Effect of varying thermal annealing temperatures on the surface and electrical properties of Mg-doped GaN

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Abstract. Gallium nitride (GaN)-based light emitting diodes (LEDs) have been widely used to produce blue light that, with phosphor, is converted into white light for everyday applications. Despite its high efficiency, the performance of GaN-based LEDs is limited by the low electrical conductivity of magnesium (Mg)-doped GaN due to the high activation energy of Mg (140 – 200 meV) as well as the presence of magnesium-hydride (Mg-H) complex, which may passivate Mg as an acceptor. In this study, the efficacy of thermal annealing treatment at temperatures in the range of 550 - 850°C was investigated to activate metal-organic chemical vapor deposition (MOCVD) grown Mg-doped GaN. Changes in the roughness and surface morphology was observed between the varied annealing temperatures by atomic force microscopy (AFM) while X-ray diffraction (XRD) data acts as supporting information for structural quality. Hall effect characterization was conducted to determine electrical properties of the annealed samples. In this study, a correlation between the resistivity and surface roughness trends was observed through the acquisition of an insight into the lattice distortion affecting the material conductivity that occurred specifically at temperatures above 750 °C.

1. Introduction

The Magnesium (Mg) as a dopant to increase the presence of holes in gallium nitride (GaN) has significantly defined the development of highly efficient GaN based light emitting diodes (LEDs) for important blue light emission. In current day, white light is produced from advanced blue GaN LEDs using phosphor converters. Applications of the solid-state light emission device are well established in the use of automotive headlamps, streetlights and general lighting, wherein an effective reduction of power consumption has been shown when compared to the previous use of compact fluorescent lamp and incandescent bulbs. However, it was evident in the past studies that initial attempts of obtaining highly efficient blue LED from GaN materials were difficult to pursue due to the unattainability of p-type GaN [1].

Before the advent of Mg to increase hole carriers in GaN, researchers attempted to dope GaN with zinc (Zn) as this was commonly used as an acceptor for p-type gallium arsenide phosphide (GaAsP) and gallium phosphide (GaP), but successful p-type GaN was not achieved [1]. It was not until the work of Amano and Nakamura et. al that successful p-type GaN was demonstrated from using Mg as a dopant instead of Zn due...
to the lower activation energy of Mg and the adoption of post thermal treatment method to increase hole concentration in the samples [2, 3]. Based on the study by Lyons et al, most acceptors for GaN exhibited deep level acceptor characteristics including Mg. However, their analysis showed that Mg characteristically exhibited itself as an accidental shallow acceptor for GaN through density and hybrid functional theory, which would make it possible to introduce enough holes in GaN compared to most acceptors [4].

Several methods have been utilized to grow Mg-doped GaN, with the most common being by metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). Through MOCVD, as-grown Mg-doped GaN would remain resistive until being thermally treated due to hydrogen (H) passivation by the pre-reactions involving ammonia. However, a few studies have described the advantage of hydrogen passivation as H itself could become a co-dopant in the magnesium-hydride (Mg-H) complex [5]. The formation of Mg-H complex in GaN denotes H as the most dominant donor impurity, which would compensate other dominant defects such as nitrogen vacancies while also increasing the presence of Mg in the material [5, 6]. Since Mg-H has a low binding energy of approximately 0.8 eV, H can easily be dissociated and removed through thermal treatment which will then ionize the Mg [6]. Through thermal treatment, optimized conditions are necessary to not induce structural damage and increase compensating defects [6, 7].

Few thermal annealing approaches have been adopted to activate Mg-doped GaN such as rapid thermal annealing [8], conventional tube furnace annealing [9], two or multiple-step annealing [10, 11], annealing in mixed ambient gases (O2, Ar, N2) [12], annealing with metal catalysts [13] or combinations of said methods. Although the results of these methods from the above citations have given substantial information on the optimum annealing conditions between optical, structural and electrical characteristics of the activated Mg-doped GaN, not much detail was emphasized on the surface quality characterization in relation to the electrical results, which are important to consider when optimizing the annealing conditions suitable for the material. Therefore, in this work, systematic investigation of the surface quality characterization was carried out on the MOCVD grown Mg-doped GaN subjected to various thermal annealing temperatures, ranging from 550 °C to 850 °C using atomic force microscopy (AFM) in congruence with electrical property analysis through Hall effect. This study gauged the most suitable annealing temperature for the application of LEDs based on the AFM and Hall effect results.

