Structural and Optical properties of Fe doped Gallium Nitride by sol-gel Method

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Abstract *:*Here we report the synthesis and characterization of Fe doped GaN nanostructure. The Fe-doped nanostructures were synthesized by Sol-gel method. The Crystalline quality and morphology of the synthesized GaN with different doping concentration was examined using X-ray diffraction, field emission scanning electron microscopy. X-ray diffraction indicates that the synthesized samples were wurtzite GaN nanostructure with high purity and no other second phase was formed during the growth. The SEM Image shows smaller individual nano particles of various sizes in the range of 30-50 nm. The band gaps of the synthesized sample were obtained using Diffuse Reflectance Spectroscopy, the band gap value increases with increasing Fe concentration. These results suggest that the Fe doped-GaN could be a promising candidate for optoelectronic and magneto electronic devices.

Keywords:- Fe doped GaN, Sol-gel synthesis, Nanostructure, XRD, SEM, Optical property.

I. INTRODUCTION

Gallium nitride (GaN) is a potential Semiconductor functional material due to its wide direct band gap 3.4 eV, at room temperature, high thermal conductivity, high chemical stability, high break down voltage [1–3], it is also important semiconductor used for optoelectronic and power application such as blue light emitting diode, laser, bipolar transistor, high temperature electronic devices, ultraviolet optoelectronic devices, photonic crystals, photodetectors and so on [4–6], gallium nitride doped transition metal offers attractive possibilities for innovation technological application and the ability to ‘‘tune’’ properties in semiconductors and generate a novel class of optical and spin dependent electronic devices [7]. Transition metal doped GaN have attracted much attention due their unique properties. Many physical properties such as electrical conductivity, piezoelectricity and defect structure, are influenced by the different type of impurities. The optical properties of GaN nanostructure can be altered by adding suitable dopant [8].

Fe-based materials have received considerable attention. The higher resistivity of p-type GaN has been found as a major obstacle for the device applications of GaN. To extent the applications of the GaN-based optoelectronic and spintronics device, the realization of band gap engineering to create barrier layers and quantum wells in devices heterostructures is vital [9-11]. Thus, the synthesis of GaN alloying for fabrication of optoelectronic devices has been hotly pursued. It is essential to search for optimal dopants to modify GaN material for improved optoelectronic devices. The study of alloys from the device fabrication and device performance is very important though GaN is immune to various environments [11-13]. The alloys can be widely introduced by doped on GaN structure. The insertion of transition metals such as Ni, Cu into the GaN structure may be changes its physical properties, which are important for GaN applications [14-15]. There are many different technique was employed to introduce dopant into the host lattice structure which include chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), sol-gel method etc [16-23]. Here we report the synthesis of 0%, 1%, 3% and 5% Fe doped GaN nanostructure for potential applications. The scope of this paper is to synthesize Fe doped GaN using simple sol-gel method by adding PVP as particle stabilizer. The effects of the Fe doping concentration on the structural, morphological, compositions, and optical properties of the GaN nanoparticles were investigated in details.

2 Experimental details

2.1 Materials

All reagents used in our experiments were of analytical purity and were used as received without further purification. Gallium nitrate hydrate ($Ga(NO_3)_3 \cdot 9H_2O$) and iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) from Aldrish, were used as precursor for preparing GaN doped iron (Fe) nanoparticles deionized water.

2.2 Synthesis of Fe doped GaN Nanoparticles

GaN samples were prepared with different atomic percentages of Fe (1, 3 and 5 at %), respectively. Firstly, the stoichiometries of GaN/Fe were dissolved in distilled water with constant magnetic stirring until the solutions became clear. Separately 10 wt% of PVP ethanol solution was prepared. The makeup solution was added into the PVP solution under constant stirring for 4 hours to obtain the clear and homogeneous viscous solution. The prepared viscous solution was annealed at 500^0C in air to decompose the gallium nitrate and polymer for 3 hr. The obtained product was kept inside the quartz reactor for ammonization. Here we used nitrogen as carrier gas and ammonia (NH_3) flow was kept constant while maintaining the constant temperature. After completion of the synthesis, the system was gradually cool to room temperature under nitrogen atmosphere. The obtained powders were subject to various characterizations. X-ray diffraction was used to analyze the crystal structure and phase purity, the particle size and morphology was obtained with FESEM. Chemical information and bonding between different atoms was collected by FTIR spectra. Diffuse Reflectance Spectroscopy was used to determine the band gap of the synthesized sample. All the measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION:

3.1 X-ray diffraction analysis (XRD)

X-ray diffraction of synthesized pure and GaN with different concentration of Fe doped GaN was shown in Fig. 1. The diffraction peaks indicate the formation of hexagonal wurtzite GaN structure and there are no anomalous peak related to other phase such as cubic gallium nitride, FeO, Fe_2O_3. This shows implantation of Fe ions does not change the crystal structure of the host GaN.

