EFFECT OF NITROGEN GAS FLOW ON STRUCTURAL, OPTICAL, AND ELECTRICAL PROPERTIES OF N-GAN THIN FILMS GROWN BY HOT WIRE PULSED LASER DEPOSITION

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Highlight

GaN thin films grown on sapphire using pulsed laser deposition with hot wire at 750°C and 120 sccm nitrogen flow exhibited a wurtzite structure with (0002) and (0004) orientations, a wide bandgap of 3.55 eV, and n-type conductivity. The films showed a carrier concentration of 1.45×10^{19} cm^{-3} and electron mobility of 18.55 cm^2/V·s, indicating good crystal and electrical quality.

Abstract
GaN thin film was successfully grown on sapphire (0001) substrate using the pulsed laser deposition method with hot wire under a nitrogen gas atmosphere. To understand the characteristics of the resulting GaN film, observations were made by changing the growth conditions, i.e., temperature up to 750°C and adjusting the nitrogen gas flow rate during the growth process up to 170 sccm. The purpose of these variations is to see how changes in temperature and gas flow affect the quality, structure, and physical properties of the GaN thin films formed. GaN thin films grown at 750°C and supplied with nitrogen gas at a rate of 120 sccm show a wurtzite crystal structure with crystal orientation directions of (0002) and (0004). The wurtzite crystal structure is a common form for GaN and the (0002) and (0004) orientations show that its crystal growth direction is parallel to the c-axis of the hexagonal crystal, which usually results in good crystal quality. This material has a bandgap of 3.55 eV, which indicates wide semiconductor properties. In addition, the film exhibits n-type conductivity properties, with a charge carrier density of 1.45×10^{19} cm^{-3}. The recorded electron mobility is 18.55 cm^2/V.s, which reflects the ability of electrons to move within the material when subjected to an electric field.

Keywords
Hot Wire Pulsed Laser Deposition (PLD); Gallium Nitride (GaN); Nitrogen Flow Rate.

Introduction
Optoelectronic devices, such as LEDs and lasers, require semiconductor materials that can emit or respond to light at specific wavelengths. Blue and ultraviolet light have high energy, so to generate or detect them, semiconductors with wide band gaps (energy band gaps between the valence band and conduction band) are required. Scientists consider that nitride-based alloy compounds such as aluminum nitride (AlN) and gallium nitride (GaN) are examples of semiconductor materials with wide band gaps, which help them to operate efficiently in high-energy regions such as the blue and UV spectra. In addition, these materials also have physical and chemical properties that support high performance and robustness under various operating conditions. Their remarkable resilience to high irradiance and temperatures makes them ideal for extreme conditions, paving the way for innovative device fabrication. Nitride alloys have a variety of uses, such as in communication devices for outer space, ozone layer condition monitors, spark detection sensors, and missile navigation system technology. Gallium nitride (GaN) is an excellent semiconductor that has great potential to be used in various applications involving high temperature and power, as well as optoelectronic devices with an energy band gap of 3.4 eV, making it ideal for developing ultraviolet (UV) sensors [1]. The development of devices based on Gallium Nitride material opens up opportunities for satellite communications that are inaccessible to earth surveillance, monitoring the ozone layer, and detecting sparks. Transistors based on group III-nitride can operate at higher temperatures. High-quality Gallium Nitride (GaN) films are essential for semiconductor applications in advanced technologies, such as LEDs, lasers, and high-power devices. One of the main methods used to produce GaN films is Metal-Organic Chemical Vapor Deposition (MOCVD) [2],[3], molecular beam epitaxy (MBE) [4],[5], and vapor

phase epitaxy (VPE) [6],[7]. Many studies have been conducted to understand the growth process and characteristics of GaN films, both in terms of optical and electrical properties, produced using this technique.

Researchers have increasingly adopted pulsed laser deposition (PLD) as a modern and widely used technique for growing III-V alloy semiconductor thin films, including GaN, AlN, and AlGaN. This method offers several advantages, such as enabling congruent ablation through short ultraviolet (UV) laser pulses, which facilitates multi-material deposition from a single target. In Pulsed Laser Deposition (PLD), this technique allows scientists to place more than one target material on a rotating stand inside a reactor chamber. When a laser beam is directed at the target, it heats and vaporizes the material from the target. Using the rotating stand, each target is exposed to the laser beam in turn, resulting in the growth of heterostructured films directly and precisely in place. By adjusting the laser's repetition rate, they can control the growth rate, making the technique suitable for both atomic-scale research and the fabrication of thick layers.

