

# Doping GaN NPs Synthesized by a Chemical Method for p-n Junction Application.

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**Abstract:** This research was devoted to studying the doping of GaN NPs at low temperature with Mg and the possibility of using them in the p-n junction. This study was subjected to a FESEM, EDX, XRD, PL and Hall Effect examination. The FESEM examination showed clear images of the NPs, the XRD peaks appear at  $2\theta = 32.5, 39.1$  and  $45.48$  which conform the crystalline of p-GaN NPs, Hole Effects measurements confirm the p-GaN with different Mg ratios. The ideality factor and series resistance of p-n junction have been measured.

**Keywords:** P-GaN; Hall Effect; p-n junction; Magnesium; FESEM; Ideality Factor and Series Resistance

## 1. Introduction

Since the past two decades, III-N has been one of the most significant materials employed in applications for optoelectronic devices due to its wide, direct, adjustable bandgap capabilities in UV (0.7-6.2 eV) areas (Akasaki and Amano, 1997). GaN is a semiconductor material with a direct band gap with a width of 3.4 MeV and an excitation binding energy of 26 MeV (Amir et al., 2022). As more active areas in LEDs, high-purity gallium nitride nanoparticles make electrical devices more practical (Amir et al., 2022).

GaN NPs have been produced using a variety of techniques, including electrochemical reaction, spin coating, RF sputtering, molecular beam epitaxy, metal-organic chemical vapour deposition (MOCVD), pulsed laser deposition (PLD), and hydride vapor phase epitaxy (HVPE) (Pang and Kim, 2015, Yusoff et al., 2013, Hu et al., 2012, Joshi et al., 2010, Mantarcı and Kundakçı, 2017, Fong et al., 2015, Kawwam and Lebbou, 2014, Braniste et al., 2017, Wang et al., 2016, Qaeed et al., 2015, Qaeed et al., 2013a). The aforementioned techniques and more, some of which require vacuum as a precondition, some of which involve costly chemicals or intense heat. In our earlier research, GaN NPs were successfully produced using a chemical process that was low cost and successful at room temperature (Qaeed et al., 2013a, Qaeed et al., 2015). Due to defects like nitrogen vacancies and oxygen and hydrogen impurities that act as electrons in the electrical polarity of the alloys, high P-type doping in alloys continues to be a difficulty. Getting rid of the contaminants that lead to electro-negativity is the difficult part (Chung et al., 2010). Given its many uses, the nano-nitride composition shown a strong capacity to address this issue (Aluri et al., 2011, Qian et al., 2005) Materials like  $\text{In}_x\text{Ga}_{1-x}\text{N}$  with  $x=0.35$  are typically predominantly n-type, and it is still very challenging to convert these materials to p-type by Mg doping. The findings suggest that greater background electron concentration management might lead to additional improvements in p-type conductivity in InGaN: Mg (Pantha et al., 2009). Mg-doped  $\text{In}_x\text{Ga}_{1-x}\text{N}$  was studied, and as the In mole percentage grew, the RT carrier concentration increased exponentially (Chen et al., 2006). By using Metal Organic Vapour phase Epitaxy with magnesium doping at 550 °C, InN and In-rich InGaN were developed. p-InGaN was produced with an acceptor concentration of  $1 \times 10^{19} \text{ cm}^{-3}$  (Chang et al., 2007a). On semi-insulating c-GaN/sapphire templates, Mg-doped  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys with a hole concentration  $\approx 5 \times 10^{18} \text{ cm}^{-3}$  and a hole mobility of  $3 \text{ cm}^2/\text{V s}$  were produced via metal organic chemical vapor deposition (Pantha et al., 2009). Due to the high activation energies ( $E_A$ ) of magnesium - acceptor, a commonly accepted p-type dopant for GaN and similar alloys, where  $E_A$  rise with increase in band gap energy, it is very difficult to get highly conductive p-type GaN and AlGaIn. It is advantageous to utilize P-type InGaIn device structures rather than P-type GaN device structures, particularly in devices like solar cells, laser diodes, and green, long-wavelength emitters where the active area must be developed at temperatures much higher than those of the P-type GaN layer. Intense study has been put into P-