2. Experimental Procedures

The sample in this experiment was grown by a Taiyo Nippon Sanso MOCVD reactor model SR4000-HT which utilizes a tri-layer gas injection nozzle and horizontal laminar flow configuration to effectively suppress pre reactions in the gas phase [14]. This reactor features a susceptor with 3 × 2” diameter wafer pockets. Precursors used during the experiment’s heterostructure growth were Ammonia (NH3), Trimethylgallium (TMG), and Bis-cyclopentadienyl magnesium (Cp2Mg). The heterostructure was grown at atmospheric pressure, 100 kPa, on a flat sapphire substrate with a miscut 0.1 deg off the m-plane and thickness of approximately 0.430 mm. A low temperature GaN nucleation or buffer layer at 520 °C was grown on the sapphire substrate followed by a high temperature (HT) GaN growths at 1125 °C and 1150 °C. The first and second HT GaN layers were about 800 nm and 2.4 μm respectively. The final layer which was the Mg doped GaN layer with Cp2Mg flow of 0.423 μmol/min was about 200 nm thick.

The 2” grown wafer was then cut into several sample pieces for post annealing treatments at different temperatures. The annealing procedure was demonstrated in a conventional furnace. The time of anneal was fixed at 15 min with ambient air. In this work, the samples were annealed in different temperatures of 550 °C, 650 °C, 750 °C and 850 °C. Surface quality of the samples was characterized by atomic force microscopy (AFM) (Model: Dimension EDGE, BRUKER) to investigate surface morphology and root-mean-square (RMS) roughness of the annealed samples. The structural properties were determined by X-ray diffraction (XRD) (Model; PANanalytical X’Pert Pro MRD) using Cu-Kα1 radiation source (λ=1.5406
Å). Electrical properties of the samples were characterized by Hall effect in room temperature (RT) to analyze resistivity, carrier concentration and carrier mobility of the samples. Hall effect samples were cut into approximately 6 x 6 mm² squares where indium was deposited on the four corners of the square, following the Van Der Pauw sample preparation requirement. The samples were then annealed at 400 °C for 15 min after metal contact to obtain better incorporation of indium on the surface. Current-Voltage (I-V) characteristics were measured to evaluate the Schottky or ohmic characteristics of the metal to semiconductor interface.

3. Results and Discussion

Figure 1 shows the AFM scans of each sample with their respective height profiles while Figure 4 displays the RMS roughness of the samples. Differences in the topography and roughness with respect to the annealing temperature were observed. The non-annealed sample had a roughness value of 0.892 nm with raised micro bumps that featured lines, indicating step flow growth. This value was similar to the AFM roughness shown by Qhalid et. al at 0.86 nm which was a higher value than their undoped GaN at 0.3055 nm [15]. The roughness value, which may be tied to the appearance of the micro-bumps, could also be caused by the effects of Mg doping into the GaN material which at increasing levels may form or progress into forming pyramidal hillocks or craters on the surface of the material [15, 16]. The content of Mg in this sample based on the Cp2Mg flow rate of 0.423 μmol/min was approximated to be 6×10¹⁹ atoms/cm³ based on data extrapolation from previous secondary ion mass spectroscopy (SIMS) Mg doping analysis that was not shown in this paper. The visible appearance of pyramids in some AFM scans might indicate that the Mg concentration level in this study was mid-range or higher, however, this study observed regions without the hillocks and observed the micro-bump features [16]. Figure 2 shows the XRD patterns of each sample where the main consistent peaks found were GaN (002) and GaN (004) which agrees well with wurtzite GaN diffraction peaks referred in database (JCPDS file No. 05-0792) [Sekaran]. However, distinguishable diffraction peak of GaN (100) was observed in each sample which support the indication of Mg’s disruptive role in the crystallinity of GaN as GaN (100) and other peaks are more prominently found in polycrystalline GaN [18].

