

Low-cost growth of magnesium doped gallium nitride thin films by sol-gel spin coating method

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Abstract. Low-cost sol-gel spin coating growth of magnesium (Mg) doped gallium nitride (GaN) thin films with different concentrations of Mg was reported. The effects of the Mg concentration on the structural, surface morphology, elemental compositions, lattice vibrational, and electrical properties of the deposited films were investigated. X-ray diffraction results show that the Mg-doped samples have wurtzite structure with preferred orientation of GaN(002). The crystallite size decreases and the surface of the films with pits/pores were formed, while the crystalline quality of the films degraded as the Mg concentration increases from 2% to 6. %. All the Raman active phonon modes of the wurtzite GaN were observed while a broad peak attributed to the Mg-related lattice vibrational mode was detected at 669 cm^{-1} . Hall effect results show that the resistivity of the thin films decreases while the hole concentration and hall mobility of thin films increases as the concentration of the Mg increases.

1. Introduction

Wide band gap gallium nitride (GaN) semiconductor has received significant attention as a promising material for the applications of the optoelectronics and high-temperature/high-power devices such light emitting diode (LEDs) and laser diode (LD). The GaN have unique properties such as wide direct band gap (3.4 eV) [1], high breakdown field and high thermal conductivity [2]. This innovation brought about ever increasing research efforts towards more high-performance nitride-based LEDs and LDs with p-type GaN. Until now, magnesium (Mg) doped GaN is the most successful in the development of GaN based optoelectronic devices. Effective research of p-type GaN:Mg layer has been one of the dynamic encounters for realizing blue and green LEDs. The main reason uses of the p-type GaN in the development optoelectronic devices is to supply sufficient concentration of holes so that, when embedded into the active layer, they will recombine with electrons and emit light effectively. Therefore, a higher hole concentration in the p-GaN layer is advantageous to increase the light intensity of LEDs. However, the dopant concentration in the Mg doped GaN layer must be optimized to obtain ohmic metal contacts [3], which is important to decrease the operating voltage of the devices [4]. Despite the steady progress in Mg-doped GaN thin films, several issues remain to be solved. For instance, there are still difficult to produce highly p-type conductivity and difficult to activate the Mg dopant in GaN thin films. Up until now, highly advanced and expensive growth techniques such as metalorganic chemical vapour deposition [5] and molecular beam epitaxy [6] were used to produce p-GaN. While few complex approaches were used to activate the Mg-dopant in GaN thin films, i.e., thermal annealing [7], low-energy electron beam irradiation [8] and microwave treatment [9].

In order to produce more economical p-GaN films, chemical synthesis process using a sol-gel spin coating method was purposed. This method has received considerable attention due to its many



benefits such as simple deposition procedure, easier composition control, low equipment cost, and large area coating capability [10-11]. At present, sol-gel spin coating growth of GaN thin films has been successfully demonstrated by Fong et. al [12-14]. Nevertheless, this method has not been applied to grow the p-GaN thin films. For this reason, sol-gel spin coating growth of Mg-doped GaN thin films with different concentrations of Mg was carried out. In this work, the influences of the Mg concentrations on the structural, surface morphology, elemental composition, lattice vibrational and electrical properties of deposited films were investigated systematically using various characterization techniques.

2. Experimental

In this experiment, Mg doped GaN thin films were deposited on commercial AlN template by sol-gel spin coating method. The AlN template was obtained from the Kyma Technologies, Inc. It consists of a thin crystalline AlN layer (thickness around 25 nm) grown epitaxially on silicon (111) substrate.

The sol-gel precursor was prepared using gallium nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), magnesium nitrate hydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), diethanolamine (DEA), ethanol (purity, 99.7 %) and distilled water. The function of each material was as Ga source, Mg dopant, stabilizer and solvent, respectively. The precursor solutions with different Mg concentrations (i.e., 0, 2, 3 and 6 %) were prepared by dissolving an appropriate amount of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into ethanol. Subsequently, DEA and distilled water were slowly added. The resulting mixture was then stirred in ultrasonic bath to form a clear and transparent homogeneous mixture. The precursor was deposited on AlN/Si substrate by the spin-coating method at room temperature with a spinning rate of 3000 rpm for 30 s. The coating process was repeated for few times to obtain films with desired thickness (i.e., approximately 0.5 – 0.6 μm). Next, the coated films were annealed in furnace at 950 °C for 15 minutes. Finally, the coated films were nitrided under ammonia gas ambient at 950 °C for 75 minutes.

