

Structural, Optical properties of AlInGaN nanocrystalline through chemical route by CVD method

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Abstract

The objective of the current study is to characterize AlInGaN nanostructure for the optoelectronic applications. Synthesize of quaternary AlInGaN nanostructure by Chemical Vapour Deposition method for different temperatures. AlInGa-EDTA complex were nitridated at different temperatures. X-ray diffraction reveals that AlInGaN samples were wurzite structure. While increasing synthesize temperature X-ray diffraction peaks were shifting higher angle side. It also represented has same in XPS and Raman studies. Raman analysis of the AlInGaN, $A_1(\text{LO})$ mode of AlGa_N-like Phonons and InGa_N-like clusters peaks were observed. When increasing growth temperature, morphology has been changes from spherical like microstructure to clusters like nanoparticles by Scanning Electron Microscopy. The particle size has been changes from 20 nm to 11 nm revealed by High Resolution Transmission Electron Microscopy and also XRD, SAED pattern represented that AlInGaN samples were poly-crystalline nature. Room temperature photoluminescence measurement shows that AlInGaN nanostructure near-band-edge emission blue shift.

1. Introduction

The groups III-nitride are wide-band-gap semiconductors. It can be recognized as very important materials for many optoelectronic devices, such as Light emitting diodes, Laser diodes, and high temperature/high-power electronic devices. The importance of Aluminum Indium Gallium Nitride (AlInGa_N) system of quaternary alloys has been offers the opportunities to modify their fundamental physical properties over a wide range by purposely varying Indium or Aluminum compositions in AlInGa_N to change the band gap while keeping lattice matched with Ga_N, which can be used to reduce dislocation density. It can be used in field emission display and optoelectronic applications [1]. AlInGa_N quaternary was attracted due to adjust independently with bandgap, lattice constant [2]. Heterostructures have strain-free and it can be achieved by varying of Aluminum (Al), Gallium (Ga) and Indium (In) to get high quality nitrides. But it is having problem to get high quality nitrides. AlInGa_N proper growth condition and optimizing need one end Indium Nitride (InN) have lower growth temperature; other end AlN requires higher growth temperature [3].

The first study was done by McIntosh et al and Yamaguchi et al; they reported the physical incorporation of Al and In into Ga_N which provided information about the bandgap versus alloy compositions [3–4]. After that, Matsuoka et al predicted the presence of an unstable mixing region (spiodal phase separation) in wurzite AlInGa_N as the indium content increases [7]. While, Peng et al reiterted based on optical absorption measurements of the sputtered films; they stated that AlInN and AlInGa_N do not seem to provide good confinement to GaInN because of the very strong bowing effect [8–14]. Furthermore, according to Narukawa et al the density of non-radiative center furthermore and possibly the non-radiative recombination mechanism itself was altered when Indium was included in the growth [9, 10].

In addition, Kumano et al suggested that the increase of the optical efficiency is due to the reduction in the non-radiative recombination center with Indium incorporation [10–14]. Binary and ternary nitride

there are few reports available, but quaternary of AlInGaN nanocrystal there is not reported yet. Synthesis of AlInGaN nanocrystal is challenging because of having different bond length, decomposition temperature and desorption of growth species. In this paper, Synthesis of AlInGaN nanocrystals have been prepared by Chemical Vapour deposition (CVD) and structural, optical properties of AlInGaN nanocrystalline have been investigated.

2. Experimental procedure

2.1 Sample preparation

AlInGaN alloy was synthesized by nitridation of $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}$ -EDTA complex at 750°C, 800°C, 850°C and 900°C for 8hrs. $\text{Al}_{0.2}\text{In}_{0.16}\text{Ga}_{0.64}$ -EDTA complex was prepared using a mixture of gallium chloride (GaCl_3), Aluminum chloride (AlCl_3), Indium chloride (InCl_3) and EDTA.NH_4 in aqueous solution at pH of 9. The solution was stirred for more than 6 hrs and dried in an oven at 70°C to obtain $(\text{Al}_x\text{In}_y\text{Ga}_{1-x-y})\text{-EDTA.NH}_4$ complex. The $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}$ -EDTA complex was taken in an alumina boat and placed inside the horizontal quartz tube reactor. Nitrogen (N_2) gas was allowed to pass through liquid ammonia (NH_3) bubbler to carry NH_3 and to react with the complex during the reaction. The complex was nitridated at 750°C, 800°C, 850°C, 900°C for 8 hrs to obtain AlInGaN alloy.

