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Modulation of structural, electrical, optical and thermoelectric properties of MOCVD grown GdN thin films by nitrogen environment annealing process

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ABSTRACT

This manuscript demonstrated the effect of nitrogen annealing on the structural, optical, electrical and thermoelectric properties of MOCVD grown GdN thin films. After growth a representative sample was cut into pieces and annealed in nitrogen environment at various temperatures ranging from 300 to 500 °C. XRD data verified the formation of hexagonal structure of GdN with preferred orientation along C-axis. It was also observed that the crystalline size and intensity of (200) plane increased as the annealing temperature increased. This behavior indicates the improvement in the crystal structure because the nitrogen vacancy related defects compensated by the incoming nitrogen atoms during annealing. Raman spectroscopy and UV/Vis spectroscopy data also strengthened the XRD data that crystal structure improved significantly with annealing in nitrogen environment. Hall data demonstrated that carrier concentration of samples decreased by annealing due to decrease of nitrogen vacancy related donor defects. Room temperature Seebeck data showed that the values of Seebeck coefficient and power factor were found to be decreased with annealing temperature. The decreased in Seebeck coefficient is understandable because the conductivity of samples was found to be decreased with annealing temperature.

1. Introduction

GdN is supposed to be potential candidate of future electronic and optoelectronic applications because it has some amazing properties. It has wide and direct band gap of 3.4 eV therefore it can find applications in high frequency and high power optoelectronic devices [1,2]. In order to utilize GdN in such devices, it has fundamental importance to grow stoichemetric GdN [3,4]. Because non-stoichemetric GdN has various intrinsic defects such as nitrogen vacancy and Gd interstitials [4–6]. These intrinsic donor defects degrade the crystal structure therefore hinder the utilization of this material in commercial devices. Various techniques have been utilized in the literature to grow defect free GdN. For example F. Natali et al optimized the growth parameters in MBE chamber to control the structural, optical and electrical properties [7]. P. Wachter et al calculated various physical parameters such as electrical conductivity and dielectric constant of stoichemetric single crystal GdN [8]. B. M Ludbrook et al studied GdN thin films having well-oriented crystallite up to 30 nm grown on Zirconium using plasma-assisted pulsed laser deposition [9]. F. Natali et al have AlN buffer layer to grow defect free GdN on Si substrate and they have assessed the crystal quality using various characterization

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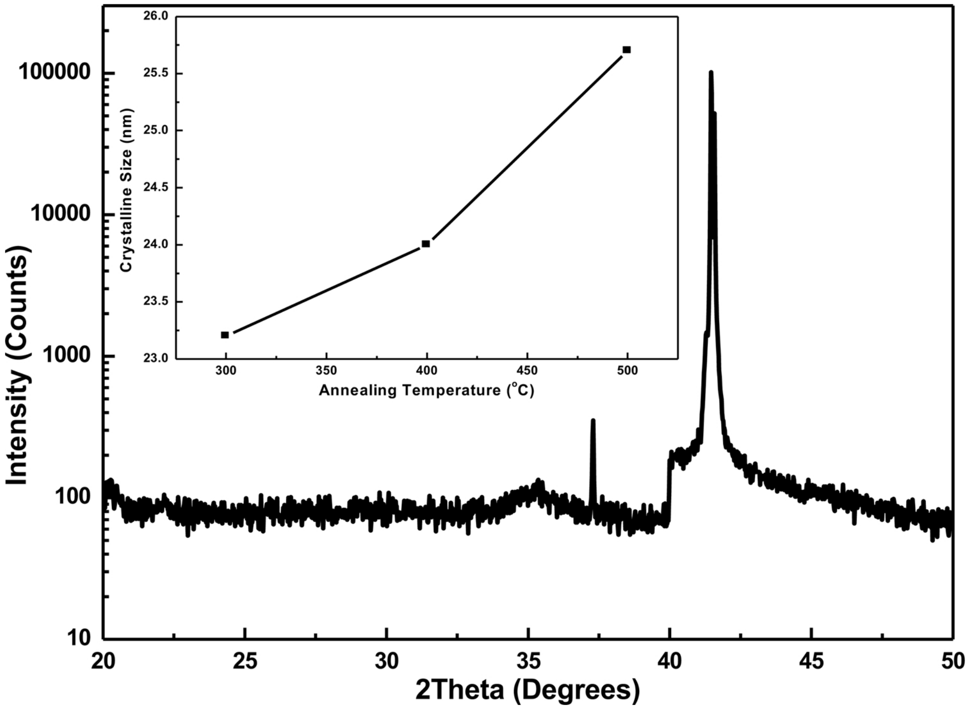