type doping of InN and In-rich InGaN. The accomplishment of their optoelectronic applications heavily rely on p-type doping. The most researched dopant functioning as a potential acceptor in InN is magnesium. Since the initial publication of evidence for p-type doping in InN and InGaN (Jones et al., 2006, Qaeed et al., 2014). In this work, we will doping GaN NPs synthesized by a chemical method via adding different amounts of magnesium to determine the best result utilize in applications

## 2. EXPERIMENTAL PROCEDURE

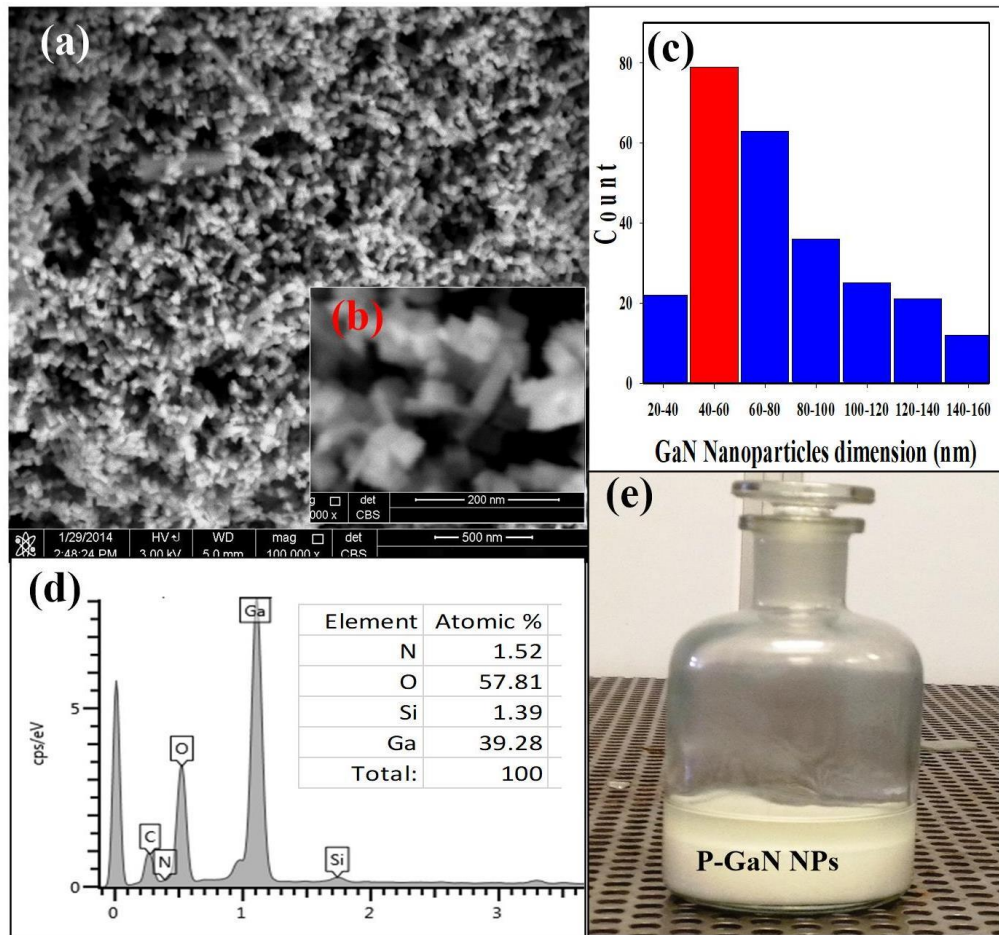
**2.3 Materials:** The ingredients used to create GaN NPs were obtained from Across Organics, and they are as follows: Methanol, Oleylamine (C18-content 80-90%), toluene, HNO<sub>3</sub> (34.5%), and NH<sub>4</sub>OH (28-30%). Gallium (III) acetylacetonate (Ga(acac)<sub>3</sub>; 99.99%) was obtained from Sigma-Aldrich.

