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Enhancing crystal quality and optical properties of GaN nanocrystals by tuning pH of the synthesis solution

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Abstract: Gallium nitride nanocrystals as a wide bandgap semiconductor material for optoelectronic applications can be synthesized using chemical methods. In this research using co-precipitation and nitridation processes gallium nitride nanocrystals have been synthesized, and by tuning pH of the synthesis solution at the co-precipitation step, crystal quality and optical property of the resultant gallium nitride nanocrystals have been enhanced. Gallium nitride nanocrystal samples were synthesized using solutions with pH values of 2.1, 4.8, 7.8, and 9.0, and then nitridation at 950 °C under the flow of ammonia gas. The synthesized nanocrystal samples were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and photoluminescence techniques. The XRD data show that the nanocrystals have hexagonal wurtzite crystal structure, and using Scherer's equation the sizes of the synthesized nanocrystals are 23.6, 26.6, 19.7, and 10.4 nm for the samples synthesized using the solutions with pH values of 2.1, 4.8, 7.8, and 9.0 respectively. The sizes of the nanocrystals obtained from SEM images are larger than the values obtained using Scherer's equation, due to the aggregation of nanocrystals. EDX spectra show that pH of the synthesis solution affects the elemental stoichiometry of the gallium nitride nanocrystals. We obtained better stoichiometry for the nanocrystal sample synthesized using solution with the pH of 4.8. Photoluminescence spectra show that for this sample the emission intensity is higher than the others.

Keywords: co-precipitation; gallium nitride; nanocrystal; nanoparticle; nitridation; semiconductor.

1 Introduction

Since 1970, III-nitride semiconductors have been considered as a promising material system for the electronic and optoelectronic device applications especially for the development of blue and ultraviolet light emitting diodes [1]. These materials have high mechanical and thermal stabilities, large piezoelectric constants, and possibility of passivation by thin layers of Ga_2O_3 or Al_2O_3 [1]. Nitride semiconductors such as: InN, GaN, AlN and their alloys comprise a direct band gap semiconductor system with the bandgap energy in the range of 1.95 eV (InN)–6.2 eV (AlN) [2]. Among nitride semiconductors, GaN has attracted considerable attention for photonic device applications due to its wide and direct bandgap of 3.4 eV and high excitonic binding energy of 28 meV [3]. Owing to its high electron mobility, small free carrier effective mass, resistance to radiation, high thermal and mechanical stabilities, and excellent optical properties, GaN has been used for fabricating high power electronic devices [4], diode lasers [5], high speed photodetectors [6] and blue light emitting diodes for solid state lighting [7].

GaN nanostructures, after silicon, have been considered as the most important semiconductor material for electronic and optoelectronic device applications [8]. Generally semiconductor nanostructures are preferred due to their size tunable properties caused by quantum confinement phenomena. Many research groups have reported on the synthesis of GaN nanocrystals using variety of synthesis techniques such as: sol-gel [9], hydride vapor phase epitaxy [10], metal-organic-chemical vapor deposition [11], pyrolysis [12], laser ablation [13], catalytic growth [14], electrochemical deposition [15], combustion [16], co-precipitation [17, 18], forced hydrolysis [19], solvothermal method [20], and another chemical method [21]. Among these techniques co-precipitation technique is a high yield, scalable, and low-cost synthesis technique.

In this paper by tuning pH of the synthesis solution at the co-precipitation step, crystal quality and optical properties of synthesized GaN nanocrystals are enhanced. The GaN nanocrystals were synthesized using chemical co-precipitation method at different pH values, and then nitridation.

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2 Experimental method

2.1 Materials

In this work for the synthesis of GaN nanocrystals, gallium metal (99.99%), 2-propanol (grade: extra pure, assay > 99.5%), ammonia solution 25% (grade: laboratory, assay ≈24–26%), nitric acid 65% (grade: extra pure, assay ≈63–67%), and ammonia gas (99.9%) were used.