Fig. 1. Representative XRD pattern of as grown GdN thin film synthesized by MOCVD. Inset of Fig. 1 demonstrated the effect of annealing temperature on the crystalline size of GdN thin films.

techniques [10]. But the issue of nitrogen vacancy is still not comprehended even using state of the art growth techniques. Therefore, a detailed study is still needed to probe this issue in order to get benefits from this amazing material.

In this paper, we have annealed MOCVD grown GdN in nitrogen environment to fill the nitrogen vacancy donor defects. The grown samples were annealed at various temperatures (300–500 ^{0}C) in nitrogen environment using flow rate of 140 sccm. The effect of nitrogen annealing on the structural, optical, electrical and thermoelectric properties was investigated using various characterization techniques such as XRD, FTIR, Raman spectroscopy, UV/Vis spectroscopy, Hall measurements and Seebeck measurements.

2. Experimental procedure

The samples used in this study were grown on sapphire substrate by MOCVD by our collaborators at UNCC, USA.

After the growth, sample was cut into small pieces of dimension 10 x 10 cm. The annealing was performed in programmable furnace at different temperatures from 300 to 500 °C with a step of 100 °C in nitrogen environment for one hour. The flow of nitrogen gas was kept constant (140 sccm) for all samples. The structure of grown GdN was confirmed with the help of X-Ray Diffraction (Brucker). The carrier concentration, mobility and resistivity of samples were measured using Hall Effect Ecopia 3000. The Seebeck measurements were performed by home made Seebeck system and Raman spectroscopy measurements were performed using Dangwoo optron system.

3. Results and discussion

Fig. 1 represents the XRD data of as grown GdN thin films grown by MOCVD technique. We have observed two XRD peaks at 42.2^{0} and 36.1^{0} which are related to the Sapphire and (002) plane of GdN [11–13]. Therefore, XRD data confirmed the hexagonal structure of annealed films with preferred orientation along c-axis. The strongest XRD peak is due to sapphire substrate and GdN peak is very weak which is due the fact that the thickness of grown GdN is very small (100 nm), therefore strongest single from the substrate is expected. It is also observed the intensity of GdN (002) plane is found to be increased as the annealing temperature increased from 300 to 500 ^{0}C in nitrogen environment (not shown here). The increase in intensity and decrease of FWHM of (002) plane suggested that the crystal structure of grown GdN is improved with annealing temperature. This behavior is related to the fact that nitrogen vacancies filled by the incoming nitrogen during annealing process and resulted in the improvement of crystal structure.

The graph in Fig. 1(inset) demonstrated the effect of annealing temperature on the crystalline size of MOCVD grown GdN thin films annealed at various temperatures ranging 300–500 °C in nitrogen environment for one hour. The crystalline size was calculated using Scherrer formula as given below [14];