2.2 Sample characterizations

The X-ray powder diffraction (XRD) patterns has been recorded using PAN analytical XPERT-PRO X-ray diffractometer with $\text{Cu K}\alpha_1$ radiation at room temperature in the range between 25 ° and 80° at a step size of 0.021. AlInGaN sample 750°C, 800°C, 850°C and 900°C has been taken for XRD spectrum. The room-temperature Raman spectrum was recorded using Olympus spectrometer Ar^+ ion laser excitation at 488 nm. The morphology of AlInGaN sample 800°C, 850°C and 900°C has been analyzed using Carl Zesis EV018 by SEM. Transmission electron microscope (TEM) analysis of the AlInGaN sample 800°C, 850°C and 900°C has been carried out using the TEM (Tecnai G2 model T-30 s-twin) with an accelerating voltage of 300 kV and X-ray photoelectron spectroscopy (Omicron Nanotechnology Instrument). Room-temperature PL spectra was recorded using spectra physics HORIBA JOBIN spectrometer Ar^+ ion laser excitation at 244 nm.

3. Results and Discussion

Figure 1 shows that X-ray diffraction (XRD) patterns of GaN and $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$ alloy samples. From the XRD patterns it was concluded that the diffraction peaks corresponding to (100), (002), (101), (102), (110), (103), (200), (112), (201) planes were well matched with wurzite hexagonal phase of GaN JCPDS (89-8624) and that the compound belongs to $\text{P6}_3\text{mc}$ space group. Also, this result shows that as-prepared products are single-phase hexagonal GaN and $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$ alloy. It was observed that there was a small shift in diffraction peaks of $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$ samples towards higher angle when compared

with GaN sample and this shift is attributed to Aluminum (Al), Indium (In) substitution at Ga site. The ionic radius of Al^{3+} (0.535Å) is smaller than that of Ga^{3+} (0.62Å) and there is a change in diffraction peak position between GaN and AlN as observed (in Fig. 1). These changes in the XRD patterns are indicative of the formation of $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$ structures. In case of 10% Al substituted, In-16% into GaN molar ratio, the shift was not appreciable. When Al substitution was increased to 20% and In-16%, there was a shift towards higher angle by 0.25° .

In Fig. 1 it is clear that with increasing compositions of Al the peak shifts to higher angles due to incorporation of Al, Indium in the GaN crystal lattice. At 20% Al substitution as well as Indium-16%, the XRD peak shifts by 0.25° , followed by nitridation 750°C to 900°C . Al, In substitution where peak shifts of around 0.25° was observed. The average size of the crystalline grain was determined by means of the Debye-Scherrer formula for the (101) XRD peak about 15 nm. Crystalline grain size was decreases with increasing concentration of Al-20%, In-16% ions samples from nitridation of different temperatures 750°C to 900°C respectively. It was observed that higher of diffraction peaks. Due Al, In atoms are incorporated into the lattice site in the GaN and also InGa_N cluster has Aberrate in Raman studies in Fig. 2. In Fig. 2 shows the room-temperature Raman spectrum of AlInGa_N alloy samples recorded in the range of $350\text{--}850\text{ cm}^{-1}$. The Raman spectrum possess vibrational modes of 567 cm^{-1} , 680 cm^{-1} and 740 cm^{-1} . The vibrational modes are related to GaN peak at 567 cm^{-1} , 680 cm^{-1} peak related are correlated to InGa_N-like cluster and 740 cm^{-1} peak related to AlGa_N. When increase the growth temperature 850°C to 900°C , InGa_N like peak is disappeared is evidenced from Fig. 6. AlGa_N like peak and GaN $A_1(L_1)$ Mode only presented is also evidenced from XPS in Fig. 5.

The Fig. 3 shows SEM images of AlInGa_N sample prepared at (a) 800°C , (b) 850°C , (c) 900°C . When increasing growth temperature from 800°C to 900°C . The morphology changes from spherical-like particles to Agglomerated particles it having a small in size and also evidence in Fig. 4 shows TEM images of AlInGa_N samples prepared at (a) 800°C , (b) 850°C , (c) 900°C . the AlInGa_N samples have decreasing particle size from 20 to 11 nm. In Fig. 4(d) shows that AlInGa_N SAED pattern of polycrystalline nature.

XPS analysis has been carried out to confirm the chemical bonding in AlInGa_N nanostructures. Figure 6 shows spectrum of photoelectron binding energies of Al 2p, N 1s, In3d, Ga3d of AlInGa_N Nanostructures. Figure 7 shows photoelectron spectra of In3d, in which a binding energy $\sim 447.5\text{ eV}$ has been observed from AlInGa_N nanostructures. When increase the growth temperature 850°C to 900°C , In3d-like peak is disappeared also evidenced for Raman studies.

Figure 7 shows room-temperature photoluminescence studies of AlInGa_N sample prepared at 800°C , 850°C , 900°C . The Near-band-Edge (NBE) emission at 345 nm for AlInGa_N sample prepared at 800°C and 350 nm for 850°C , and 900°C samples. Some of defect like peaks at 425 nm, 440 nm and 470 nm are due to InGa_N like cluster formed in samples is due to various defects such as Ga vacancy (V_{Ga}), N interstitial (N_i), and the N anti-site (N_{Ga}), oxygen point defect and impurities. This broad peaks are associated with donor-acceptor pair and band has been attributed to recombination between the

residual donors [12]. In future studies will be making high crystalline AlInGaN material going to be prepared at different compositions. The prepared material can be used in optoelectronic applications and Photo-catalytic as well as AlInGaN can be utilized for sublimation growth of single crystals.