### 2.4 Preparation of GaN NPs and P-Type GaN

The creation of GaN NPs involved mixing 200 mg of Ga(acac)<sub>3</sub> with 10 ml of oleylamine at room temperature. This mixture was added to a rotary evaporator flask that was placed in a 90°C water bath. After that, 10 ml of HNO<sub>3</sub> and 20 ml of NH<sub>4</sub>OH were added to the solution. 12 hours were spent stirring the fluid to thoroughly dissolve the combination (Qaeed et al., 2013a). The solution was then purified five times using centrifuge equipment and 10 millilitres each of methanol and toluene. In order to create Mg-doped p-GaN NPs, 0.015 mg of MgO was dissolved in 5 ml of HNO<sub>3</sub>. This Mg source was mixed after being added to several solutions in various amounts. To determine the samples' hole concentration, hole mobility, and resistivity, hall effect tests were carried out.

## 3. RESULTS AND DISCUSSIONS

In Fig. 1 (a and b), respectively, FESEM images of GaNNPs synthesized at 90°C are displayed with various scales (50 and 200 nm). According to past studies, the van der Waals forces of attraction between the particles cause the GaN NPs to aggregate (Gopalakrishnan et al., 2014, Qaeed et al., 2013b). Figure 1(c) displays the typical particle size histograms for the related FESEM picture. The geometric mean diameter of the GaN NPs, which was estimated, was found to be between 40 and 60 nm. The Scherrer equation and XR D analysis both show that the material contains aggregated nanocrystallites with near diameters. The FWHM of diffracted peaks and variations in crystallite size are factors in the Scherrer equation. However, temperature and time are important growth parameters that play a significant role in controlling the size of the GaN NPs. The results of the elemental analysis utilizing EDX measurements are displayed in Fig. 1(d), and they confirm the existence of the elements N and Ga. However, the growth factors, including temperature and time, are crucial in regulating the size of the GaN NPs. The elemental analysis performed using EDX measurement is shown in Fig. 1(d), and it verifies the presence of N and Ga elements. However, due to low temperatures, which cause the Ga to evaporate at higher temperatures, the proportion of Ga is higher than that of N(Gopalakrishnan et al., 2014).

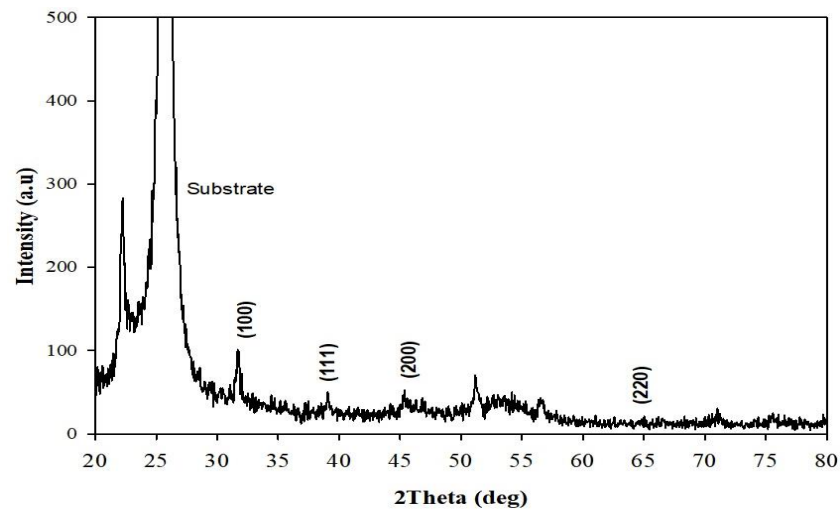


**Fig.(1)** p-GaN NPs synthesized by a chemical method (a) FESEM with 500nm scale (b) FESEM with 200 nm scale (c) particle size Histograms of p-GaNNPs (d) ESX of p-GaNNPs (e) image of p-GaNNPs

