Femtosecond-Laser Induced Two-Photon Absorption of GaN and $Al_xGa_{1-x}N$ Thin Films: Tuning the Nonlinear Optical Response by Alloying and Doping

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Abstract

Semiconductors thin films are the foundation of modern technology. While the nonlinear optical (NLO) properties of bulk semiconductors have been systematically studied in the last three decades, it is still a great challenge to obtain them for semiconductors thin films, as the high laser irradiance in NLO experiments tends to irreversibly damage the thin films. In addition, tuning the NLO response of semiconductor thin films by alloying and doping has not been explored yet. Here, we study the influence of the Aluminum content in $Al_xGa_{1-x}N$ thin films and the n-type doping concentration in GaN thin films on their two-photon absorption (2PA) coefficients. For this, we investigate five different GaN-based thin films: an unintentionally doped one with no Al as a reference, two n-type doped GaN films with distinct concentrations of silicon impurities, and two $Al_xGa_{1-x}N$ alloys with an aluminum content of 5.5 % and 9.0 %, respectively. The femtosecond 2PA spectra reveal that doping impurities reduce the non-linear coefficients (~10%), while alloying with Al enhances the 2PA coefficient up to 30%. We use the model of Brandi and Araujo to determine Kane´s energy parameter related to the transition matrix element for each sample and compare them with recent theoretical studies based on the k·p theory where an excellent agreement is found.

I – INTRODUCTION

Gallium Nitride (GaN) is a wide bandgap semiconductor that is widely known for its excellent optical and electronic properties.[1-8] Its bandgap can be tuned by alloying it with In or Al, and n-type doping is typically achieved by introducing Si or Ge as shallow donor centers. GaN exhibits low compressibility, thermal stability, chemical, and radiation inertness. GaN and also AlN have very interesting nonlinear optical (NLO) properties, making them also suitable for optical power limiting, second harmonic generation, frequency comb generation, and parametric down-conversion.[9-12]

Due to its versatility and importance for technological applications, the optical and electronic properties of GaN continue to be extensively studied.[13-19] However, two-photon absorption (2PA) studies are yet on demand. For example, comprehensive studies on the impact of impurity concentration and alloying on the 2PA have not yet been performed. Even for pure GaN, there are no experimental results on 2PA using femtosecond pulses and low repetition rate over a broad spectral range. Moreover, some of the reported results are conflicting. For instance, Toda et. al [20] reported 2PA coefficients on the order of 5 cm/GW at 0.4 $\hbar\omega/E_g$ (here we will use the form 0.4 $\hbar\omega/E_g$, where $\hbar$ is the reduced Planck's constant, ω is the excitation photon frequency and E_g is the band gap energy). This large value for the nonlinearity has been attributed to interactions with impurities and defects that are related to the yellow luminescence band. Also, 2PA coefficients of about 3.5 cm/GW were reported by Fang et. al[21] at 0.7 $\hbar\omega/E_g$ using picosecond pulses, which can be ascribed to the contribution of excited state absorption, given the longer pulse duration. Large values, on the order of ~15 cm/GW, have been observed at UV wavelengths (close to 1 $\hbar\omega/E_g$) by Sun et. al. [22] However, in this spectral region, resonance enhancement takes place, contributing enormously to these high values. Even values as high as 1500 cm/GW have been reported by Lin et al.,[23] however, in this case the authors have used an excitation photon energy larger than the bandgap of the material, characterizing a reverse saturable absorption effect.[24] It is worth mentioning that these studied were performed in bulk materials.

Therefore, given the lack of studies over a broad spectral range with femtosecond laser pulses at low repetition rates, as well as the scarcity of

investigations on the influence of impurities and alloying on the 2PA, in this work we investigate five different GaN-based thin films samples: an unintentionally doped one used as reference, two n-type GaN with distinct concentrations of silicon impurities and two $Al_xGa_{1-x}N$ alloys with an aluminum content of 5.5 % and 9.0 %. We observed the highest 2PA coefficient for the alloy with the higher content of aluminum, while the higher n-type doping displayed the smallest one.