4. Conclusion

The AlInGaN nanocrystalline material has been prepared through CVD method. The prepared material exhibit high crystalline nature and its evidenced for XRD, XPS and Raman studies. From SEM image shows that when increasing growth temperature 800 to 900 C, morphology changes could be observed as well particle size decreases evidenced from TEM. The NBE emission peaks at 345 nm and 350 nm for AlInGaN samples in photoluminescence. The AlInGaN materials can utilized for sublimation growth of single crystals and optoelectronic, Photo-catalytic application.

Declarations

Author Contribution

It is certified that the paper entitled “Structural, Optical properties of AlInGaN nanocrystalline through chemical route by CVD method” is an original work, has been written by the stated authors and it is well aware about the content. Further it has been approved for the submission. It is not published previously in any other publication elsewhere and there is no conflict of interest. All authors have checked the manuscript and have agreed to the submission. It does not contain any copyrighted material which is reproduced without permission of the original author. AlInGaN nanocrystalline can be used in energy harvesting and Optoelectronic application

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Figures

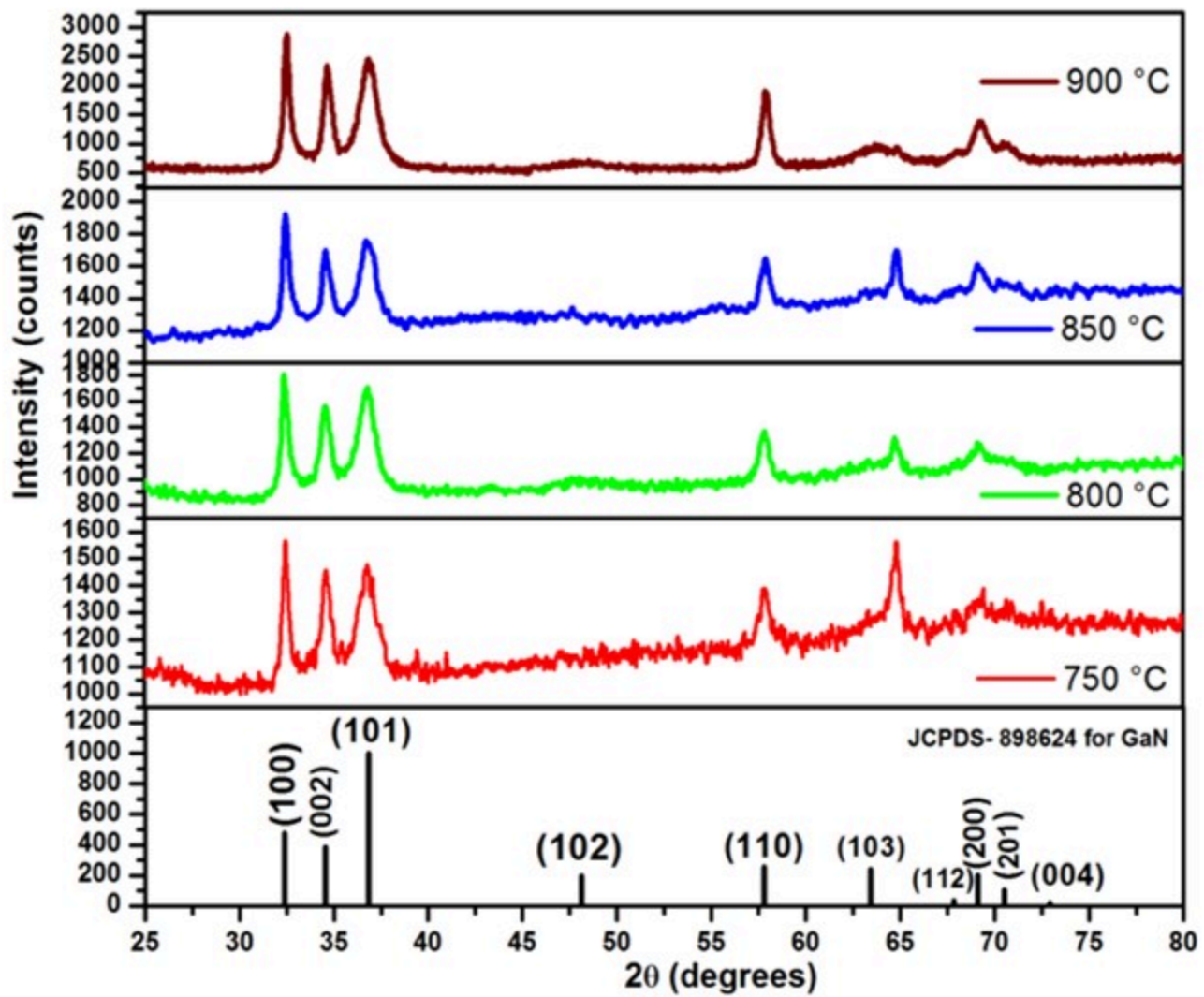


Figure 1

shows XRD pattern of AlInGaN alloy samples Nitrated at 750°C, 800°C, 850°C, 900°C.