The samples displayed in Fig. 2 were created within eight hours using the nitrogen sources illustrated in Fig. 1: 20 ml NH<sub>4</sub>OH and 10 ml HNO<sub>3</sub>. The samples' high intensity peaks match the PET substrate(Qaeed et al., 2013a). The sample's findings show two c-GaN peaks at 2θ = 39.1 and 45.48 that correlate to the cubic phase and reflect from (111) and (200), as well as h-GaN nanoparticle peaks at 2θ = 32.5 that reflect from the (100) plane (Wright and Nelson, 1995, Balkaş and Davis, 1996, Falter et al., 1993). This result of the XRD result indicates that the quantity of Nitrogen source affect in the chemical reaction controls the structure formation of GaN nanoparticles. The average crystallite sizes ( $D_p$ ) of the of the sample were estimated using Scherer's formula (Qaeed et al., 2013b).

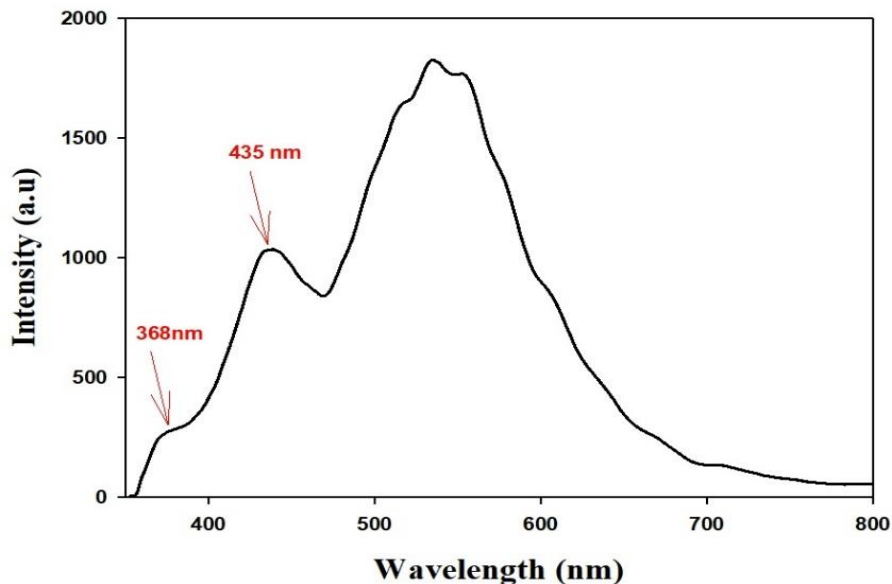
$$D_p = \frac{0.9\lambda}{\rho \cos\theta} \quad (1)$$

where  $\lambda$ ,  $\theta$  and  $\rho$  are X-ray wavelength, Bragg's diffraction angle and full width at half maximum (FWHM) of the peak respectively. The average diameter of cubic and hexagonal structure of p-GaN NPs diameter was found to be approximately 55 nm.