II – EXPERIMENTAL DETAILS

GaN and $Al_xGa_{1-x}N$ samples were epitaxially grown in an Aixtron AIX2600G3 HT MOVPE reactor on a 650 μm thick, double-side-polished 4" sapphire substrate. Following a standard procedure for GaN growth, the bare sapphire substrate was thermally cleaned in an H_2 atmosphere. Afterward, a GaN nucleation layer was deposited using trimethylgallium (TMGa) and ammonia (NH_3) at a low temperature before a high-temperature recrystallization step. Subsequently, different epilayers were grown with a group III metalorganic (trimethylgallium and trimethylaluminium) supply of 450 μmol/min and V/III ratio of 725 at a temperature of 1020 ºC and a reactor pressure of 5 mbar under H_2 carrier gas, resulting in a growth rate of approximately 2 μm/h. Table 1 summarizes the characteristics of the samples used in this work.

Table 1 – GaN films characteristics

Sample	Type	Concentration	Thickness (μm)
GaN	i	$<< 10^{17}$ cm^{-3} (Si impurities)	11.13
GaN_{n1}	n	10^{17} cm^{-3} (Si impurities)	11.43
GaN_{n2}	n	4.5×10^{18} cm^{-3} (Si impurities)	9.3
$Al_{0.055}Ga_{0.945}N$	alloy	5.5 % of Al	10.8
$Al_{0.09}Ga_{0.91}N$	alloy	9.0 % of Al	10.0

Linear absorption spectra were measured using a UV/Vis spectrophotometer Shimadzu UV-1800 to determine the bandgap energy of the samples. The spectra of the two-photon absorption coefficient (β) of all GaN-

based samples were obtained using the open-aperture Z-scan technique. The experiments were performed using a Clark MXR-2000 fs-amplifier system, which delivers 150-fs pulses with 0.6 mJ pulse energy at 775 nm and a repetition rate of 1 kHz. This system is the excitation source for an Optical Parametric Amplifier (OPA) that provides 120-fs pulses in the wavelength range between 470 and 2000 nm, allowing the excitation of samples over a broad spectral range in the fs regime. Also, to ensure a TEM_{00} Gaussian beam profile required for the Z-Scan, spatial filtering of the laser beam is performed. It is important to point out that prolonged laser exposure can damage the thin film. Details about the Z-scan setup can be found in Ref.[25].

III – RESULTS AND DISCUSSION

The steady-state absorption spectra of the samples, measured at room temperature, are displayed in Figure 1.

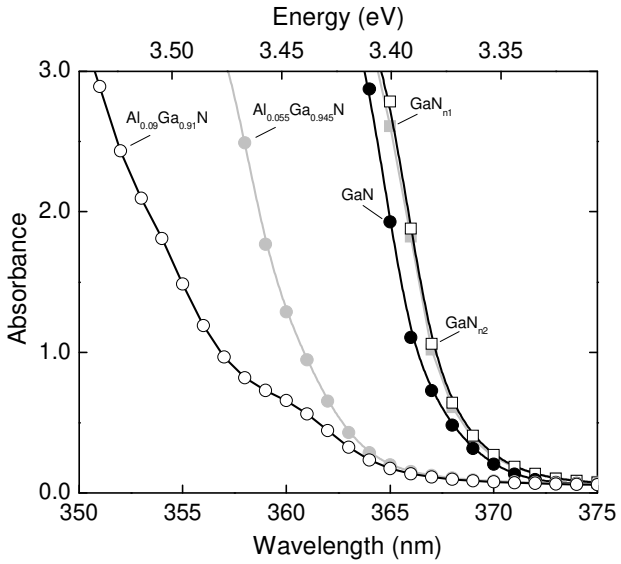

Figure 1: Absorption spectra of GaN and $Al_xGa_{1-x}N$ films. From left to right, $Al_{0.09}Ga_{0.91}N$, $Al_{0.055}Ga_{0.945}N$, GaN, GaN_{n1}, and GaN_{n2}.