The roughness value was observed to slightly degrade and showed bigger bump size when annealed at 550 °C in comparison to the non-annealed sample. At 650 °C, the bumps appeared more thread-like, which could indicate coalescence between the micro-bumps and the sample exhibited roughness improvement from the non-annealed sample with an RMS value of 0.699 nm. According to Guha et. al, Raman spectroscopy results on Mg-doped GaN annealed at 650 °C demonstrated that the material strain inherited by lattice mismatch from the substrate, the Mg dopant itself, or point defects in Mg doped GaN was more relaxed at this temperature [17]. The study also noted that an increase in temperature to 750 °C increased the strain again causing lattice distortion, which may explain the increase in RMS value compared to annealing temperature at 650 °C. Rana et al. also described annealing temperatures between 700 °C – 800 °C as the start of lattice disruption where nitrogen would start to evaporate while gallium was displaced from their lattice sites [7]. At 850 °C, the AFM scan showed no bump or threadlike formation but specks with consistently spiky height profile, which would indicate further lattice distortion caused by increasing nitrogen evaporation as mentioned previously. The evaporation of nitrogen is an important factor to discuss with regards to the electrical properties of the samples, as it may give rise to nitrogen vacancies and compensate the Mg dopants [6].
Figure 1. 10 x 10 μm 2D AFM scanned images of a) non-annealed sample, b) annealed sample at 550 °C, c) at 650 °C, d) at 750 °C, and e) at 850 °C with their respective height profiles corresponding to the white lines in the 2D images.
Further investigation on possible lattice distortion of annealed samples were evaluated through XRD analysis on the crystalline size, \( D \), derived from the FWHM of the GaN (002) diffraction peaks through Scherer’s equation [19].

\[
D = \frac{0.95 \lambda}{\beta \cos \theta}
\]  

(1)

The wavelength of the X-ray source, \( \lambda \), 0.15406 nm and \( \beta \) is the FWHM value in radians. The in plane lattice strain was also determined by equation (2) where \( c \) is the calculated lattice constant from samples and \( c^0 \) is the lattice constant of unstrained GaN [20].

\[
\varepsilon = \frac{c - c^0}{c^0}
\]  

(2)

Figure 3 displays the calculated value and it was observed that the crystallite size is shown to increase with increase in annealing temperature. This supports the above analysis from AFM of the occurrence of coalescence between the lattice structures with increase in temperature. However the calculation for strain shows very small differences between the samples with the highest strain value being at annealing temperature 650 °C which disagrees with the notion from Guha et. Al. [17] With the small values of strain that may allow inaccuracy perhaps future work would incorporate other methods of evaluating strain such as through reciprocal space mapping (RSM) and Williamson Hall method [21].

![Figure 2. XRD pattern of a) non-annealed sample and thermally annealed samples at temperatures b) 550 °C, c) 650 °C, d) 750 °C and e) 850 °C.](image)
Figure 3. Calculated relative strain ($\varepsilon$) and crystallite size D for thermally annealed samples.

Figure 4. RMS roughness values of non-annealed sample and annealed samples.

Figure 5. Resistivity of annealed samples as shown by Hall effect.