Structural properties of the Mg doped GaN thin films were evaluated by High-resolution X-ray diffraction (XRD, PANalytical X'Pert Pro MRD) with a $\text{Cu-K}\alpha_1$ radiation source, ($\lambda = 1.5406 \text{ \AA}$). Field emission scanning electron microscopy (FESEM, NOVA NANOSEM 450) and the energy dispersive X-ray spectroscopy (EDX, attached to the FESEM system) were used to examine the surface morphology and elemental compositions of deposited films, respectively. Raman spectroscopy (Horiba Jobin Yvon HR800UV) with a 514.5 nm argon (Ar) ion laser as the excitation light source was used to investigate the lattice vibrational properties of films. Lastly, Hall effect system (Accent HL5500PC) was used to measure the resistivity and the hole concentration of the deposited films.

3. Results and discussion

Figure 1 shows the XRD patterns of Mg-doped GaN thin films with different Mg concentrations grown on AlN/Si substrate. A sharp and intense diffraction peak located at 34.58° and a weak diffraction peak found at 73.03° are correspond to the wurtzite structure GaN(002) and GaN(004) (JCPDS file No. 05-0792), respectively. Besides that, two diffraction peaks originated from the Si substrate and the AlN layer can be observed at 28.47° and 35.73° , respectively. From Figure 1, it can be seen that the intensity of GaN(002) diffraction peak increases with increasing Mg concentration. This is an indication of the incorporation of the Mg atoms into Ga sites. Further increase the Mg concentration to 6% has caused the degradation of the GaN(002) diffraction peak intensity. In other words, the crystallinity of the 6% was deteriorated. Generally, the incorporation of the Mg atoms into the Ga sites will induce disorder arrangement of the Ga and N atoms due to the difference in the ionic radii of magnesium and gallium [3]. While the degree of the disorder is depends on the Mg concentrations. It worthy to mention here that the degradation of the GaN(002) diffraction peak intensity of sample with 6% Mg concentration may most probably due to its porous surface morphology, as will be shown later.

Further investigation on the structural properties of the deposited was conducted. The crystallite size of deposited GaN thin films were calculated using Scherrer's formula [15]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Here the k is a dimensionless shape factor ($k = 0.94$), the λ is the wavelength of the X-ray ($\lambda = 1.5407\text{\AA}$), the β is the full width at half maximum (FWHM) of the diffraction peak, and the θ is the diffracting angle in radian. The in-plane stress of Mg doped GaN thin films were estimated by [14]:

$$\sigma_{xx} = \frac{\varepsilon_{zz} B}{\nu} \quad (2)$$

where B is the bulk modulus ($B = 200$ GPa) and ν is the Poisson ratio ($\nu = 0.23$) [16]. The ε_{zz} is the relative strain of the c -axis in the sample and can be expressed as:

$$\varepsilon_{zz} = \frac{c - c_0}{c_0} \quad (3)$$

Here, c is the calculated lattice parameter and c_0 is unstrained lattice parameter for wurtzite GaN ($c_0 = 5.185$ Å) [16]. In this work, the GaN(002) diffraction peak information was used for the calculation of the crystallite size and the strain because it has the highest intensity.

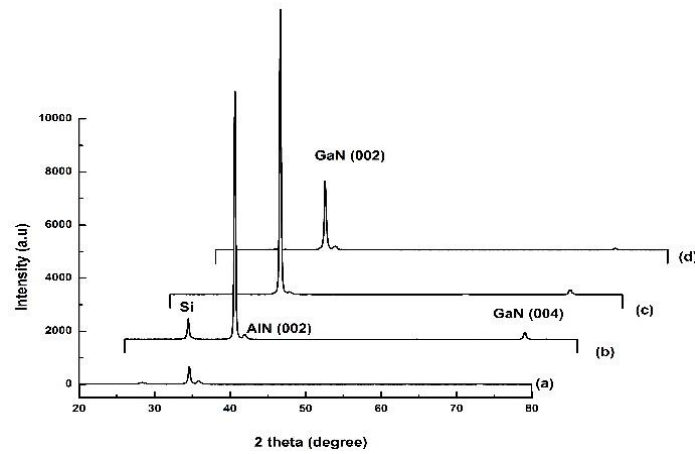


Figure 1. XRD patterns of sol-gel spin coated Mg-doped GaN thin films with different Mg concentrations grown on AlN/ Si: (a) as-grown (0%), (b) 2%, (c) 4 % and (d) 6%.

