Effect of Nitrogen Gas on the Growth of Magnesium Doped Indium Nitride Thin Films via Sol-gel Spin Coating Method

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Abstract. The growth of magnesium doped indium nitride (InN:Mg) thin films via sol-gel spin coating method followed by nitridation process was reported in this paper. In this work, the nitridation processes were carried under ammonia with and without nitrogen ambiences. X-ray diffraction patterns reveal that InN:Mg thin film grown under nitrogen ambiences show formation of InN (101) preferential orientation wurtzite structure. Field emission scanning electron microscopy results show that both deposited films exhibit coalesced island morphology with hexagonal like structure. Energy dispersive X-ray spectroscopy revealed that sample grown under ambient with N₂ gas has lower oxygen atomic percentage and higher ratio of indium to nitrogen. Two allowed Raman modes of wurtzite InN, namely, E₂(High) and A₁(LO) modes, were clearly detected for the deposited films under N₂ gas ambient. Nevertheless, the film grown under the present of N₂ gas shows an additional feature corresponding to ν₄ vibration of the MgN₄ tetrahedron at around 564 cm⁻¹. The presence of this feature indicates that the magnesium acceptors were activated and the compensation of Mg[N₄]⁻(LVM) was occurred. Finally, all the results suggest that present of N₂ gas during nitridation process will induce better grow of InN:Mg thin films.

1. Introduction

In 1986, Tansley and Foley achieved very high electron mobility and high crystalline quality n-type indium nitride (InN) thin film grow by reactive sputtering at low temperature [1]. Since then, the InN-based electronic and light emitting devices have made a great development. However, the poor hole mobility and electrical conductivity of p-type InN remained unsolved and continue to hinder the development of InN-based electronic devices.

Up to date, magnesium (Mg) is a common acceptor impurity for p-type InN and most of the studies used molecular beam epitaxy (MBE) [2] and metal organic vapor phase epitaxy (MOVPE) techniques [3] to grow Mg doped InN. However, these techniques require the ultrahigh vacuum system, high maintenance cost, as well as complicated in setup and procedures. Therefore, the cost spent in the equipment and maintenance can be noticed. In present work, the sol-gel spin coating could be an alternative method to grow Mg-doped InN. In general, this technique is relatively simpler, cheaper, safer, and scalable as compared with the conventional techniques as mentioned previously. Recently, Fong et al. (2015) and Lee et al. (2017) have successfully demonstrated the growth of GaN and InN thin films by means of this technique [4][5].
Moreover, the growth of high quality p-type InN thin films is challenging due to the difficulties in compensating Mg in InN [6] and passivation effect of hydrogen toward magnesium [7]. There are two mechanisms which can cause the passivation of Mg acceptors: one is self-compensation caused by the formation of a deep donor, $\text{Mg}_{\text{In}}-\text{V}_N$, namely a nearest-neighbor association between Mg acceptor and nitrogen vacancy. The nitrogen vacancy ($\text{V}_N$) which functions as a donor for InN, thus the $\text{V}_N$ and Mg acceptors, which are oppositely charged tend to attract each other to form $\text{Mg}_{\text{In}}-\text{V}_N$. The other mechanism is the hydrogen passivation effect which results in electrically inactive Mg–H complex defects in InN during deposition. The present of too much of Mg-H complex can not only degrade the crystalline quality but also affect the electrical properties of the deposited thin film [8]. Nitrogen (N$_2$) is a common gas for Mg doped GaN thermal annealing activation, and it has been considered to be capable of compensating nitrogen vacancies during annealing. Therefore, similar approach can be applied to InN:Mg thin films. Nevertheless, sol–gel spin coating growth of Mg doped InN thin films with N$_2$ thermal treatment remains unexplored and depth investigation is absolutely necessary.

2. Experimental Detail
Commercially available aluminum nitride on silicon [AlN/Si(111)] templates was used. The substrates were cleaned through immersion into the chemical solution of hydrofluoric acid and distilled water (with a ratio of 1:50) for 20 s to remove the native oxide layer. The substrates were then rinsed with distilled water, dried with nitrogen gas, and subjected to plasma treatment to enhance the wetting process. Indium nitrate hydrate powder (99.99% purity) and magnesium chloride 6-hydrate (98% purity) powder were dissolved in ethanol (99.7% purity) and subjected to the ultrasonically agitation. The prepared precursor was dropped onto the substrates and rotated for 25 s at 2000 rpm by using spin coater. The spin coating process was repeated for several times until the desired thickness was achieved. Annealing was performed at 300°C for 2 hours to refine and dry the deposited films. Finally, nitridation was performed in a furnace system under ammonia and nitrogen or without nitrogen atmosphere for 45 minutes with a constant flow rate of 400 and 60 sccm, respectively, to transform the deposited film into InN polycrystalline. The furnace was set at 600°C to break ammonia bonds and to generate active nitrogen radicals for chemical reactions. The samples were then cooled to room temperature.