2.2 Synthesis method

In order to synthesis GaN nanocrystals, 2.8 g of the gallium was dissolved in 34 cc of the nitric acid with agitation using ultrasonic bath. It takes about 45 min until the complete dissolution of gallium in nitric acid. Then in order to dilute the solution 240 cc of the 2-propanol was added to the solution. The resultant solution was divided to four solution samples. By addition of double distilled water to the ammonia solution a diluted 4% ammonia solution was prepared. The diluted ammonia solution was added dropwise into each of the solution samples very slowly, about one droplet in every 5 s, until that four solution samples with pH values of 2.1, 4.8, 7.8, and 9.0 were prepared. Then each solution sample left for 10 h while it was stirred vigorously using magnetic stirrer. After this period the white precipitate was separated from each solution sample by centrifugation. The resultant white power samples were dispersed in ethanol using ultrasonic bath and centrifuged again. This process repeated for three times, in order to the white powders are washed thoroughly. The powder samples dried in an electric oven set to 80 °C for 15 h. Then the samples were placed in alumina boats into an electric furnace with quartz tube. The ammonia gas was set to flow inside the tube at a rate of 500 sccm. The furnace temperature increased from room temperature to 950 °C at a rate of 40 °C/min, and remained at this temperature for 2 h. Then the samples inside the quartz tube left to cool down to room temperature while the ammonia gas was flowing on the samples. At the end of the nitridation process yellow colored powder samples obtained. During the cool down step, instead of high purity ammonia gas high purity nitrogen gas can be used. High purity is a requirement because the presence of oxygen not only oxidizes GaN but also makes GaN *n*-type [22].

3 Results and discussion

Energy dispersive X-ray spectroscopy (EDX) analyses of the samples are shown in Figure 1. It is evident that the pH of the solution at the co-precipitation step affects the stoichiometry of the synthesized GaN nanocrystals. The GaN nanocrystal sample synthesized using the solution with the pH value of 2.1 shows larger gallium atoms deficiency relative to other samples. For this sample the weight percent of gallium and nitrogen atoms are 73.52 and 26.48%, respectively. The chemical formula for this sample can be written as: $Ga_{0.56}N$. With using the weight present of gallium and nitrogen atoms, indicated on Figure 1, for the samples synthesized using the solutions with the pH values of 4.8, 7.8, and 9.0, the chemical formula for these samples can be written as: $GaN_{0.91}$, $Ga_{0.77}N$, and $Ga_{0.72}N$, respectively. These results have been indicated in Table 1. In this research we obtained better stoichiometry for the GaN nanocrystals synthesized using the solution with the pH value of 4.8, where the weight percent of gallium atoms is 84.48% and the weight percent of nitrogen atoms is 15.52%.

Figure 2 shows X-ray diffraction (XRD) patterns of the synthesized powder samples. The XRD patterns obtained using Cu-Kα radiation (wavelength 1.5406 Å). The diffraction peaks are in agreement with the peaks of hexagonal wurtzite GaN crystal structure, and have been indexed on the figure with the relevant crystal planes, indicating that only one GaN crystal phase exists. As the figure shows the intensities of XRD peaks increase with the increase of the pH of the synthesis solution and then decrease, which are highest for the GaN nanocrystals synthesized using the solution with the pH value of 4.8. This is due to the larger nanocrystal size of this sample, and higher crystalline quality of nanocrystals of this sample because of its better stoichiometry as evidenced from EDX analysis.

Using the XRD data the sizes of the nanocrystals (D), shown in Table 1, were calculated using Scherer's equation:

$$D = \frac{K\lambda}{\beta Cos(\theta)} \tag{1}$$

where β, θ, λ, and K are respectively: peak width at half maximum intensity, i. e., Full Width at Half Maximum (FWHM) expressed in radians, location of the peak, the wavelength of the X-ray radiation, and a constant factor that for spherical particles is equal to 0.9. For calculating the sizes of nanocrystals the position and FWHM of the (101) peaks were used. As Table 1 shows, with the increase of the pH of the solution samples the size of nanocrystals increases and then decreases.