Table 1 summarizes all the structural parameters extracted from the XRD patterns of the sol-gel spin coated Mg-doped GaN thin films with various Mg dopant concentrations. From Table 1, it was found that films deposited with 2% Mg concentration have the smallest FWHM and biggest crystalline size, however, it has the largest magnitude of the in-plane stress. Note that the positive and negative signs of the in-plane stress indicate the type of tensile and compressive stress, respectively.

TABLE 1. Structural parameters of the sol-gel spin coated Mg-doped GaN thin films with different Mg concentrations extracted from the XRD and Raman results.

Sample	XRD				Raman	
	FWHM	Crystallite size (nm)	Relative Strain ($\times 10^{-4}$)	Lattice constant, c ($\times 10^{-10}$ m)	In-plane Strain (GPa)	Stress (GPa)
0%	0.31	46.72	3.857	5.187	0.34	0.24
2%	0.26	55.70	-9.643	5.180	-0.84	-0.73
4%	0.27	53.64	-6.557	5.182	-0.57	-0.49
6%	0.29	49.94	1.929	5.186	0.17	0.24

Figure 2 shows the FESEM microstructure images of the Mg-doped GaN thin films with different Mg concentrations (0, 2, 4 and 6%). It can be seen that all the deposited films exhibit smooth surface morphology and fine granules were well distributed over the surface of the films. As the Mg concentration increases, it can be observed that the granules size gradually increases and more pits or pores (i.e., black colour dots) were gradually formed on the surface. From Figure 2, it was found that the Mg-doped GaN sample with 2% Mg concentration exhibits the densest and compact surface morphology; while the sample with 6% Mg concentration exhibits porous surface morphology with largest pits/pores.

Table 2 summarizes the elemental compositions of Mg-doped GaN thin films with Mg different concentrations. It can be clearly seen that the Ga and the Mg compositions increase with increasing of Mg doping concentrations. The oxygen is the most commonly found impurity in GaN films grown by sol-gel spin coating approach. Under atmospheric conditions, it was found that the oxidation reaction is more favor as compared to that of the nitridation reaction. Consequently, sol-gel spin coating growth of GaN thin films without oxygen contamination is most challenging task.

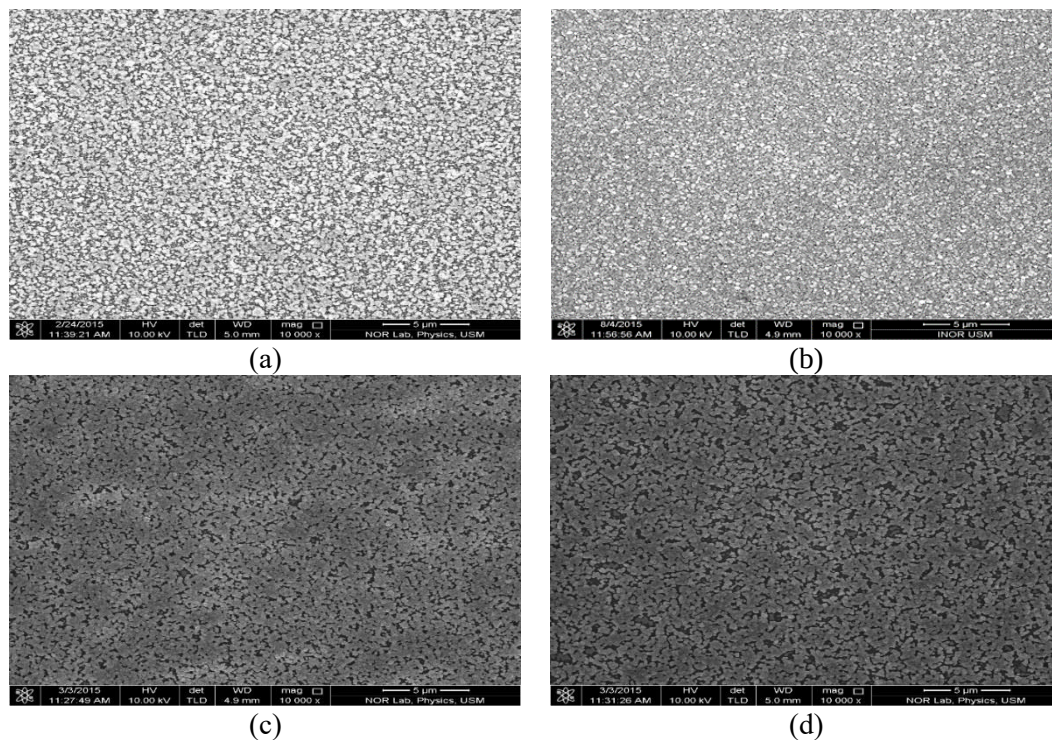


Figure 2. FESEM microstructure images of the Mg-doped GaN thin films with different Mg concentrations: (a) as-grown (0%), (b) 2 %, (c) 4 % and (d) 6%.