The PLD technique has become a subject of interest among researchers due to its numerous advantages. This method has been employed in the field of GaN deposition, with researchers achieving successful epitaxial growth of GaN thin films on silicon substrates [8],[9] and sapphire substrates [10],[11],[12],[13]. A paucity of research has been conducted on the parameters involved in the growth of GaN thin films using the PLD technique, particularly with regard to the effect of nitrogen flow rate during deposition on the properties of the resulting films.

The primary challenge associated with the PLD growth technique pertains to the prevalence of columnar defects in GaN thin films. Morphological analysis of these films reveals the presence of Ga droplets or GaN particles of diverse dimensions. The formation of Ga droplets on GaN films is attributed to the interaction between the GaN target and the laser, resulting in the emission of nitrogen atoms from the GaN molecules. This process enables the growth of Ga atoms on the substrate [14]. A number of researchers have examined the density of columnar defects and target material particles in thin films cultivated through the PLD method. For instance, Huang's research [15] demonstrated the efficacy of mitigating columnar defects by incorporating a ZnO buffer layer during the growth of GaN thin films. As demonstrated by Norton [16] and Kennedy [17], the modification of a PLD reactor through the incorporation of a mechanical filter has been shown to effectively reduce the formation of target material particles in oxide-based thin films.

In this study, the objective is to minimize the formation of target material particulates on the surface of GaN thin films. This is achieved by flowing hot nitrogen gas (1000°C) into the growth reactor through a tungsten filament. The rationale behind this approach is that the nitrogen gas molecules entering the reactor become reactive with high kinetic energy. The objective of this study is to examine how variations in nitrogen flow rates affect the electrical, optical, and structural characteristics of GaN films grown by the hotwire PLD technique.

EXPERIMENTAL PROCEDURES

The growth of GaN thin films was carried out under vacuum conditions by flowing nitrogen gas into the reaction chamber through a filament wire heated to 1000°C during the deposition process, as shown in Figure 1. Nitrogen flow rates varied from 65 to 170 sccm. In the GaN film growth process, a sapphire substrate (0001) is used as the base to grow the GaN layer due to its mechanical and thermal properties that are compatible with GaN. The substrate temperature used in this process ranges from 600°C to 750°C. The 0.59-inch diameter GaN target pellets utilized in this study were prepared from high-purity GaN powder (99.99%) that was compressed at a pressure of 7×10^4 $N.cm^{-2.}$ The laser source used is a "neodymium-doped yttrium aluminum garnet (Nd: YAG)" laser, operating at a wavelength of 355 nm. The laser parameters included an energy of 250 mJ and a repetition rate of 10 Hz. The growth parameters for the various films are listed in Table 1.

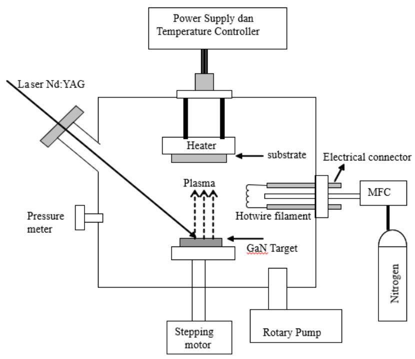

Fig.1. Schematic of Hot-Wire Pulsed Laser Deposition system

Table 1. Growth variables for GaN thin films*

Sample	S0	S1	S2	S3
Growth Pressure (mbar)	0.15	0.20	0.35	0.40
Nitrogen flow rate (sccm)	-	65	120	170
substrate temperatures (ºC)	750	750	750	750
Growth time (min)	180	180	180	180
Film thickness (nm)	60	80	176	205