The bandgap energies (E_g) of all samples as extracted from these spectra according to Ref.[26] are given in Table 2. The influence of the sample composition on the E_g can be clearly observed in Figure 1. As expected, Si impurities lead to a slight narrowing of the room-temperature band gap due to the introduction of new donor states slightly below the conduction band (red-shift observed in Figure 1).[27] They can also lead to tensile strain in the layers,

which could modify the bandgap energy via the respective deformation potential. On the other hand, alloying GaN with Al increases E_g (blue-shift showed in Figure 1) due to the high bandgap of the wurtzite AlN semiconductor (~ 6 eV) [30].

The 2PA coefficient (β) spectrum of GaN was determined in the range from 0.53 $\hbar\omega/E_g$ up to 0.63 $\hbar\omega/E_g$. Figure 2 displays typical open aperture femtosecond Z-Scan measurements obtained at 0.60 $\hbar\omega/E_g$, 0.56 $\hbar\omega/E_g$ and 0.53 $\hbar\omega/E_g$ for $Al_{0.055}Ga_{0.945}N$. The solid lines represent the fitting obtained, from which the 2PA coefficient β was determined. Similar measurements were obtained for the other samples in the same spectral range, which allowed determining the 2PA spectra for the different samples, displayed as symbols in Figure 3. We observed a monotonic increase of the 2PA magnitude as the excitation photon energy increases, up to 0.63 $\hbar\omega/E_g$, after which resonance enhancement of the nonlinearity starts to be observed. No nonlinear absorption signal was observed for $\hbar\omega/E_g$ smaller than 0.50, as expected for a 2PA process.

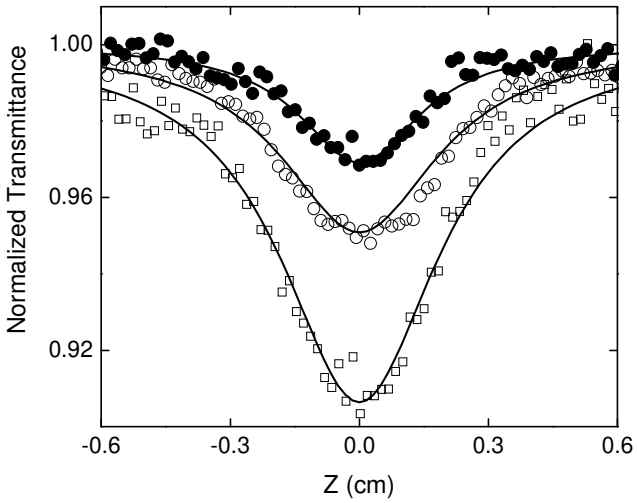

Figure 2: Z-scan transmittance measurements for the $Al_{0.055}Ga_{0.945}N$ at three different photon energies, from top to bottom, 0.60 $\hbar\omega/E_g$, 0.56 $\hbar\omega/E_g$ and 0.53 $\hbar\omega/E_g$ respectively. The solid line is the theoretical fitting obtained with Eq. 1.

From Figure 3, it is noticeable that the Si impurities tend to decrease the 2PA coefficient, while the alloying increases the 2PA. It is important to observe that these results agree with the ones obtained by Miragliotta et al.,[28] who investigated the 2PA coefficients by measuring the photocurrent generated in

GaN films using a tunable laser. They observed negligible 2PA coefficient below 0.5 $\hbar\omega/E_g$ and values up to 1.5 cm/GW at 0.57 $\hbar\omega/E_g$. These results are in good agreement with our experimental data showing negligible 2PA coefficients for excitation energies lower than 0.53 $\hbar\omega/E_g$ and β values ranging from 1.31 to 2 cm/GW at 0.57 $\hbar\omega/E_g$ depending on the sample composition. More specifically, our result for the unintentionally doped sample yielded exactly 1.5 cm/GW at 0.57 $\hbar\omega/E_g$.