Cohen's method, with applying Nelson–Riley extrapolation function, [23] was used to determine the values of lattice parameters (a, and c). These parameters have been

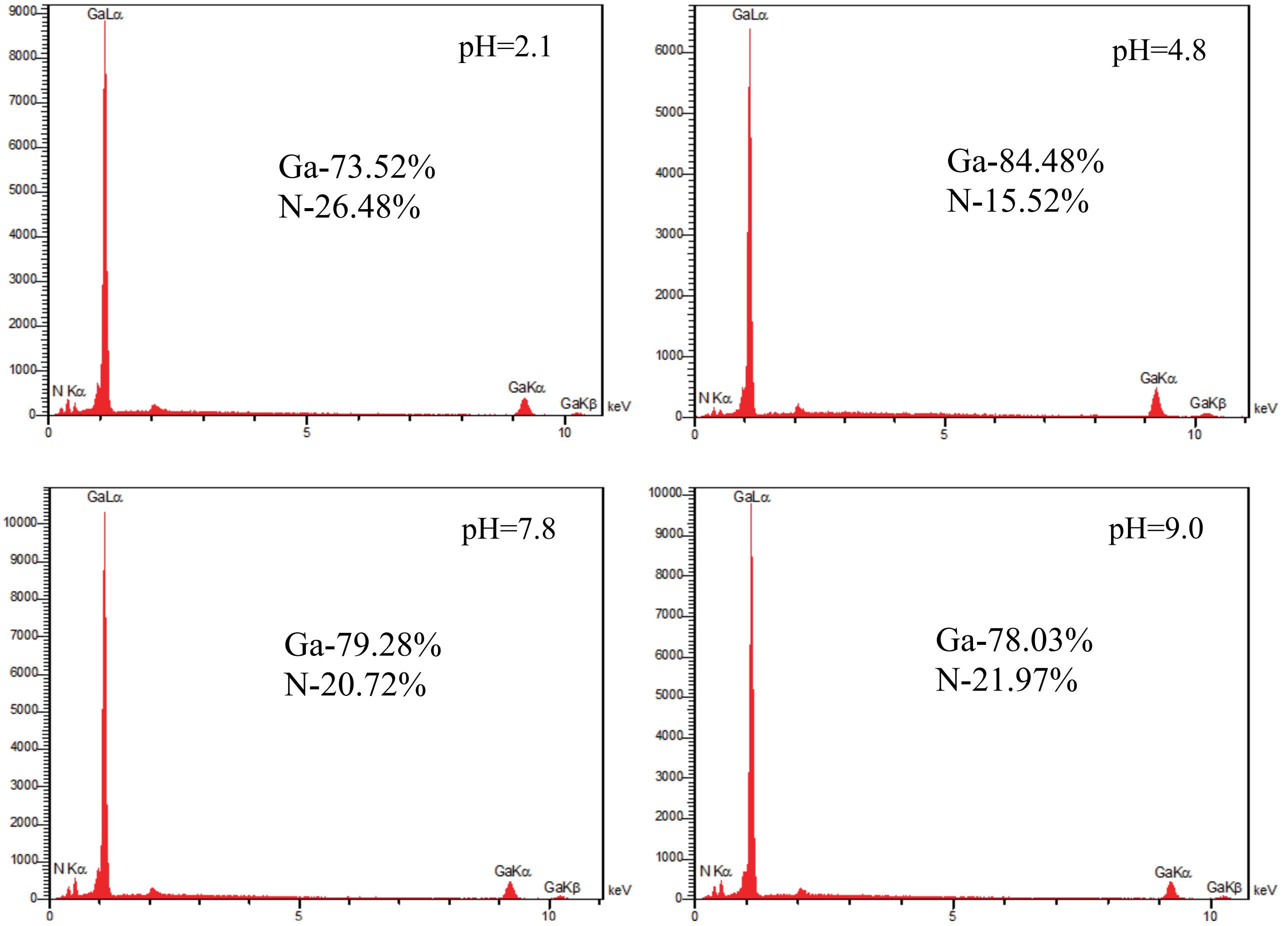

Figure 1: EDX spectra of GaN samples synthesized using solutions with different pH values. The weight percent of gallium and nitrogen atoms have been indicated.

indicated in Table 1. Using the lattice parameters, unit cell volumes and densities of the samples were determined with using chemical formulas of the samples. The results, indicated in Table 1, show that the samples with larger gallium atoms deficiencies have smaller unit cell volumes and lower densities.