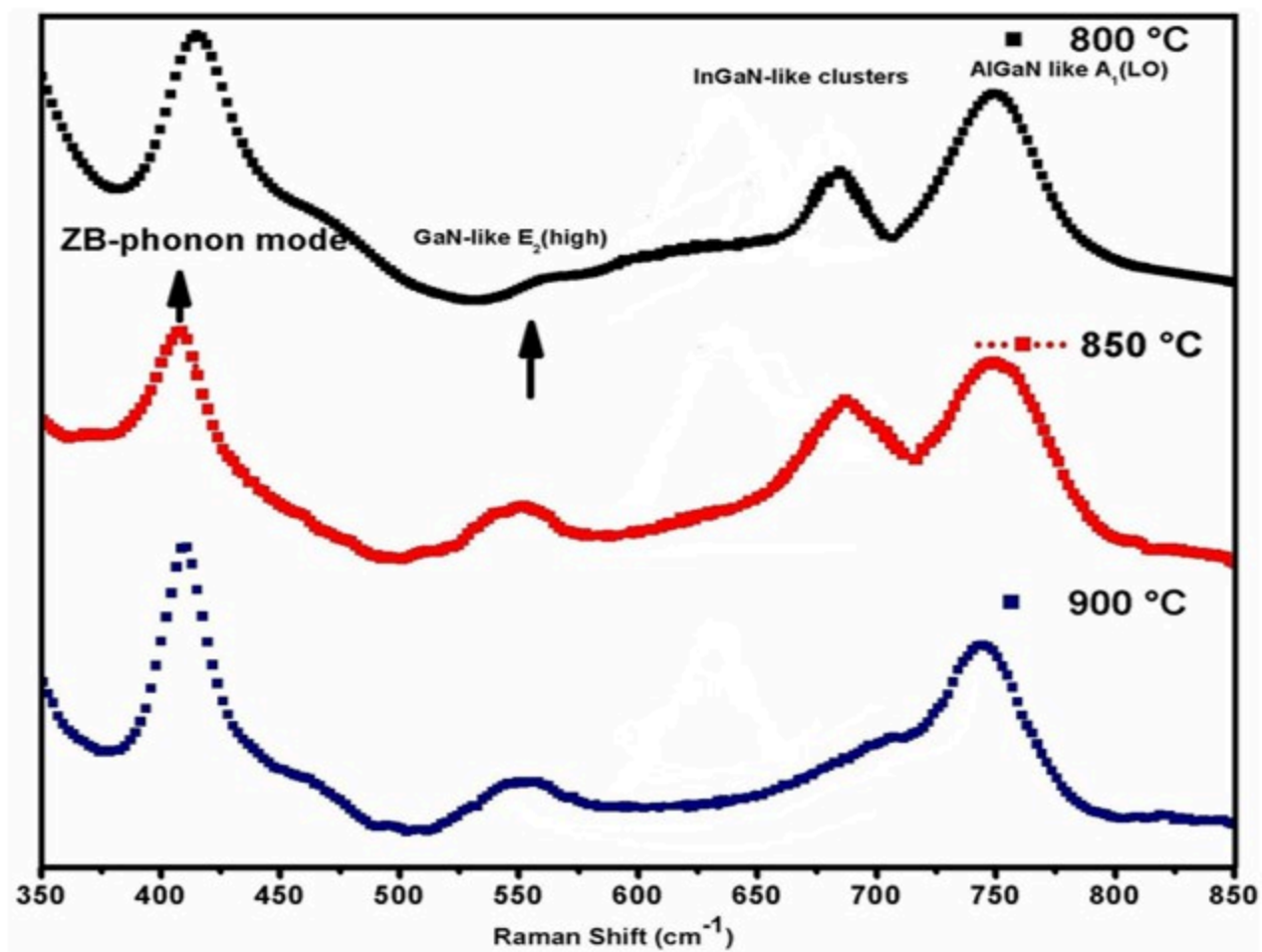


Figure 2

shows Raman spectrum of AlInGaN alloy samples Nitrated at 800°C, 850°C, 900°C.

