the peaks 111, 200 and 220 correspond to face center cubic (fcc-) AlN phase with space group F-43m. Based on previous high resolution transmission electron microscopy studies of various as-deposited AlN:Er samples [26], it was observed that 84% of the total NPs analyzed had hexagonal crystal structure and thus the focus of this analysis and calculations is for h-AlN:Er NPs.

The crystallite size and lattice strain are calculated using the DS method using the formulae

$$D = \frac{K\lambda}{\beta_{Size}\cos\theta} \tag{1}$$

and

$$\epsilon = \frac{\beta_{strain}}{4\tan\theta} \tag{2}$$

where D is the crystallite size, K is the shape factor (~1), λ is the wavelength of the CuKα radiations (~0.154 nm), β is the integral broadening of XRD peaks and ε is the lattice strain. The β parameter was corrected for instrumental broadening in all DS and W–H type analysis.

Using (Eqs. (1) and 2), the average crystallite size and lattice strain for h-AlN is found to be 23 ± 6 nm and $4.3\times10^{-3}\pm0.4\times10^{-3}$ respectively. Debye formula only considers crystallite size effects of individual diffraction lines and thus gives a lower bound for the crystallite size.

Additionally, the AlN:Er crystallite size and lattice strain were computed using an alternative method, namely W–H UDM analysis. Assuming that the total peak broadening (β) has two

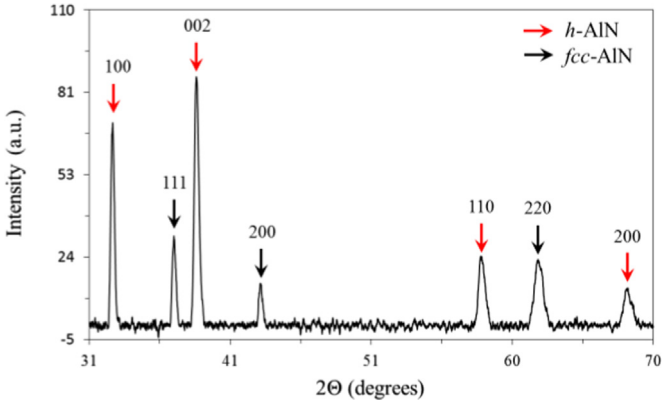

Fig. 1. XRD Spectrum for as-deposited AlN:Er NPs synthesized using Inert Gas Condensation technique.