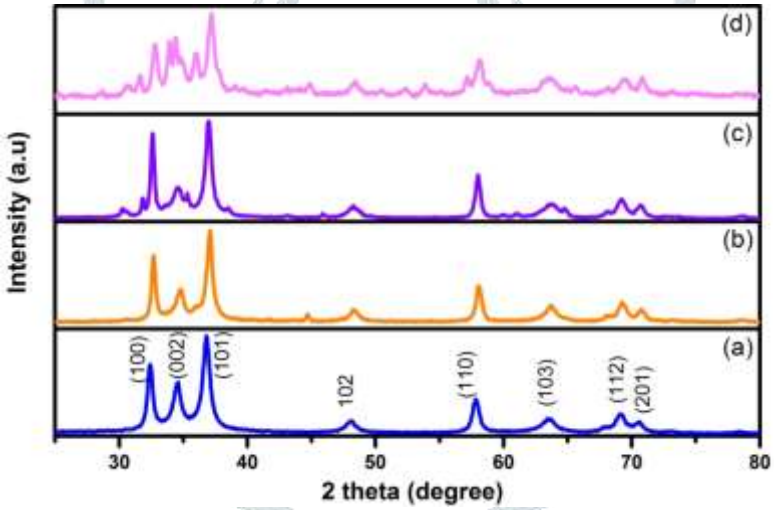

Fig.1 XRD patterns of (a) GaN undoped and Fe-doped: (b) 1at%, (c) 3at% and (d) 5at%

The X-ray results indicate that the pure GaN and Fe doped GaN sample has a polycrystalline structure and it grows with a hexagonal wurtzite type. The significant peaks for the pristine GaN were, GaN (100), GaN (002), GaN (101), GaN (102) , GaN (110) ,GaN (103) ,GaN (112) and GaN (201) centered at 2θ = 32.42°, 34.54°, 36.80°, 48.52°, 57.90° , 63.70°, 69.27° and 70.58° respectively. This corresponds to the single-phase wurtzite hexagonal structure of GaN . All of the reflection peaks of the XRD pattern of the synthesized GaN sample are in agreement with the nanocrystalline GaN by the sol–gel method [24]. Interestingly, the X-ray patterns show diffraction peaks with line broadening and high intensities, When the Fe doping percent increases the intensities of diffraction peaks also increases. The highest peak at 2θ = 36.80°, corresponds to the (101) crystallographic direction of GaN, indicates that the sample are highly c-axis orientated. And the sharp diffraction peaks also reveal that the samples thus prepared are highly crystallized and high crystal quality. It is worthily to note that, Fe-related impurity phases such as those of metallic Fe, iron oxides, and other compounds were not detected in the doped samples, indicating that Fe^{3+} replaced Ga^{3+} in the GaN lattice without changing the wurtzite structure.

In order to evaluate the variation of the crystallite size (D) with increasing Fe-doped GaN nanofibers, the Debye– Scherrer formula neglecting peak broadening due to residual stresses in the films is given by [3]:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where k is the shape factor, k is the wavelength of the X-ray used, β is the full width at half maximum of a distinctive peak in units of radians, and θ is the Bragg angle of the X-ray diffraction peak. The crystallite size of the samples was determined using (101) peak. It can be seen from the figure that the mean crystallite size decreases with increasing Fe-doped GaN. The crystallite sizes were found to be in the range of 30–60 nm. The obtained crystallite size is bigger than that of nanocrystalline GaN by the sol–gel method [24].

3.2 SEM Analysis

The morphology of pure GaN and Fe (1%, 3% and 5%) doped GaN nanostructure were studied by FESEM as shown in Fig. 2. The figure of the pure GaN shows the particle are tried to form hexagonal structure and the particle are closely packed, particle size are found to be vary 30-40 nm. The surface properties of GaN are influenced from the incorporation of dopant [25]. Especially the amount and kind of dopant can play an important role on the surface properties. These figures show the aggregates of smaller individual nano particles of various sizes. The SEM images depict the grain size increases as the concentration of the Fe increases. The size of nanoparticles of Fe doped GaN ranges from 50-150 nm [26]. From the above observations, it can be noticed that the doping concentration of Fe affects the parent GaN, thus agglomerates were of the nano- and submicron sizes [27].