TABLE 2. Atomic percentages of Mg-doped GaN thin films grown on AlN/Si substrate.

Sample	N	O	Mg	Al	Si	Ga
As grown	30.08	6.87	-	2.26	38.54	22.25
2%	34.51	2.89	0.35	1.62	37.01	23.62
4%	33.06	2.80	0.63	1.37	27.08	35.06
6%	30.77	4.23	0.92	2.35	41.08	20.66

Figure 3 shows the Raman spectra of Mg-doped GaN thin films with different Mg concentrations deposited on AlN/Si substrate. Under Raman configuration of $z(x,-)\bar{z}$, the allowed Raman active modes for wurtzite structure GaN are the $E_2(\text{high})$ and $A_1(\text{LO})$ phonon modes [17]. From Figure 3, it can be seen that these allowed Raman modes can be detected from all the samples. This result implies

that all the deposited GaN thin films have wurtzite structure, i.e., in agreement with the XRD results as discussed previous. For the as-grown sample (Mg concentration = 0%), the $E_2(\text{high})$ and the $A_1(\text{LO})$ phonon modes were observed at 569 cm^{-1} and 730 cm^{-1} , respectively. As the Mg concentration increases, it was found that the $E_2(\text{high})$ phonon mode was shifted towards lower wavenumber. However, for the Mg concentration of 6%, the $E_2(\text{high})$ phonon mode remains unchanged and the underlying cause still remains unknown.

The $A_1(\text{LO})$ phonon mode for all the samples was shifted towards higher wavenumber with increasing Mg concentration. Besides that, the feature of this $A_1(\text{LO})$ phonon mode became broader and weaker as the Mg concentration increases. The behavior of the $A_1(\text{LO})$ phonon mode as a function of the Mg concentration can be explained by the coupling effects of the longitudinal optical phonon and plasmon. Apart from the Raman active modes, all the Mg-doped samples also exhibit a broad peak centered at 669 cm^{-1} . This broad peak corresponds to the local vibrational mode (LVM) induced by the Mg dopant [18]. The presence of this LVM is a good indication of the incorporation of the Mg atoms into the Ga sites. Note that the strong Raman peak located at 522 cm^{-1} is originated from the Si substrates. It is known that the shift of Raman $E_2(\text{high})$ peak can be directly related to the residual stress in the deposited films. Typically, the $E_2(\text{high})$ peak of an unstressed GaN crystal is located at 568 cm^{-1} [19]. It is reported that the presence of 1 GPa of compressive stress will induce a shift of 4.12 cm^{-1} on the $E_2(\text{high})$ peak [20]. Based on these information, the residual stress in the Mg-doped GaN thin films were estimated and the obtained results were tabulated in Table 1. Overall, it was found that the residual stresses estimated Raman results were comparable to that extracted from the XRD patterns.

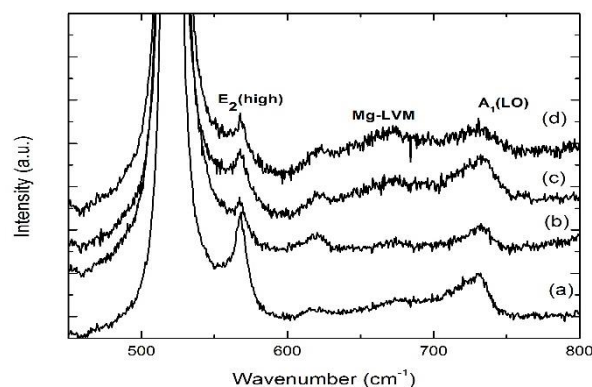


Figure 3. Raman spectra of the Mg-doped GaN thin films deposited on AlN/Si substrate with different Mg concentrations: (a) as-grown (0%), (b) 2%, (c) 4% and (d) 6%.