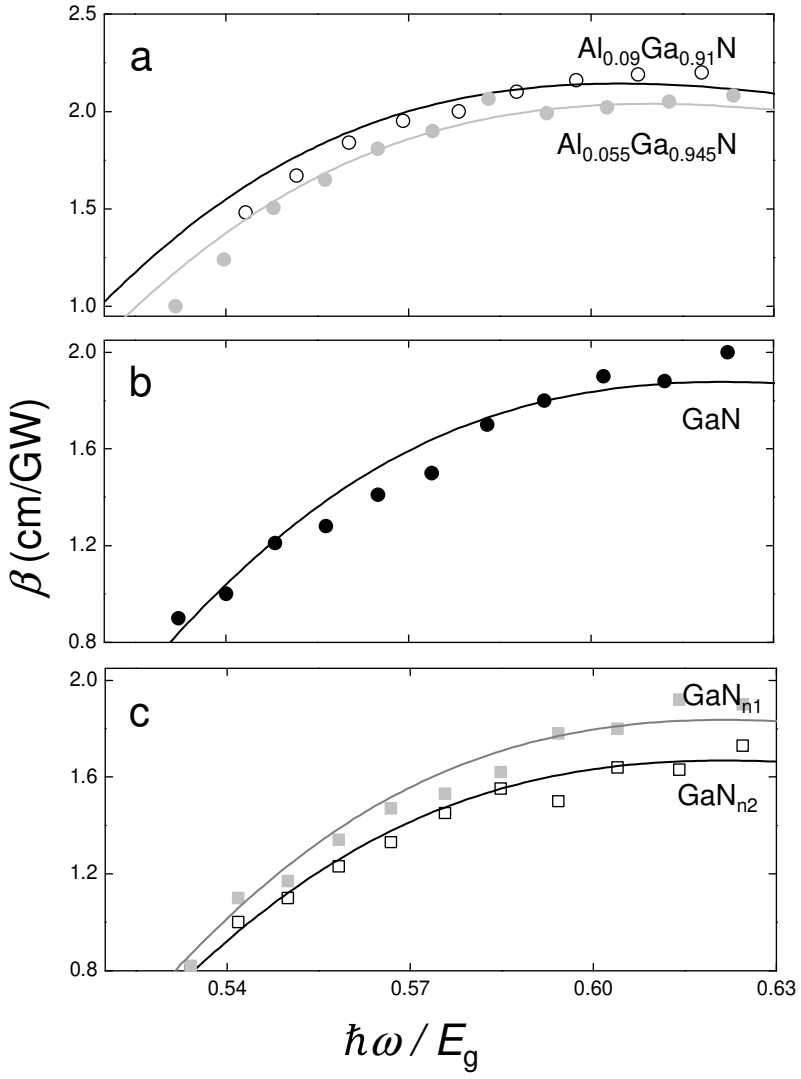

Figure 3: Two-photon absorption coefficient (β) spectra for GaN samples. a) $Al_{0.09}Ga_{0.91}N$ and $Al_{0.055}Ga_{0.945}N$ represented by open and closed circles, respectively. b) GaN unintentionally doped. c) Closed and open squares are the results for GaN_{n1} and GaN_{n2} respectively. The solid lines are the theoretical fits using Brandi-Araujo's model.[29]

To interpret the 2PA coefficient for the different samples, we have employed the Brandi and Araujo model,[29] which provides a universal

description for the frequency dependence of the multi-photon absorption coefficient in solids, considering a linearly polarized field. This model is based on the S matrix formalism and the dipole approximation of the Hamiltonian. For the absorption of two degenerate photons, the 2PA coefficient is given by

$$\beta = \frac{2^{7/2}\pi e^4}{3c^2}\frac{{p_{c,h}}^2\left(\mu^*\right)^{5/2}}{m_0^2 m_e^2 n^2 E_g^{7/2}}\frac{\left(2\frac{\hbar\omega}{E_g}-1\right)^{3/2}}{\left(\frac{\hbar\omega}{E_g}\right)^{15/2}} \quad (1)$$

where *e* is the electron charge, *c* is the speed of light in vacuum, m_0 and m_e^* are the electron rest and the electron effective mass, respectively, *n* is the refractive index and μ* is the reduced effective mass ($\frac{1}{\mu^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$), where m_e^* is the hole effective mass. $p_{c,h}$ is the momentum matrix elements, which give the strength of 2PA transitions.

According to Ref. [30], the electron and hole effective mass for GaN are m_e^* =0.20 m_0 and m_h^*=0.80 m_0, and m_e^* =0.32 m_0 and m_h^*=1.33 m_0 for AlN. From these data, we have estimated the effective mass for the alloys using a linear interpolation function between these values considering the Al concentration, allowing us to determine the values of effective masses for the alloy.[31] The values used to fit the model to our experimental data are given in Table 2.