* Growth parameters in this study using the Hot wire PLD technique

RESULTS AND DISCUSSION

Crystallinity

X-ray diffraction (XRD) is an analytical technique used to examine the crystal structure of materials. In thin film growth using PLD, XRD is used to identify and confirm the crystallinity of the resulting film. That is, XRD helps to determine the extent to which the film has a regular and high-quality crystal structure. As illustrated in Figure 2, the XRD patterns of GaN film samples exhibited variation with respect to the nitrogen gas flow rate (S1, S2, and S3). The outcomes demonstrate that the GaN and sapphire planes are aligned, i.e., GaN(0001) // sapphire (0001), for samples S1 and S2. Figure 2 shows that the conditions in the deposition process, such as the flow rate of nitrogen gas, play an important role in affecting the crystal quality of the resulting GaN films. When the nitrogen flow rate was increased from 65 sccm to 170 sccm, the GaN film exhibited better crystal growth, as evidenced by the appearance of diffraction peak (0004) at 2-theta angle 74.50°, which indicated a regular and high-quality crystal orientation. However, after the nitrogen flow rate was further increased, the crystal quality decreased. This is reflected by the appearance of an orientation peak (1011) at a 2-theta angle of 36.1°, which indicates the presence of irregularities or defects in the crystal structure.

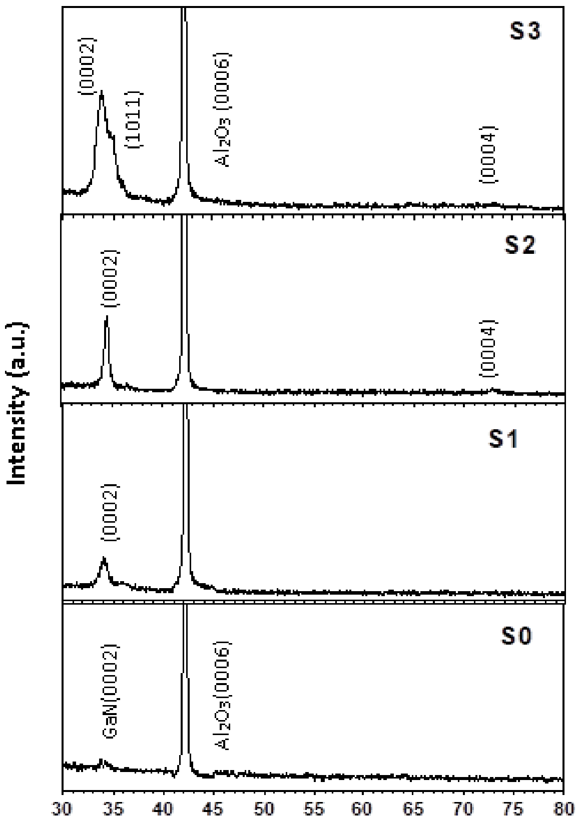

Fig.2. XRD patterns for GaN film samples grown by Hotwire PLD as influenced by Nitrogen flow rate: S0 (without N_2 flow), S1 (with N_2 flow 65 sccm), S2 (with N_2 flow 120 sccm), S3 (with N_2 flow 170 sccm)

This finding aligns with the observations reported by Huang [15], which demonstrated that the kinetic energy of the GaN species arriving at the substrate exhibits an optimal value for the production of a high-quality film. It was further noted that increasing the nitrogen gas flow leads to an enhancement in the collision rate between the GaN species and the energetic nitrogen atoms. This, in turn, results in a reduction in the kinetic energy of the

GaN species that arrives at the substrate surface, lowering it below the optimal kinetic energy threshold required for the formation of a GaN epitaxial layer.

Electrical Properties

In this study, GaN films were grown using the Hotwire PLD method, in which the nitrogen gas flow rate was changed to see its effect on the film quality. The substrate temperature used was 750 °C, which is a common temperature for GaN growth to optimize the crystal structure. After film growth, characterization was performed using the Van der Pauw-Hall method at room temperature to measure the electrical properties of the GaN film. The results of the Van der Pauw-Hall measurements shown in Figure 3 provide insight into the electrical properties of GaN layers grown at different conditions. At a nitrogen flow rate of 65 sccm, the carrier density (number of charge carriers per volume) is 3.5×10^{19} cm^{-3}, and the electron mobility (electron velocity per unit electric field) is recorded as 13.5 cm^2/V.second. When the nitrogen flow rate was increased to 120 sccm, changes occurred in the electrical properties of the GaN film. The carrier density decreased to 1.45×10^{19} cm^{-3}, which means there are fewer charge carriers in the material. However, although the carrier density decreases, the electron mobility increases to 18.55 cm^2/V.second, which indicates that electrons can move faster in the material. Meanwhile, when increasing the nitrogen flow rate to 170 sccm, the carrier density increased to 2.85×10^{19} cm^{-3}, while the electron mobility decreased to 14.45 cm^2/V.second. All the grown GaN film samples (S1, S2, and S3) exhibit n-type conductivity.