Figures 4 (a), (b) and (c) show the resistivity, hole concentration and Hall mobility as a function of the Mg concentration of Mg doped GaN thin films on AlN/Si substrate, respectively. As the Mg concentration increases, it was found that the resistivity of the thin films decreases; while the hole concentration and hall mobility of thin films increases. The decrease resistivity with increase in Mg concentration can be attributed due to increase in carrier concentration and also due to increase in mobility, which is seen in the figure. The results indicate that the number of the Mg atoms incorporated into the GaN sites increases with increasing Mg concentration [21].

4. Conclusions

In summary, Mg-doped GaN thin films with different Mg concentrations were successfully grown by low-cost and simple sol-gel spin coating method. The effects of the Mg concentration on characteristics of the deposited films were investigated. All the deposited films exhibit smooth surface morphology and crystalline in wurtzite structure with GaN(002) preferred orientation. The XRD results reveal that the Mg-doped samples have better crystallinity than that the as-grown (undoped) sample. As the Mg concentration increases from 2% to 6%, the crystallite size decreases and the crystalline quality of the films degraded. In addition, pits/pores were gradually formed on the surface

of the films with increasing Mg concentration. The crystalline structure of the deposited films was again confirmed by the Raman measurements where all the allowed Raman active phonon modes of the wurtzite GaN were detected. Apart from that, a feature attributed to LVM was observed at 669 cm^{-1} . The resistivity and hole concentration of the deposited films were determined by Hall effect measurements. The results show that the resistivity of the thin films decreases while the hole concentration and hall mobility of thin films increases with increasing concentration of the Mg. For sample with 6% Mg concentration, the hole concentration around $1.36 \times 10^{19}\text{ cm}^{-3}$ was obtained.

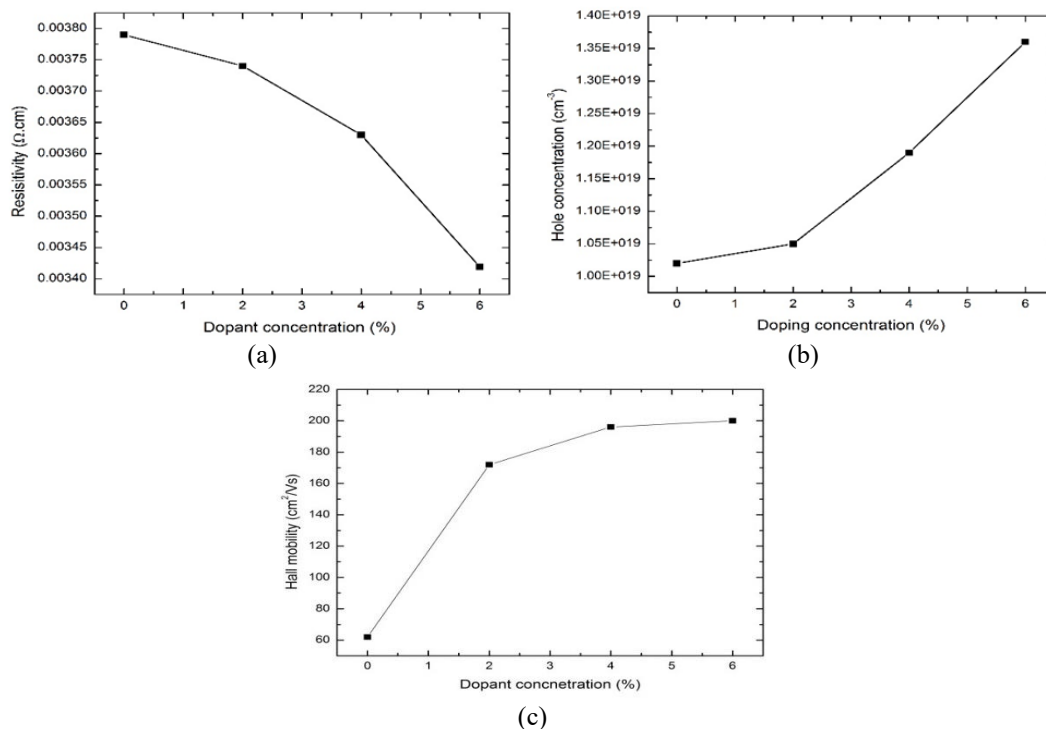


Figure 4. (a) Resistivity versus dopant concentration, (b) Hole concentration versus dopant concentration, and (c) Hall mobility versus dopant concentration of Mg doped GaN thin films on AlN/Si substrate.

5. References

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