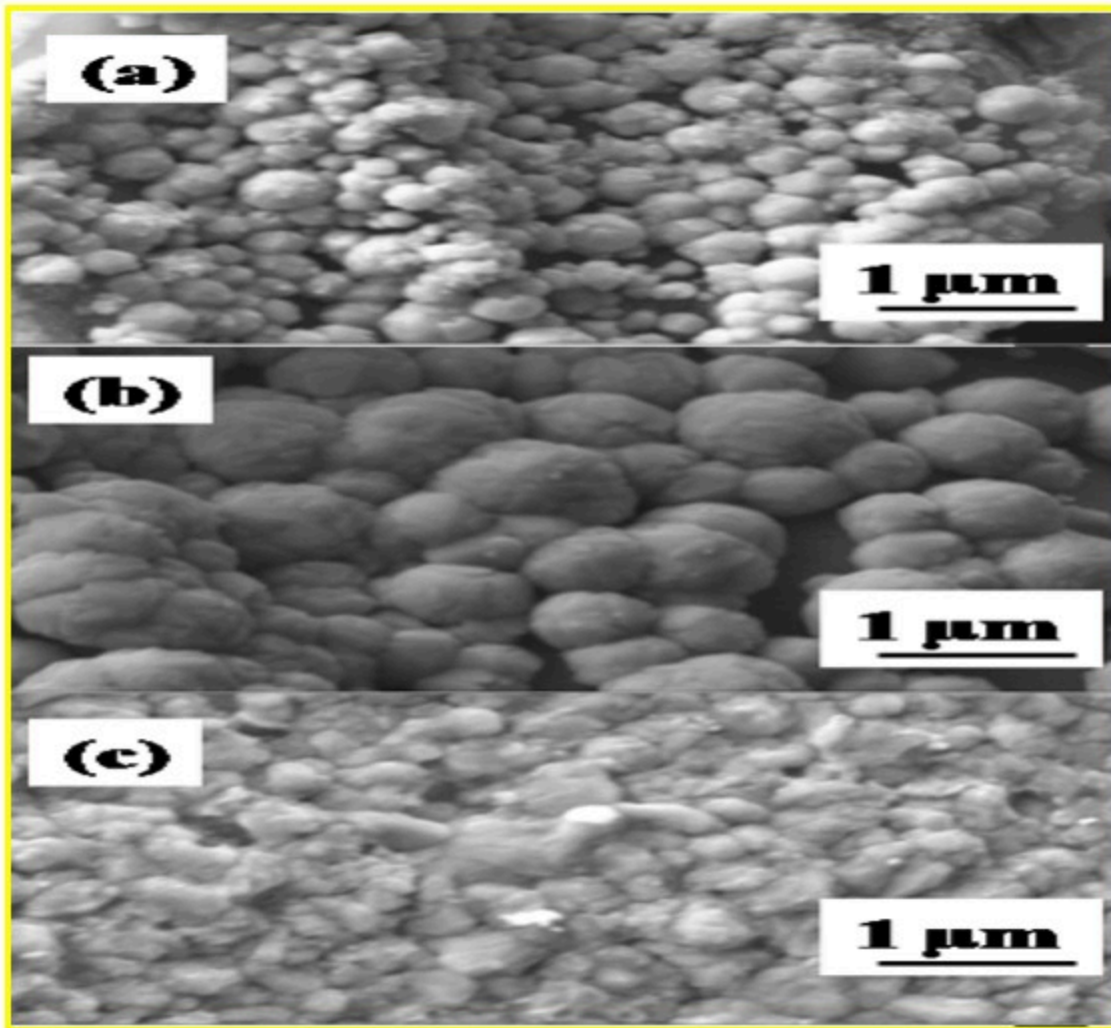


Figure 3

shows SEM images of AlInGaN alloy samples Nitrated at (a)800°C, (b)850°C, (c)900°C.