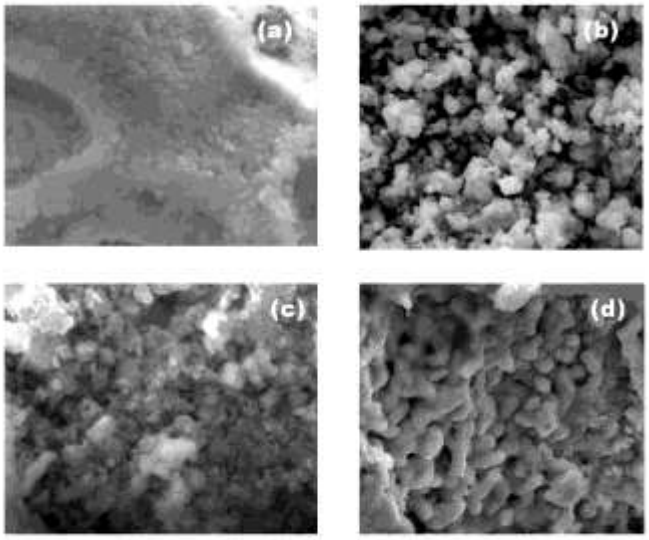

Fig.2 SEM Image of GaN nanoparticles Fe-doped: a) pure, b) 1at% , c) 3at% and d) 5 at%

3.3 FT-IR Analysis:

Figure 3 shows the Infrared spectra of Pure and Fe doped GaN nanostructures were recorded in the range of 4000-400 cm^{-1} using FTIR spectroscopy at room temperature. The spectra clearly depict the existence of GaN stretching mode by showing the peak in the range of 450-550cm^{-1}. This is an evidence for the incorporation of Fe^{3+} ions into the GaN upon Fe doping. It can be seen from that an increase in Fe concentration produces a broad absorption band at the position of the Fe^{2+} absorption around 3226 cm^{-1} this are most likely inter-center interaction and localized strain, which occur due to Fe densities and cause the lines to broaden. The absorption peak around 655cm^{-1} was recorded in the doped sample which is assign to O=C=O stretching. The presence of C in the synthesized Fe doped GaN may be due to the polymer PVP, during the decomposition it may have leaved some carbon in the sample, because of low quantity it was not deducted in the XRD spectra, the presence of oxygen was due to the unavoidable exposure of the sample to atmosphere. The strong absorption band at 453 cm^{-1} is due to Ga-N stretching mode of GaN nanoparticles and no major impurity peaks were found.

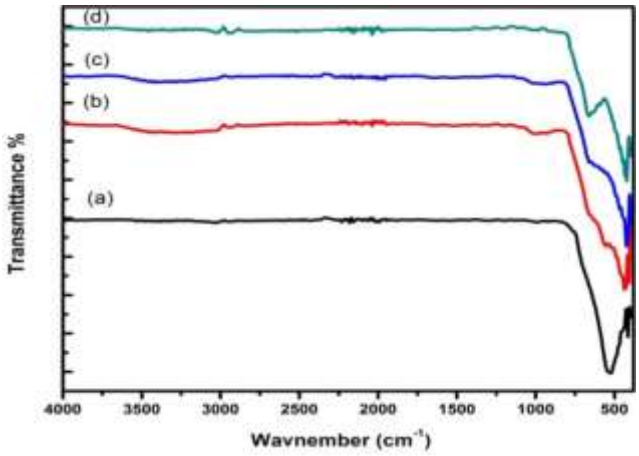

Fig.3 FTIR Spectra of a) Pure GaN and Fe doped GaN b) 1at%, c) 3at% and d) 5at%

3.4 UV/Diffused Reflectance Spectroscopy Analysis

The UV–visible reflectance spectra of pure and Fe doped GaN nanostructure were recorded using Diffuse Reflectance Spectroscopy at room temperature are plotted shown in Fig. 4, we can find that the optical reflectance spectra change after doping Fe from the spectra. The absorption spectrum of the synthesized GaN and Fe -doped GaN consists of ultraviolet bands around 290 respectively, but it is without absorption bands in the visible region. Fe doping shifts the absorption onset to lower wavelength (blue shift), indicating an increase in the optical band gap. This blue shift is known as the blocking of the lowest states in the conduction band taken place with the increase in carrier concentration, and it leads to the energy band broadening [9]. The increase in optical reflectance with Fe doped can be attributed to the increase in structural homogeneity and crystallinity [11].