$$P = 1.54\ A^{o}/\beta \mathrm{Cos}\theta$$

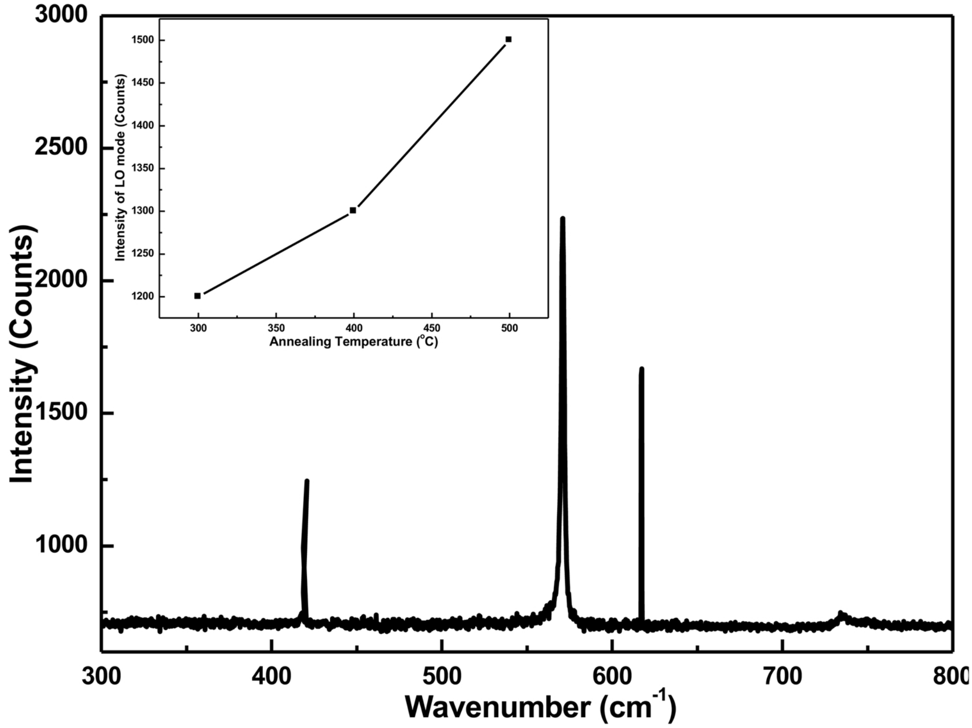

Fig. 2. Raman spectra of representative GdN thin film grown by MOCVD growth technique. Inset showed the effect of annealing temperature on the peak intensity of Raman Lo mode .

Where P is crystalline size, β is full width half maximum of GdN (200) plane and θ is the angle. It was observed that crystalline size was increased from 23.2 nm to 25.6 nm as the annealing temperature increased from 300 to 500 °C.

Raman spectroscopy graph consisted of four peaks at 420, 560, 625 and 748 cm^{-1} shown in Fig. 2. The peak at 420 cm- is related to LO mod of GaN and other two peaks are the characteristics peak of natural sapphire substrate. The peak at 748 cm^{-1} is due the point defect in sapphire substrate. The graph in inset of Fig. 2 demonstrated the effect of annealing temperature on the intensity of LO mode of GdN thin films [15]. The intensity of LO mode generally describes the quality of GdN i.e high intensity mean better crystal structure. The graph shows that intensity of LO mode increases as the annealing temperatures increases. This data suggested that quality of annealed films improved with annealing temperature.

Fig. 3 demonstrated the effect of annealing temperature on the carrier concentration of GdN thin films grown by MOCVD and annealed in nitrogen environment for one hour. The graph is evident that carrier concentration decreased from 1.9×10^{18} -1.65×10^{18} cm^{-3} as the annealed temperature increased from 300 to 500 °C. This behavior is due the fact that as annealing temperature increases, more and more nitrogen vacancies are filled by the incoming nitrogen atoms. As the nitrogen vacancy is a donor defect and donote electrons to the conduction band therefore reduction in nitrogen vacancy type defects causes a decrease in the carrier concentration.

The graph in Fig. 4 showed the effect of annealing temperature on the band gap energy of GdN thin films grown by MOCVD and annealed at various temperatures in nitrogen environment. The graph is evident that band gap is increases with the annealing temperature. This result can be explained as; annealing temperature causes the GdN more crystalline with improved structure as evident by XRD and Hall data. Therefore, band gap energy is also close to experimental value, when the sample annealed at 500 °C. This result is also justified by XRD and Hall Effect data.