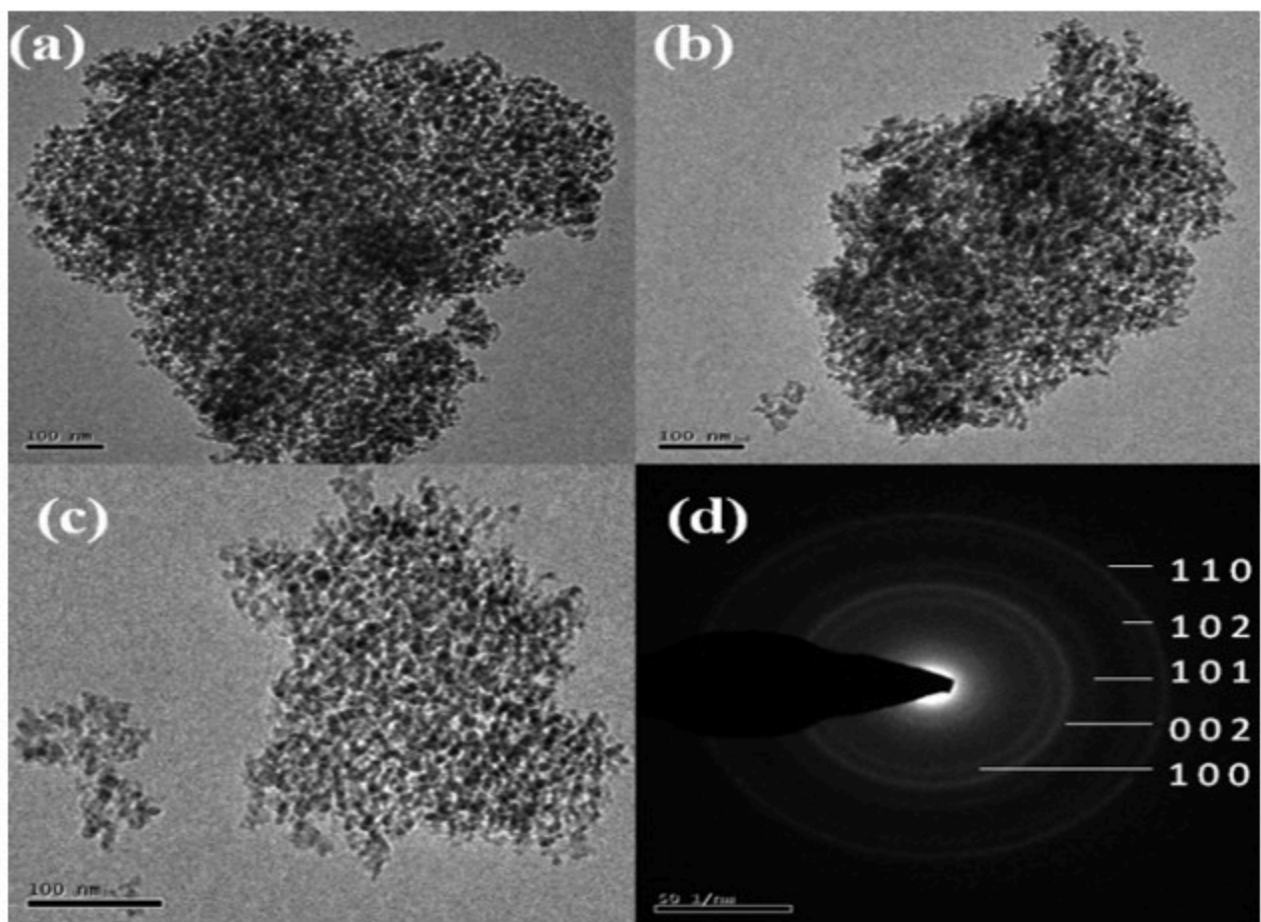


Figure 4

shows TEM images of AlInGaN alloy samples Nitrated at (a)800°C, (b)850°C, (c)900°C (d) SAED pattern