With regards to the Hall measurement, the resistivity measurements in Figure 5 of this study indicated that the lowest resistivity was 0.9152 Ohm-cm by temperature anneal at 650 °C, however, at 550 °C the value was slightly higher at 1.0373 Ohm-cm. For the temperatures higher than 650 °C in this study, the resistivity values were significantly higher, which presented the resistivity trend to be similar with the roughness trend obtained from AFM as seen in Figure 4. This could indicate a correlation between the lattice distortion explained previously and the resistivity in the material. The characterization within this analysis does not present sufficient information on the exact lattice distortion induced in the material, although it is plausible to assume that the distortion may give rise to certain defects which can be characterized through photoluminescence (PL), Raman spectroscopy and RSM.
Results demonstrated by RT Hall effect only gave readings on the annealed samples and no results could be taken from the non-annealed sample. The attempt failures were due to the obvious Schottky or diode I-V characteristic in Figure 7 for the non-annealed sample with deposited indium contacts. In Figure 6, the higher hole concentration values were obtained from annealing temperatures 550 °C and 650 °C, with the value at 550 °C being slightly higher than the value 650 °C at 1.195 x 10^{18} \text{ cm}^{-3}. The annealing temperatures after 650 °C showed a decrease in hole concentration which may be explained by the lattice quality degradation due to the previously mentioned suspected increase in nitrogen evaporation with increasing temperature [7]. Although the increase in temperatures was understood to increase the dissociation of hydrogen from Mg as shown in a study by Nakagawa et. al, a trade-off occurs as the accompanying increase in nitrogen dissociation gives rise to nitrogen vacancies which compensates the ionized Mg [22]. In optimizing a suitable temperature for an LED Mg-doped GaN activation, it is important to weigh mobility along-side the hole concentration as higher mobility of carriers will ensure better hole injection efficiency to aid radiative recombination and produce photons. Based on Figure 6, annealing temperature at 650 °C was the most suitable pick for an LED application as although the resistivity and hole concentration value was quite similar to that obtained at 550 °C, the mobility value was almost twice as high.

It could be observed from the I-V curves shown in Figure 7 that, although most of the samples were ohmic with an exception to the sample annealed at 850 °C, the slope of the linear plots were shown to decrease with increasing temperature, indicating an increase in the resistance of the semiconductor to metal interface. This trend agreed well with the trend of hole concentration as a higher hole concentration reduces the barrier width between the metal and semiconductor interface which induces carrier tunneling and causes less resistance [23]. The acquisition of Schottky characteristic for the sample annealed at 850°C, as being shown via the I-V curve would make the Hall effect measurement to be not accurate. However, the values were also in agreement to the conclusion between the I-V curve and carrier concentration as well as resistivity of the material, which makes them valid to an extent.

4. Conclusion
In annealing MOCVD grown Mg-doped GaN for the purpose of dissociating and removing H from the material, careful consideration must be taken with regards to the chosen annealing temperature. The surface roughness and morphology could offer a good indication of the material’s quality when assessing the effects
of temperature. The impact was especially obvious at higher temperatures for the Mg-doped GaN as evidently shown for the sample subjected to annealing temperature of 850 °C. This study identified annealing temperature of 650 °C to be the most suitable temperature to activate Mg-doped GaN as the lower surface roughness and sample morphology most likely indicated better lattice arrangement while values from Hall effect result from this annealing temperature showcased the best electrical properties specifically for the use of LEDs. Higher temperatures such as 750 °C and 850 °C would cause increased lattice distortion through a possible increase of strain or defects and would provide poor electrical characteristics due to self-compensation by deep donor defects such as nitrogen vacancies. Although the latter may hold true in terms of the trend in temperature variation, this study did not conclude similar effects of temperature of the same values in different ambient gas changes as different ambient gases would present different thermodynamics and affect the samples differently. Furthermore, this temperature was conducted on a certain Mg doping level which would affect the lattice structure differently than other doping levels. Extended studies on temperature effects on different doping levels would be useful for advanced p-type cladding in LED structures for the purpose of increasing hole injection efficiency.

Acknowledgement
The authors would like to acknowledge the support given by OSRAM Opto Semiconductors (Malaysia) Sdn. Bhd., Malaysia Ministry of Education (MOE) under LRGS grant (Wide Band Gap Semiconductor, Project No: 203/CINOR/6720013), Collaborative Research in Engineering, Science & Technology Center (CREST) and Universiti Sains Malaysia for their support in this research.

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