Fig. 5 demonstrated the effect of annealing temperature on Seebeck coefficient of GdN thin films grown by MOCVD. The graph shows that Seebeck coefficient decreases from 405-343 μV/K as the annealing temperature increases from 300 to 500 °C. The reduction in the Seebeck coefficient with annealing temperature is related with the carrier concentration. As the the annealing temperature increased, the carrier concentration decreased therefore decrease in Seebeck coefficient was expected.

The graph in Fig. 6 demonstrated the effect of annealing temperature on the power factor of GdN thin films. The power factor of samples was calculated from the following formula [16]

$$\text{Power Factor} = \text{Seebeck Coefficiennt} \times \text{electrical conductivity}$$

The electrical conductivity of samples was measured with the help of Hall effect. As it is evident from Hall data that electrical conductivity was increases with annealing temperature, therefore it was expected that power factor would be also increased.

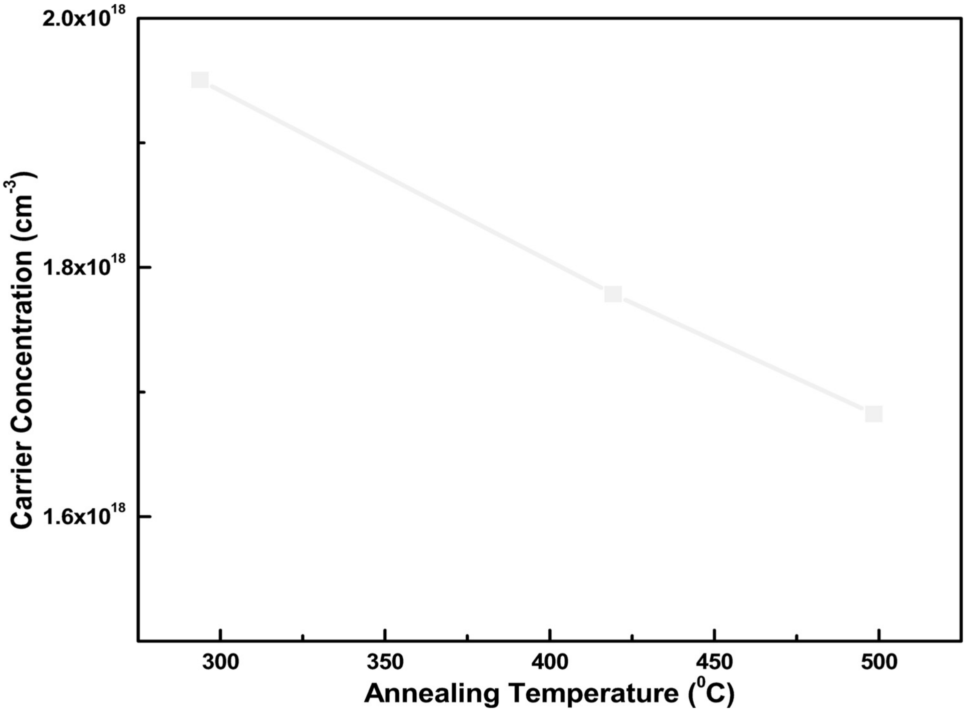

Fig. 3. Effect of annealing temperature on the carrier concentration of MOCVD grown GdN thin films annealed at different temperatures in nitrogen environment.