Table 2 – Effective mass and bandgap energy for the five semiconductors thin films. [31]

Sample	m^*_e	m^*_h	μ*	Band Gap (eV)
$Al_{0.09}Ga_{0.91}N$	0.21	0.86	0.169	3.470
$Al_{0.055}Ga_{0.945}N$	0.2055	0.83	0.165	3.429
GaN	0.20	0.80	0.16	3.376
GaN_{n1}	0.20	0.80	0.16	3.365
GaN_{n2}	0.20	0.80	0.16	3.365

Thus, the only fitting parameter in Eqs. (1) is the transition matrix element ($p_{c,v}$). This parameter is related to the Kane Energy (E_p) through $E_p = \frac{2p_{v,c}^2}{m_0}$.[32]

Therefore, it is possible to determine the E_p value for each sample. Figure 4 shows the results obtained for E_p as a function of the E_g for each sample. As can be observed, the E_p value obtained for the unintentionally doped GaN sample is 19.76 eV. In general, E_p is determined through theoretical calculations employing basically two approaches, i.e., the Hartree-Fork and k·p approximation.[32] Shokhovets and Gobsch [33] compared the imaginary part of the dielectric function of GaN measured by spectroscopic ellipsometry and obtained a value of 19.8 eV for E_p, while Rodina and Mayer [34] also used the k·p for the interband Kane matrix elements and reported a value of 18.7 eV. These values are very close to the experimental result reported here for the intrinsic sample and, therefore, corroborate our 2PA experimental outcomes.

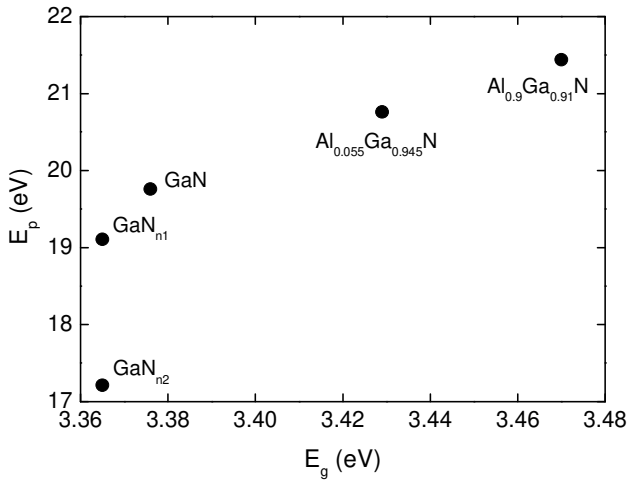

Figure 4: Kane Energy (E_k) as a function of Energy Gap (E_g) for each studied sample.

As the 2PA coefficient is proportional to E_p, it is important to notice that both exhibit the same behavior, i.e., the increase of the impurities decreases E_p and β, leading to a smaller absorption probability. However, for the alloy samples, an increase of the E_p is observed along with the 2PA increase even with E_g increasing, which indicates that the alloying contributes to enhancing the nonlinear polarizability, which is desired for nonlinear optics applications like photonics devices based on semiconductor materials.

IV – FINAL REMARKS

In summary, we have reported an experimental study of the impurities and alloying effects on the 2PA coefficient in GaN and $Al_xGa_{1-x}N$ thin films. Our results showed that for spectral regions far from linear resonance, the 2PA

coefficient increases up to 30 % for the alloy $Al_{0.09}Ga_{0.91}N$ as compared to the pure GaN, while the incorporation of Si impurities decreases β between 10 and 20%. Furthermore, the 2PA spectra were modeled with Brandi and Araujo´s approach showing good agreement between experimental results and theory. Such fitting allows us to determine Kane´s energy parameter, and the values obtained are in excellent agreement (a difference between 5-10% for GaN) with theoretical calculations based on robust models such as the 18×18 band k·p framework.[34] Thus, the results yield important information about the 2PA properties of GaN thin films in a wide spectral range as a function of composition and for different doping concentrations. Such knowledge allows for a proper choice of the material composition when designing photonic devices based on semiconductors.

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