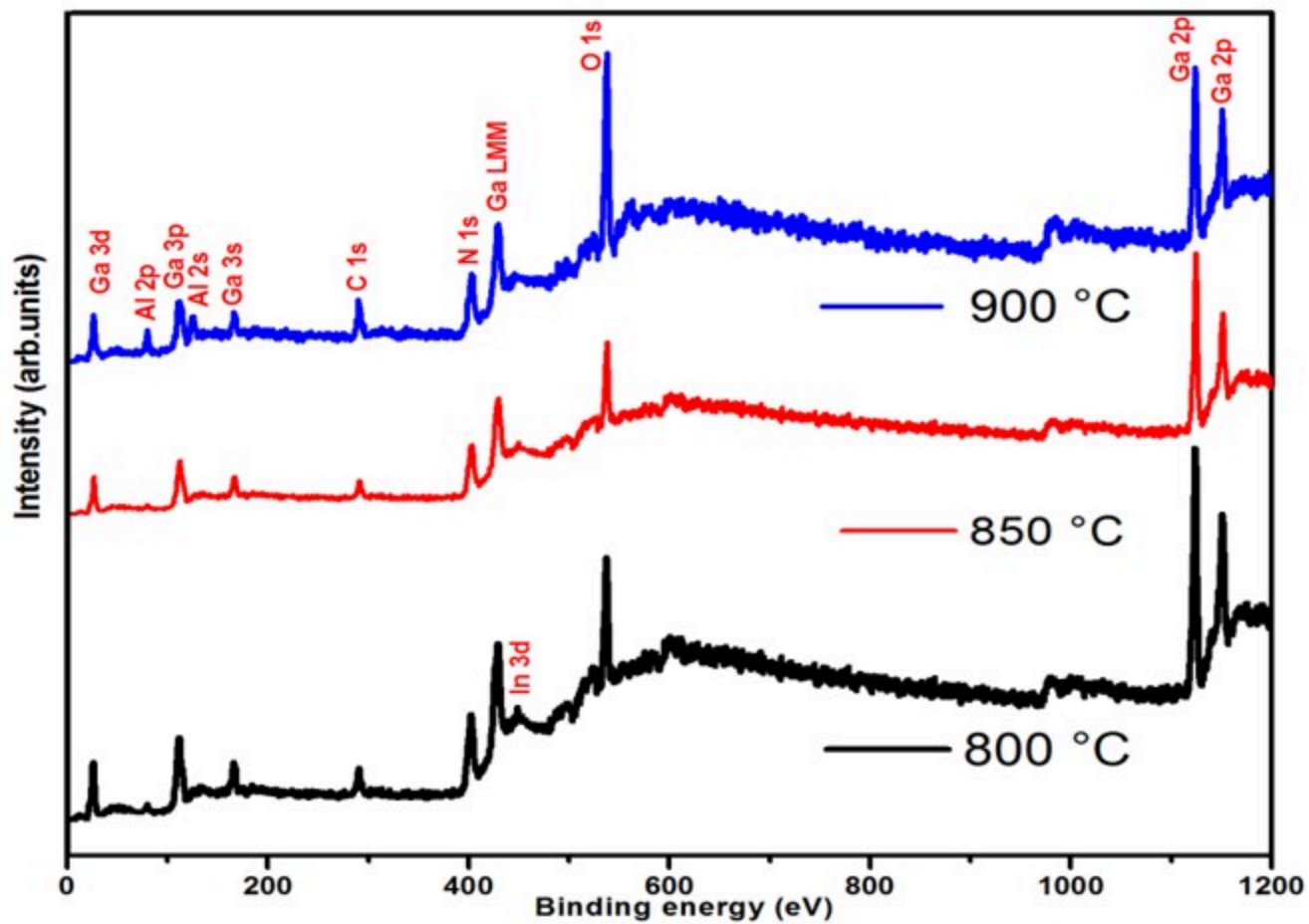


Figure 5

shows XPS Spectrum of AlInGaN alloy samples Nitrated at 800°C, 850°C, 900°C

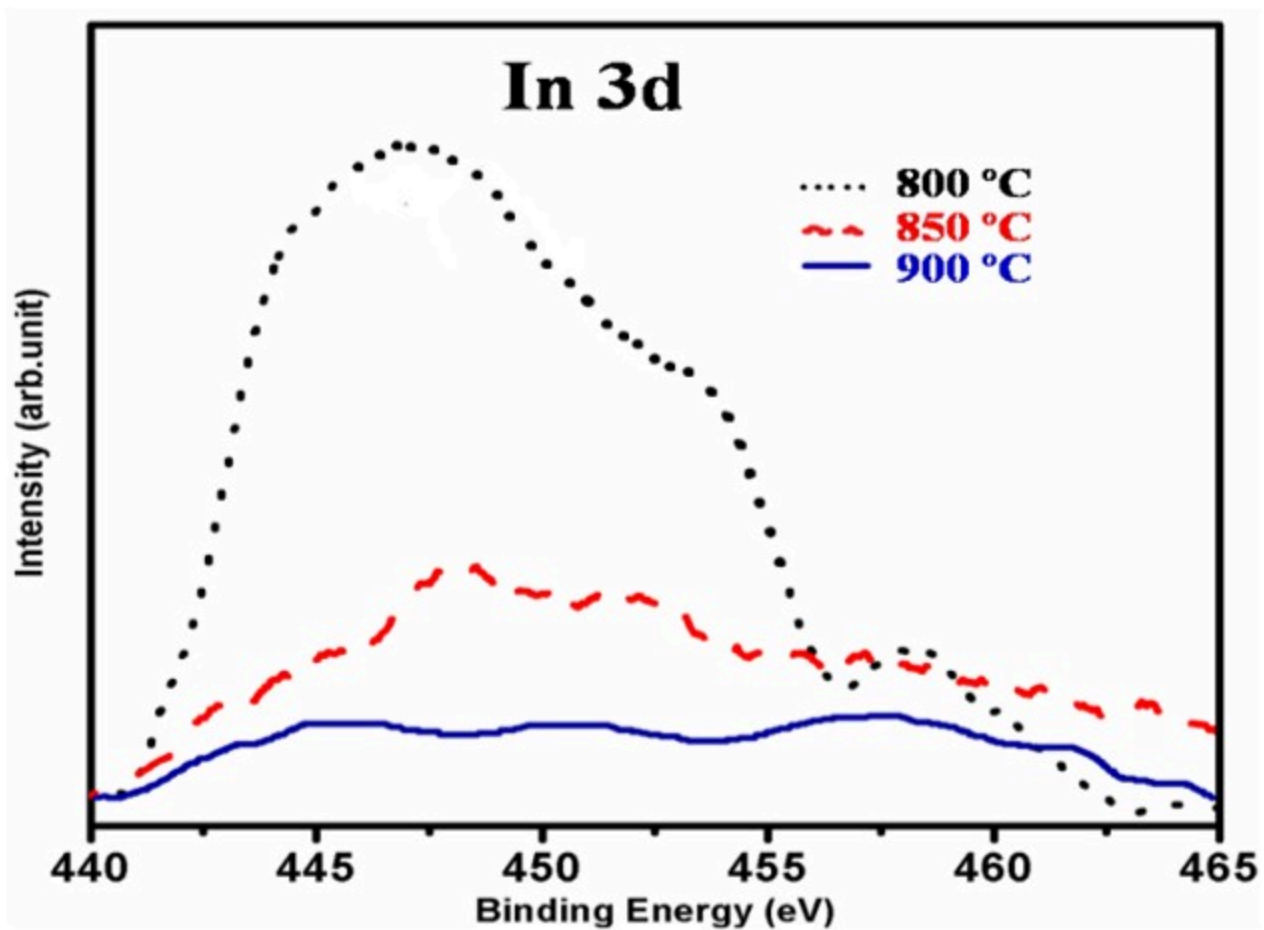


Figure 6