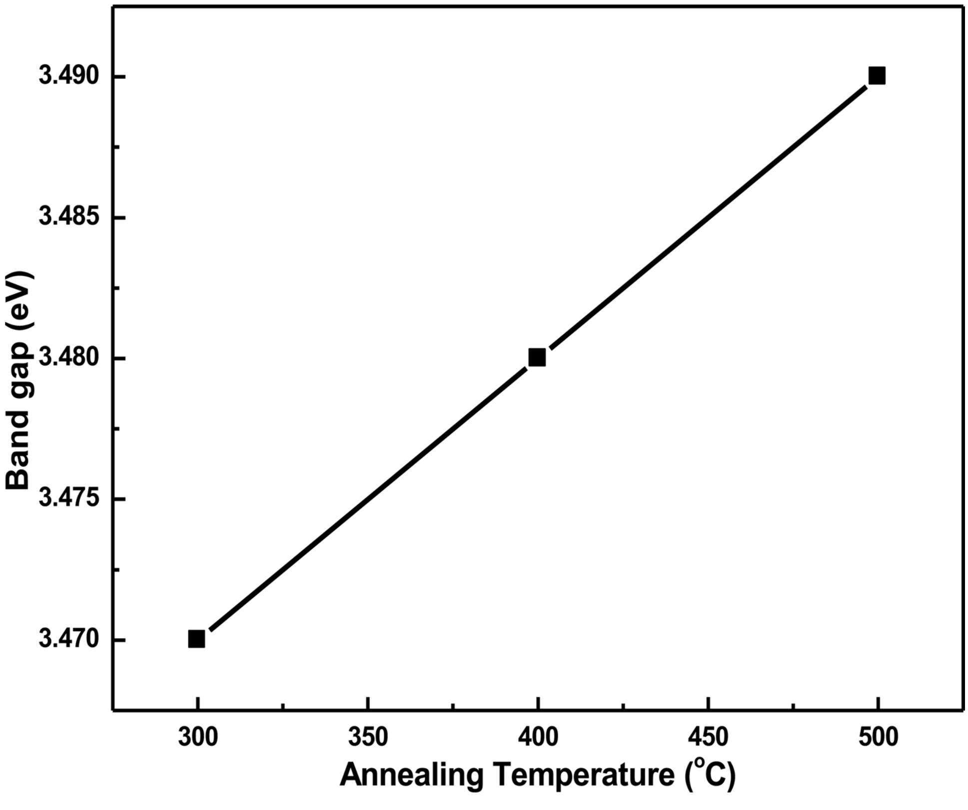

Fig. 4. Demonstrated the effect of annealing temperature on the band gap of GdN thin films grown by MOCVD and annealed in nitrogen environment for one hour at different temperatures.