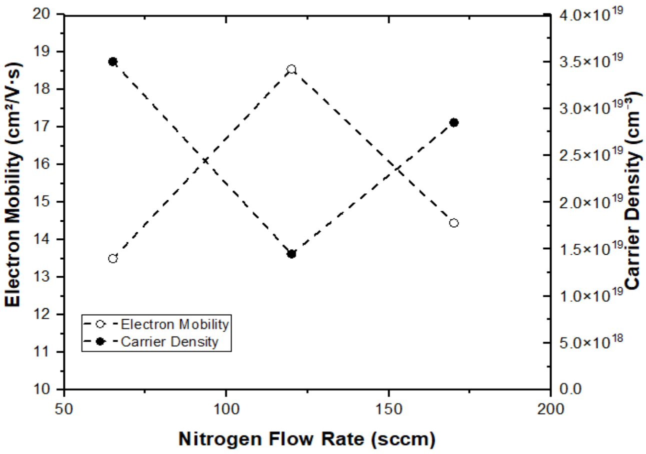

Fig. 3. Electron mobility and carrier density of GaN thin films with varying Nitrogen Flow Rate

The reduction in the electrical properties of GaN films resulting from variations in nitrogen gas flow rate is associated with the kinetic energy of GaN molecular species reaching the substrate [18]. At low nitrogen flow rates, the ablated GaN species undergo minimal collisions before arriving at the substrate surface, retaining high kinetic energy that may cause lattice damage in the growing film. By increasing the nitrogen flow rate, researchers can induce more frequent collisions between the ablated GaN species and nitrogen gas molecules, thereby lowering their kinetic energy and minimizing lattice damage. However, when the nitrogen flow rate is increased beyond 120 sccm, excessive collisions occur between the nitrogen gas and the growing GaN species. These collisions cause the energy of GaN species to become lower, so their kinetic energy is not enough to support efficient epitaxy growth. If the energy of GaN species drops below the threshold required for the formation of ordered crystals, the quality of the crystal structure decreases, which eventually harms the electrical properties of GaN films, such as carrier density and electron mobility.

The present findings are consistent with those reported by Chin [19], which demonstrated that nitrogen vacancy defects in high-density GaN thin films result in elevated electron density, thereby leading to a decline in electron mobility. This phenomenon is exemplified by samples S1 and S3, which exhibit high electron density and low electron mobility values.

Optical Properties

Figure 4 shows that the absorption ability of GaN thin films with variations in Nitrogen flow rate produce different curves in the UV-Visible wavelength range. The absorption peak was detected in the range of 200-350 nm in all variations. Table 2 summarizes the absorption peaks in GaN thin film samples. Although the absorption curves look similar, in the UV-Visible light range there are differences in absorption intensity that are so significant with the order from the lowest to highest, namely at a nitrogen flow rate of 170 sccm >120 sccm >65 sccm.

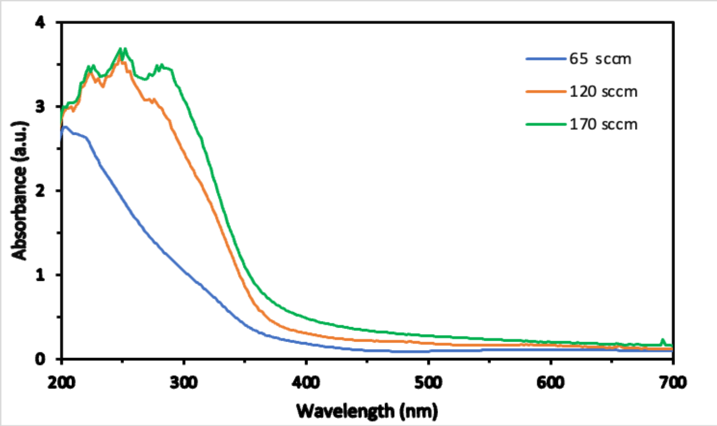

Fig.4. Absorption spectra of GaN thin films with varying Nitrogen Flow Rate in the UV-Vis range