Scanning electron microscopy (SEM) images of the nanocrystals are shown in Figure 3. As the figure shows nanocrystals have been aggregated due to van der Waals forces between the nanocrystals. The size distributions of the nanocrystals are shown on the images as inset figures, as well. The mean size of the nanocrystals are 31, 35, 26, and 14 nm for the samples synthesized using solution samples with the pH values of 2.1, 4.8, 7.8, and 9.0 respectively. The sizes of the nanocrystals obtained from SEM images are larger than the values obtained from XRD

Table 1: Sizes of nanocrystals, lattice parameters, unit cell volumes, chemical formulas, and densities (ρ_{XRD}) determined using XRD and EDX data, for the GaN nanocrystal samples synthesized using solutions with different pH values.

pH of the synthesis solution samples	FWHM of (101) peaks (radians)	2θ position of (101) peaks (degrees)	Nano-crystal size (nm)		Lattice parameters (Å)		Unit cell volume (Å^3)	Chemical formula	(ρ_{XRD}) (g/cm^3)
			XRD	SEM	*a*	*c*			
2.1	0.062	36.89	23.6	31	3.1875	5.1828	45.60	$Ga_{0.56}N$	3.84
4.8	0.055	36.89	26.6	35	3.1892	5.1969	45.78	$GaN_{0.91}$	5.98
7.8	0.074	36.89	19.7	26	3.1878	5.1886	45.66	$Ga_{0.77}N$	4.92
9.0	0.140	36.89	10.4	14	3.1899	5.1781	45.63	$Ga_{0.72}N$	4.67