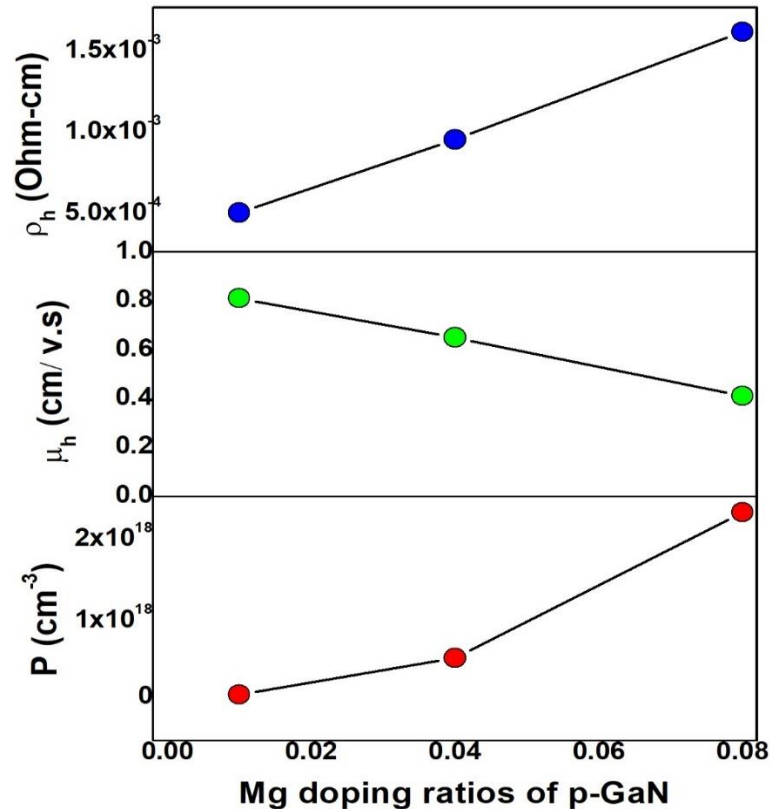
**Fig.(2).** XRD measurement of p-GaN NPs synthesized by a chemical method

The GaN-NPs' PL spectra are shown in the picture. GaN-NPs' PL peaks are dispersed in the UV (335–360 nm) and gradually become red when excitation wavelengths are increased. At 368 nm, the p-GaN NPs exhibit the first PL peak intensity. Doping is typically the reason for the phenomena of shifting PL peaks of NPs at various wavelengths. GaN NPs' PL peak spectra revealed another another peak between 425 and 440 nm (Hao et al., 2020). In our research, p-GaN NPs also demonstrated another peak at 435 nm with a little redshift in their spectra. The two peaks are caused by the various NP sizes. From earlier research that demonstrated that the ultraviolet PL of GaN was induced by the radiation recombination of shallow DAP (donor-acceptor pairs), it may be assumed that the PL spectra are spread in the ultraviolet light range (Hao et al., 2020). Due to the very low DAP radiation recombination intensity and relatively weak PL intensity of GaN-NPs, P-GaN-NPs 368 nm UV PL is further verified.



**Fig.(3)** Photoluminescence of p-GaN NPs synthesized by a chemical method

It takes a lot of work to get p-GaN to have a high conductivity since the Mg -acceptors that are frequently employed in doping processes have a high activation energy ( $E_a$ ). Studies have demonstrated the p-type dopant's complexity in relation to p-GaN NPs. This may indicate the presence of defects like oxygen or nitrogen vacancies that are the cause of the elevated background electron concentrations (Pantha et al., 2009). The electrical characteristics of p-GaN were studied using the Hall Effect, and the hole concentration was drawn as a function of the doping ratio in Figure. The graph demonstrates how raising the dopant ratio raises resistivity and hall concentration while lowering mobility. The material's excellent quality is reflected in the sample's notable value, which results in lower values of  $\mu_h$  and higher values of  $\rho_h$  that boost the currents in optoelectronic devices, considerably enhancing device performance for a wide range of applications. The hole compensating effect by background electrons is responsible for the observed drop in hole concentration for p-GaN with a doping ratio of 0.02mg (Chang et al., 2007b).



**Fig. (4)** Variation of the hole concentration ( $p$ ), mobility ( $\mu_h$ ), and resistivity ( $\rho_h$ ) with doping ratio of p-GaN NPs films.