Table 2. Absorption peaks in GaN thin film samples with varying Nitrogen flow rate

N_2 Flow Rate	λ_{max}(nm)	A_{max} (a.u.)
65 Sccm	203	2.75
120 Sccm	224	3.42
170 Sccm	252	3.69

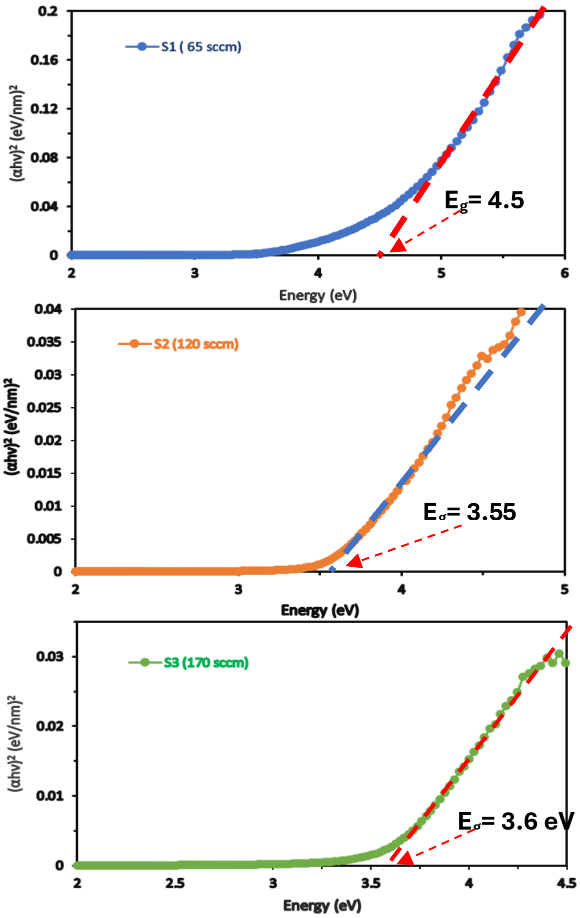

Fig.5. Tauc's plot of GaN Thin Film samples with N_2 Flow rate variation

To analyze the band gap in materials such as GaN, one commonly used method is to plot $(\alpha h\nu)^2$ against photon energy (hv). In this case, α is the absorption coefficient, which describes the extent to which a material absorbs light of a particular wavelength, and hv is the photon energy, which relates to the wavelength of light received by the material. The relationship between absorption coefficient and photon energy is described by an empirical equation, as follows (1) [20]:

$$\alpha h\nu = C\,(h\nu - Eg)^{1/2} \qquad (1)$$

In this equation, $h\nu$ is the photon energy, Eg is the band gap of the semiconductor, and C is an empirical constant that describes the relationship. A Tauc plot is used to extrapolate the linear part of this curve, which gives an accurate estimate of the band gap of the material. The absorbance of the material, which measures how much light is absorbed at a particular wavelength, was obtained for various GaN samples grown with varying nitrogen flow rates. By measuring the absorption of light at different wavelengths, the Tauc plot can help determine the band gap value of the material. Figure 5 shows the Tauc plot analysis, it can be seen that the band gap of GaN thin films grown with different nitrogen gas flow rates shows varying values. This difference in band gap value indicates that the nitrogen gas flow rate affects the band gap formation of the material. For sample S1, the band gap energy found is 4.5 eV, which indicates a material with a wider band gap, while for samples S2 and S3, the band gap energies are 3.55 eV and 3.6 eV, respectively, which are smaller compared to sample S1.

CONCLUSION

From the results, it can be concluded that the GaN film produced using the Hotwire PLD method shows good crystal quality. The growth process was carried out on a sapphire substrate with a temperature of 750°C and a nitrogen flow rate that has been set at 120 sccm. These conditions resulted in a film that has n-type conductivity, which means that electrons act as the main charge carriers. In addition, the measured electron concentration is 1.45×10^{19} cm^{-3}, and the electron mobility is high at 18.55 cm^2/V-s, which indicates the ability of electrons to move efficiently in the material. The band gap energy of the GaN film grown under these conditions is 3.55 eV, which indicates that the film has a fairly large band gap, suitable for applications in the blue and ultraviolet (UV) light spectra. The film exhibits high quality, which can be used in various semiconductor applications, such as LEDs and lasers.

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