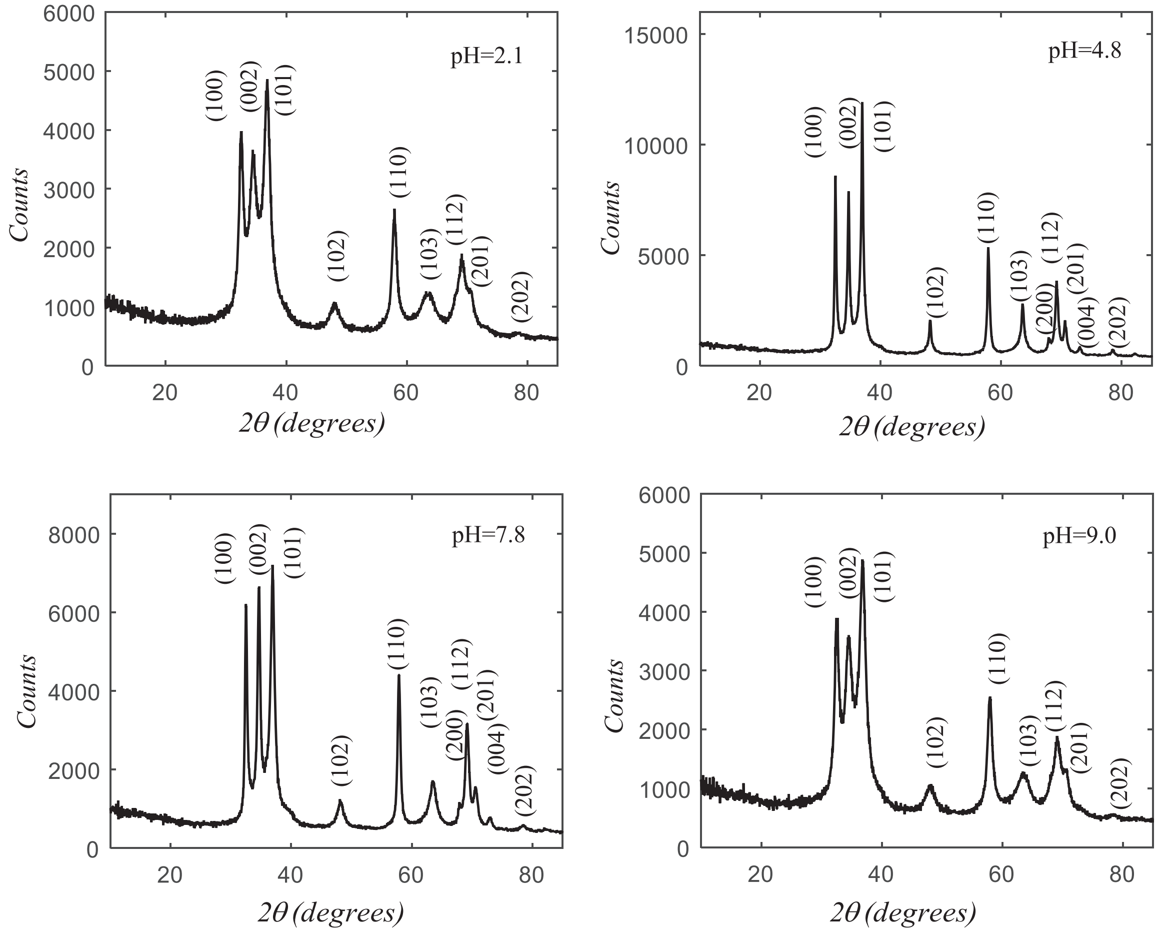

Figure 2: XRD patterns of GaN samples synthesized using solutions with different pH values.

data. This could be due to the aggregation of the nanocrystals, as evidenced from Figure 3.

Investigating optical properties of synthesized GaN nanocrystals is important from optoelectronic device applications point of view. For this purpose photoluminescence spectra of the samples were obtained using excitation wavelength of 280 nm, and are shown in Figure 4. The emission peaks are at about 3.3 eV which is near to the band gap energy of bulk GaN. The emission peak for the GaN nanocrystals synthesized using the solution sample with the pH value of 4.8 is higher than the others. It should be noted that two factors could lead to higher photoluminescence intensities: higher crystalline quality due to lower defect density, and larger nanocrystals due to the decrease of grain boundaries to volume ratio. It is true that the size of GaN nanocrystals synthesized using the solution sample with the pH value of 4.8 is larger than the others, but this is not the only fact for the highest photoluminescence intensity of this sample relative to the other samples. Because if it was the only reason then the photoluminescence intensity of the GaN nanocrystals synthesized using the solution sample with the pH value of 2.1 should be higher than the ones synthesized using the solution samples with the pH values of 7.8 and 9.0, but as Figure 4 shows this is not true. These facts indicate that the highest photoluminescence intensity of the GaN nanocrystals synthesized using the solution with the pH value of 4.8 is not only due to its larger nanocrystal sizes but also due to its higher crystalline quality of this sample as explained before using EDX and XRD data.

4 Conclusions

GaN nanocrystals were synthesized using co-precipitation and nitridation processes. Solutions with different pH values were used at the co-precipitation process step, and the nitridation process performed under the flow of ammonia gas inside a quartz tube at a temperature of 950 °C. The results show that GaN nanocrystals have single phase hexagonal wurtzite crystal structure, and