The optical band gap (Eg) of pure GaN and Fe-doped GaN can be obtained from the intercept of $(\boldsymbol{\alpha h\vartheta})^2$ versus $\boldsymbol{h\vartheta}$ for direct transitions. It is observed that for all the samples, the best straight line is obtained for n = ½ which is expected for direct allowed transition as plotted in Fig. 4b. It is seen that the optical band gap increases from 3.1 ± 0.01 to 3.25 ± 0.01 eV as the Fe doped increases. Based on quantum confinement theory, the band gap energy of a material increases with the decrease in size of the quantum dot [2, 3]. The number of oxygen vacancies and defects increases the charge carrier concentration in the conduction band with increasing Fe doping. Another reason can be attributed to the fact that with increasing Fe doping, the crystallinity and the crystallite size decrease resulting in increasing defects, and therefore, band gap energy is increased. After Fe is doped, a structural deformation is taken place in the GaN samples due to the replacement of either substitution Ga ions in the GaN lattice by Fe ions or the different in iconicity between Fe–O and Ga–N bonds. We believe that this causes an increase in the optical band gap of Fe-doped GaN with the sublattice modification.

This suggests that the Fe ions substitute uniformly for Ga^{3+} in the lattice. This is attributed to the increase in defects, which could be the number of oxygen vacancies and/or grain boundaries. Increasing Fe doped will result in increasing oxygen vacancies which lead to an increase in the carrier concentration in the conduction band. On the other hand, Fe doped improves crystallinity and increases average crystallite size that result in increasing defects, and therefore carrier concentration is increased [10, 11]. Moreover, the Fe and Ga atoms have strong mismatch in electronegativity, which is also a reason for the increase in the carrier concentration.

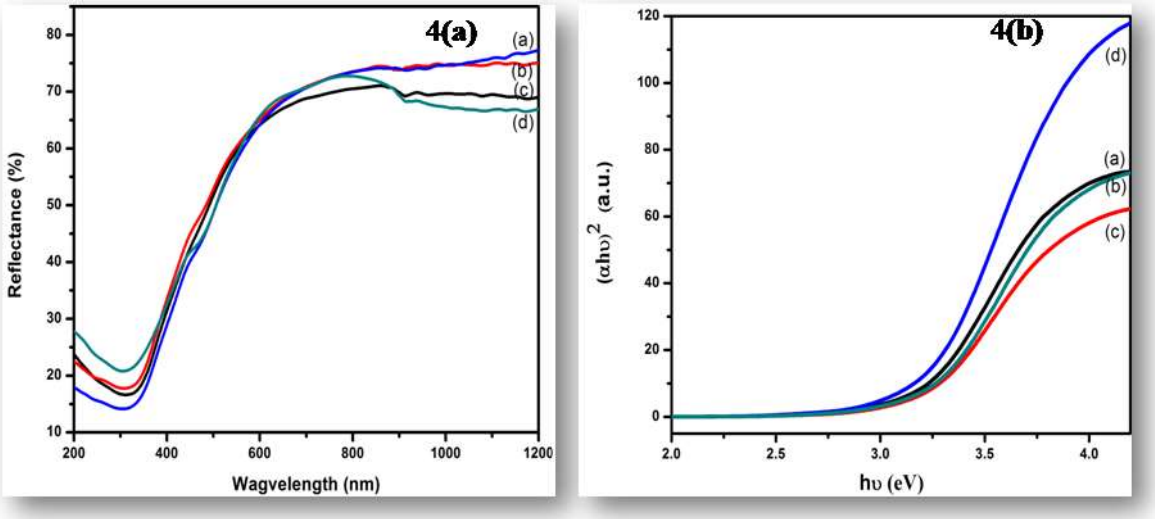

Fig. 4a Reflection spectra of (a) GaN undoped and Fe-doped: (b) 1at%, (c) 3at% and (d) 5at%
Fig. 4b Band gap plot of of (a) GaN undoped and Fe-doped: (b) 1at%, (c) 3at% and (d) 5at%

4.Conclusions

Here we conclude, The Fe-doped GaN nanostructures have been synthesized by Sol-gel method. X-ray diffraction indicates that the synthesized samples were wurtzite GaN nanostructure with high purity and no other second phase was formed during the growth. The SEM Image shows smaller individual nano particles of various sizes in the range of 30-50 nm. The band gaps of the synthesized sample were obtained using Diffuse Reflectance Spectroscopy, the band gap value increases with increasing Fe concentration. The FTIR spectra clearly depict the existence of GaN stretching mode by showing the peak in the range of 450-550cm^{-1}. This is an evidence for the incorporation of Fe3+ ions into the GaN upon Fe doping. These results suggest that the Fe doped-GaN could be a promising candidate for optoelectronic device applications.

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