The crystallite quality, crystallographic structure, and growth orientation of the deposited films were investigated through high-resolution X-ray diffraction spectroscopy (HR-XRD, PANalytical X'Pert PRO MRD) analysis with CuK$_{\alpha 1}$ radiation source of 0.154 nm. Field-emission scanning electron microscopy (FESEM, NOVA NANOSEM 450) was used to study the surface morphologies of the deposited films. Furthermore, energy dispersive X-ray spectroscopy (EDX) was used to analyze the chemical composition of the deposited films. The lattice vibrational properties of the films were evaluated through Raman spectroscopy (Horiba Jobin Yvon HR800UV) with a 514.5 nm Ar ion laser as excitation light source.

3. Results and discussion
The XRD patterns are shown in Figure 1. The polycrystalline structure can be clearly observed for InN: Mg film grown on both samples. Three dominant diffraction peaks can be observed at 2$\theta$ = 29.1°, 2$\theta$ = 31.1° and 2$\theta$ = 33.1° in both samples. All the diffraction peaks were ascribed to the formation of wurtzite structure InN (JCPDS file ID 00-050-1239). All the samples somewhat preferred orientation along the axis has been observed similar to the reported work by Lee et al. (2017) [5], Chen and Kuo (2012) [9] and Mann et al. (2008) [10]. Nevertheless, the results of 0-2$\theta$ angular scans for InN: Mg film that grows under N$_2$ gas ambient show highest InN (101) peak intensity with smallest FWHM which indicating a strong orientation and better crystallinity along the axis (refer Table 1). This result suggests that nitrogen addition during the nitridation process favors the preferential growth orientation of InN crystallites along (101) direction. To calculate the average crystallite size of the samples, the Debye-Scherrer equation was used,
where \( D = \) crystalline size, \( K = \) shape factor (0.94), and \( \lambda = \) wavelength of CuK\( \alpha \) radiation. The values of crystallite sizes for with and without N\(_2\) gas samples for InN (101) diffraction peak were found to be around 51.72 and 39.14 nm, respectively (refer Table 1). It is observed that the InN:Mg grown in N\(_2\) gas ambient has the largest crystallite growth compare with absent N\(_2\) gas condition. This indicates that N\(_2\) gas has successfully activating the Mg atoms in InN and increase the crystallite growth of InN [11]. Furthermore, lattice parameter \( a \) and \( c \) values for the films were calculated using following equation,

\[
\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}
\]

here \( d \) is the inter-planar distance and \( h, k, l \) are the Miller Indices. It was also found that lattice parameters \( (a \) and \( c) \) increase as the InN:Mg thin film grown under N\(_2\) gas condition, as shown in Table 1. From table 1, it can be clearly see that the lattice parameters \( a \) and \( c \) values for Mg doped InN were smaller than the undoped InN \( (a = 3.55 \, \text{Å}, c = 5.71 \, \text{Å}) \) as reported by Amirhoseiny et al. [12]. This phenomenon can be correlated to the compensation of Mg into InN. Since the ionic radius of Mg\(^{2+}\) (0.065 nm) is smaller than In (0.080 nm) and N (0.146 nm) the decreasing of the lattice parameter implies the substitution of Mg into In and N lattice site [13]. Hence, the calculated lattice constant smaller than that of undoped InN film, confirming that Mg was introduced into the film and compensated In or N lattice site. On the other hand, the \( a \) and \( c \) values for InN:Mg grown without N\(_2\) gas condition was found smaller than with N\(_2\) gas ambient. Mg\(^{2+}\) and H\(^+\) has ionic radius of 0.065 nm and 0.012 nm, respectively. When there is no assistance from N\(_2\) gas, the substitution of H atom into In and N lattice site occurred and passivation Mg-H or Mg-O complexes formed which cause the decreasing of lattice parameter.
Figure 1: XRD patterns for InN:Mg thin films grow (a) without N₂ gas and (b) with N₂ gas ambient.

Table 1. Full–width at half maximum (FWHM) of InN (101) diffraction peak, crystallite size, lattice constant for InN:Mg thin films grown without N₂ gas and with N₂ gas ambient.

| Sample       | FWHM (°) | Crystallite size, (nm) | Lattice Parameter (Å) | Reported Lattice Parameter (Å) |
|--------------|----------|------------------------|-----------------------|-------------------------------|
| With N₂ gas  | 0.28     | 51.72                  | \(a=3.5475\)          | \(a=3.55\)                   |
|              |          |                       | \(c=5.6680\)          |                               |
| Without N₂ gas | 0.37    | 39.14                  | \(a=3.5475\)          | \(c=5.6533\)                 |