The  $I$ - $V$  curve of sample showed with poor rectifying behaviors because of the formation of the interfacial defects (Bhat et al., 2011, Roul et al., 2011, Miller et al., 2004). At lower voltages, it is found that the diode has a rectifying behavior. Using the standard diode Eq. (1), the diodes ideality factor  $n$ , barrier heights ( $\phi_B$ ) and saturation current density ( $J_S$ ) are extracted by fitting the forward  $I$ - $V$  curves. From  $I$ - $V$  curves, the values of  $J_S$ ,  $\phi_B$ , and  $n$  are measured. The values of  $n$  in these hetero-junctions are found to be greater than 2, indicate that the diodes are not an ideal one. This is probably due to the presence of surface states and/or formation of an insulating layer of  $\text{SiO}_2$  at the interface (Wang, 2010). Such high values are commonly attributed to carrier tunneling via deep levels in the space charge region due to high-density localized states (Wang, 2010). The ideality factors measured in these devices however are in good agreement with that measured in GaN/Si diodes (Manna et al., 2010, Cheng et al., 2003).

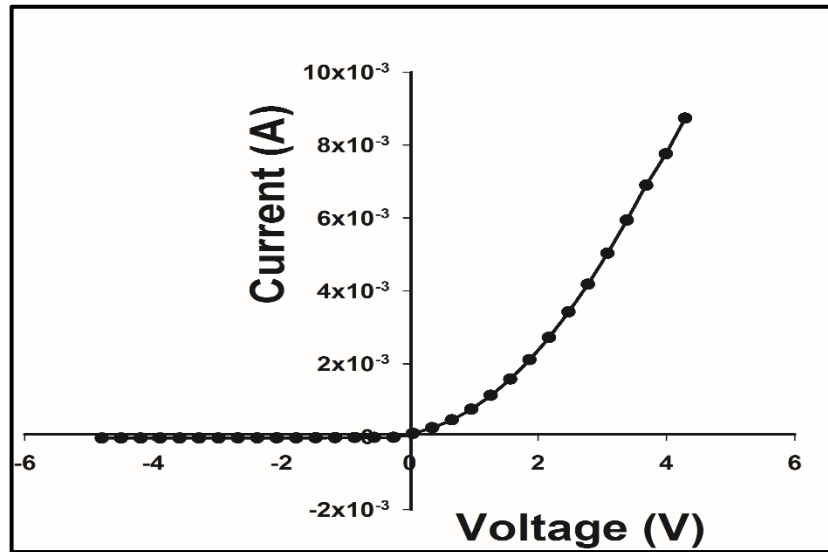


Fig. (5) Forward and reverse bias of p-n junction n-Si/p-GaN

The ideality factor of p-n junction calculated from Cheung's method where the current flows through the forward bias is given by Equation (1)

$$I = I_s e^{\frac{q(V-IR_s)}{nkT}} \tag{1}$$

$$\frac{dV}{d\log(I)} = IR_s + \frac{nkT}{q} \tag{2}$$

where  $R_s$  is the series resistance,  $T$  is the room temperature,  $k$  is the Boltzmann constant and  $q$  is the electronic charge. The ideality factor in the region suggested to be between (1-2) calculating from equation (2) and resulting from the mixture of the combined processes of diffusion and recombination processes in the neutral region and the depletion region respectively. The high value of the p-n junction ideality factor is related to the high carrier concentration (Hudait and Krupanidhi, 2001). In addition to, the high ideality factor value resulting from the high injection and series resistance effect.