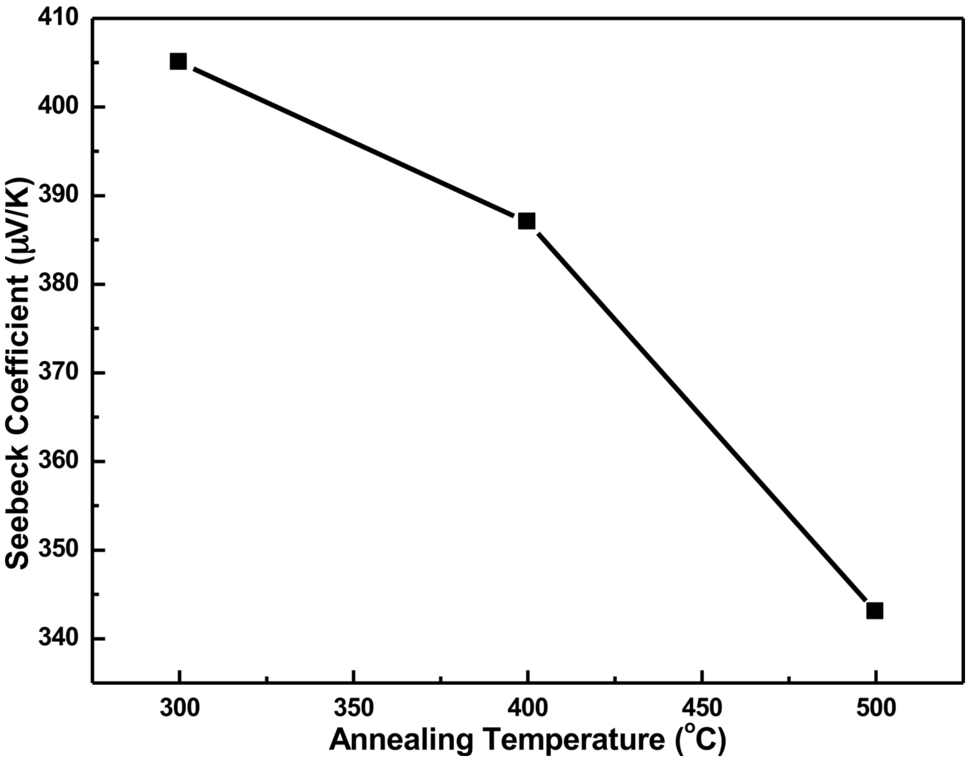

Fig. 5. The variation of room temperature Seebeck coefficient with annealing temperature of GdN thin films.

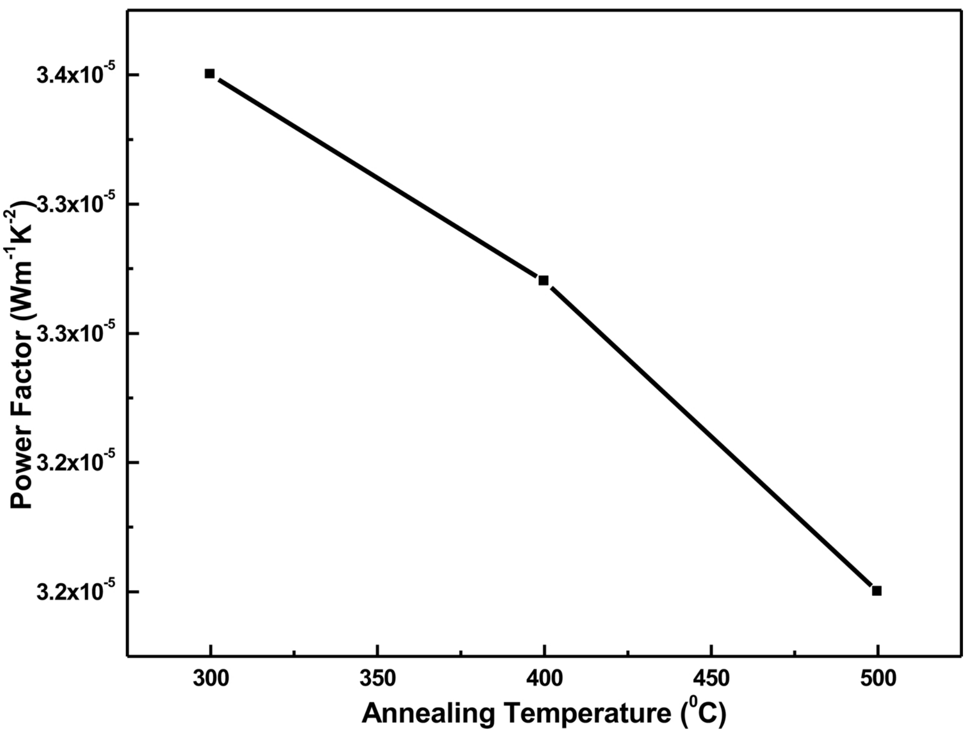

Fig. 6. The decreasing trend of power factor with annealing temperature of annealed GdN thin films.

4. Conclusion

In this thesis, effect of nitrogen environment annealing on GdN thin films was investigated. The samples were grown by MOCVD on sapphire substrate at University of North Carolina Charlotte, USA. After growth a representative sample was cut into pieces and subjected to post growth annealing in nitrogen environment at various temperatures from 300 to 500 °C for one hour. The annealed samples were characterize using XRD, Hall effect, UV/Vis spectroscopy and Seebeck effect to study the annealing influence on the structural, optical, electrical and thermoelectric properties. XRD data confirmed that all samples have hexagonal structure and crystalline structure was improved by annealing temperature. Hall data suggested that carrier concentration decreases with annealing temperature. The value of Seebeck coefficient and power factor was found to be decreased with annealing temperature.

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