Figure 2 shows surface morphology FESEM images of the InN:Mg thin films grown on AlN/ Si(111) substrate captured with 100kx magnifications. It can be seen that the crystallite size increases after grown under N₂ gas ambient which is consistent with the results indicated in Table 1. Moreover, the images show that both samples were shaped in nearly hexagonal structure; while for sample grown without N₂ gas some flat and plane surface still observed. The absent of N₂ gas might lead to inactivated the Mg atoms in InN, which impede the crystallite growth rate. On the other hand, most of the crystals were form hexagonal structure when grow under of N₂ gas ambient.
EDX analysis was conducted on the Mg doped InN thin films. The quantitative amounts of each element as measured with the EDX are shown in Figure 3. From the EDX measurements, it was noticed that the atomic percentage for In, N and Mg atoms were detected. Similar results were obtained from different areas for several times. It can be clearly see that the atomic percentage ratio of indium to nitrogen was almost 1:1 for both samples. This observation confirmed the formation of InN. Other than that, the sample with N2 gas showed the highest percentage ratio of indium to nitrogen. This indicated that N2 gas able to promote formation of InN. Moreover, there were existed of 6% of oxygen (O) in the sample grown under N2 gas ambient, this might be due to oxygen contaminated during cooling sample at atmosphere ambient. On the other hand, for the sample grown without N2 gas showed higher O atomic percentage. The chemical reaction during the nitridation process are as below [5][14]:

\[
\begin{align*}
2\text{NH}_3 & \rightarrow \text{N}_2 + 3\text{H}_2(g) \\
\text{NH}_3(g) & \rightarrow \text{H} + \text{NH}_2 \\
\text{In}_2\text{O}_3(s) + 2\text{NH}_3(g) & \rightarrow 2\text{InN}_{(g,s)} + 3\text{H}_2\text{O}(g)
\end{align*}
\]

In-O broken and the N atom tend to react with In to form InN during the nitridation process. Consequently, the released O atom tends to combine with H atom to form H2O as a side product. Without the N2 gas during nitridation process, the excessive O atoms tend to stay in furnace and might diffuse into the thin films again which cause the increase of the O atomic percentage in EDX measurement. Therefore, addition N2 gas during the growth of InN:Mg thin films act as a role to purge out the side product, excessive O atoms and impurities in furnace.
Figure 3. EDX spectra for InN:Mg thin films grown at without N2 gas and with N2 gas ambient.

Figure 5 shows the Raman spectra of Mg doped InN thin films with In:Mg thin films grown on AlN/Si(111) template. The Raman measurements were conducted under backscattering geometry \( z(x, x)z \) configuration, where the \( z \)-axis is parallel to the \( c \)-axis of InN. From the Raman results, the \( E_2 \) (high) and \( A_1 \) (LO) modes of wurtzite structure InN were observed for the sample grown with N2 gas which located at 495 cm\(^{-1}\) and 576 cm\(^{-1}\), respectively. For the sample grown without N2 gas, only \( A_1 \) (LO) modes was observed. This is mainly due to low crystalline quality of the deposited InN films. For Mg-doped InN thin film grown under N2 gas ambient, a peak around 564 cm\(^{-1}\) was detected. According to Davydov et al. (2008) [15], this mode can be assigned to the local vibration mode (LVM) of Mg-N. To further verify the origin of this peak, the theoretical LVM frequency was calculated by equation as shown in below [13],

\[
\frac{\omega_{InN}}{\omega_{LOM}} = \sqrt{\frac{\mu_{LVM}}{\mu_{InN}}}
\]

The reduced mass of LVM and InN (\( \mu_{LVM} \) and \( \mu_{InN} \)) were calculated using following equation,

\[
\mu_{LVM} = \frac{m_{Mg} m_{N}}{m_{Mg} + m_{N}}
\]

\[
\mu_{InN} = \frac{m_{In} m_{N}}{m_{In} + m_{N}}
\]

where the \( m_{Mg} \) is the atomic mass of Mg (24.305 u), \( m_{N} \) is the atomic mass of N (14.0067 u) and \( m_{In} \) is the atomic mass of In (114.818 u). Here, the Mg is assumed to be incorporated on In lattice site and the \( \omega_{InN} = \omega[E_1(LO)] = 477 \text{ cm}^{-1} \) [16]. The calculated theoretical value of the LVM for Mg-N is 565 cm\(^{-1}\), which is in good agreement with the experimentally found value of 564 cm\(^{-1}\). These results imply that the Mg atoms were successfully incorporated into the InN. This might be due to the present of N2 gas has activated the Mg dopant in the InN, which can be seen in figure below [11].
4. Conclusion
In this work, Mg-doped InN (In:Mg) thin films were deposited on AlN/Si(111) substrates by sol-gel spin coating method in combination with the nitridation process in different N2 gas ambient. The XRD results revealed the formation of wurtzite InN:Mg thin films for both samples. The growth of the InN:Mg thin film with additional nitrogen carrier gas resulted smallest FWHM and highest intensity for the InN (101) diffraction peak. FESEM results revealed that the film grown under N2 gas ambient exhibits largest coalesced island morphology with hexagonal symmetry. The EDX results showed that the InN:Mg film grown under N2 gas ambient formed with almost 1:1 atomic percentage ratio of indium to nitrogen and possesses small amount of oxygen atomic percentages. Raman results revealed Mg–N mode was detected which indicting the existed of compensation between Mg–InN. In conclusion, further works are needed to improve the crystalline quality of the Mg-doped InN thin films as well as to investigate its electrical properties. Nevertheless, the results obtained here are vital for researcher to explore the sol-gel spin coating technique for the growth of InN:Mg.

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