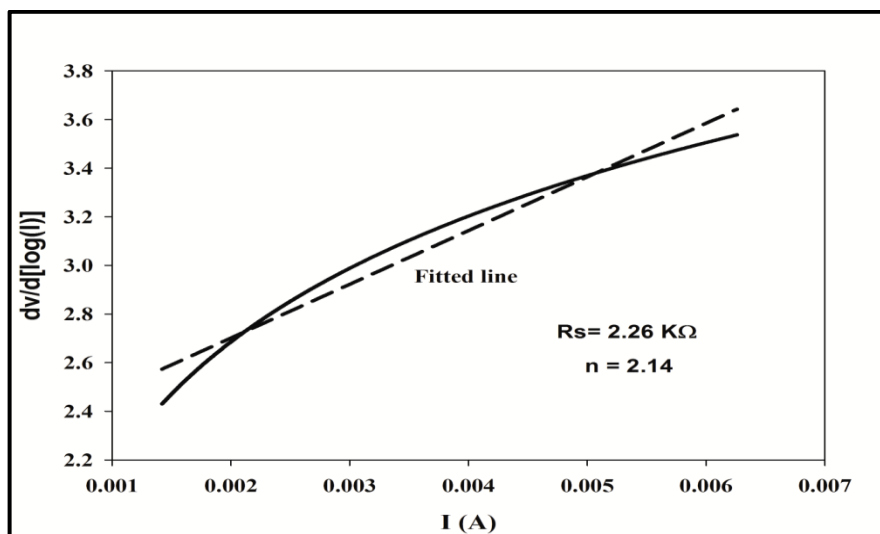


Fig. (6) Ideality factor of p-n junction calculated from Cheung's method

The barrier height ( $\Phi_B$ ) for p-n junction could be calculated from Eq (3)

$$\Phi_B = \frac{kT}{q} \ln \frac{A^* T^2}{I_s} \quad (3)$$

Where  $A^*$  is the Richardson's constant ( $32 \text{ Acm}^{-2}\text{K}^{-2}$ ),  $I_s$  is the reverse saturation current,  $k$  is the Boltzmann constant,  $q$  is the carrier charge and  $T$  is the absolute temperature. The reverse saturation current can be determined by extrapolating the  $\log(I)$  versus  $V$  curve to  $V=0$ .  $I_s = 3.1 \mu\text{A}$ . The barrier height obtained is a little high ( $\Phi_B = 0.689\text{V}$ ) because it was calculated based on the higher region of forward bias voltage. In comparison with report (Gupta et al., 2009) most of the carrier can flow in the forward bias of p-n junction because the lower barrier height of our p-n junction than compared report as the forward bias showed with high current than the mentioned report.

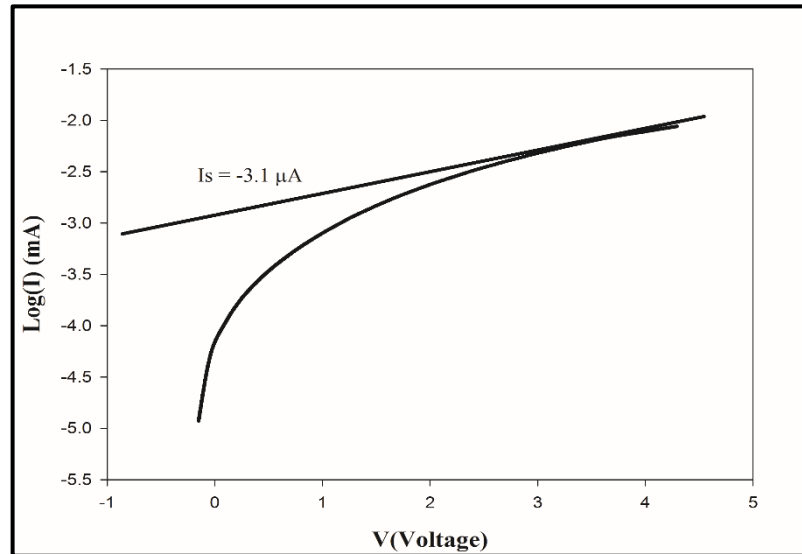


Fig. (7) Calculation the saturation current

## CONCLUSION

This research presented an easy and simple method for doping gallium nitride, as well as controlling the percentage of gallium, which in turn enables us to control conductivity and resistivity, which is the greatest thing in semiconductors. The measurements demonstrated the formation of the doped p-GaN NPs and their application with n-silicon to form the p-n junction. The rectifying behaviour was proven. Finally, the study succeeded in measuring the ideality Factor and Series resistance, which made it easy to apply this method in the upcoming doping processes for the manufacture of devices such as solar cells and photodetectors.

**Conflict of interest:** The author declare no conflicts of interest

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