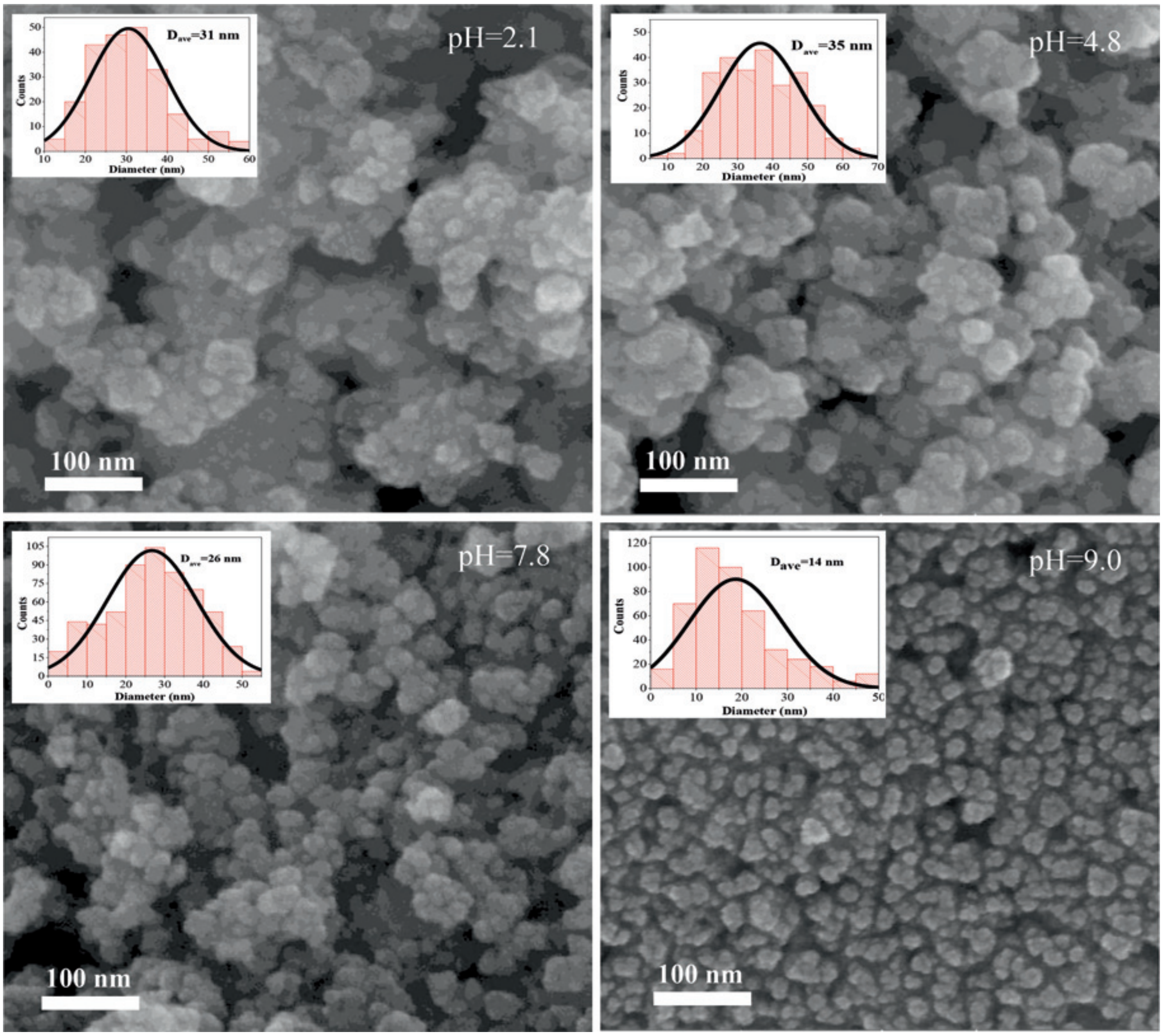

Figure 3: SEM images of GaN samples synthesized using solutions with different pH values. The inset figures show the size distribution of GaN nanocrystals.

the pH of the synthesis solution, at the co-precipitation step, affects the size and crystal quality of the synthesized nanocrystals. With tuning pH of the synthesis solution it is possible to obtain high quality GaN nanocrystals with high photoluminescence emission performance.

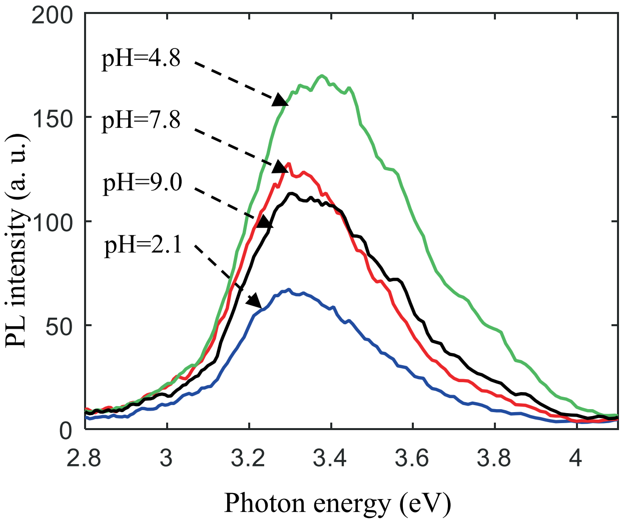

Figure 4: Photoluminesence spectra of GaN samples synthesized using solutions with different pH values.

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