shows XPS spectrum of In3d peaks position for AlInGaN alloy samples Nitrated at 800°C, 850°C, 900°C

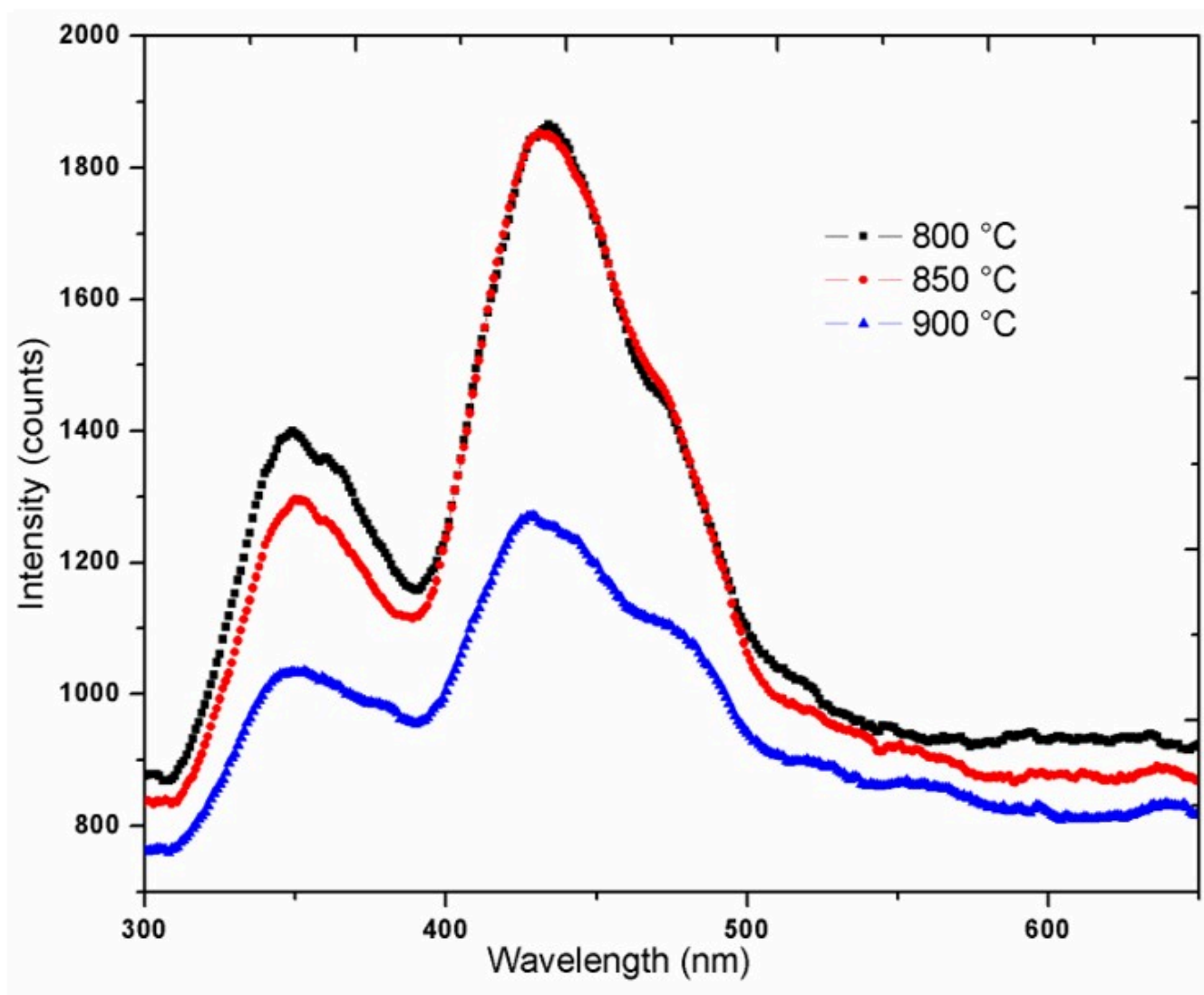


Figure 7

shows PL spectrum of AlInGaN alloy samples Nitrated at 800°C, 850°C, 900°C