Thermo-optical nonlinearity of GaN grown by metalorganic chemical-vapor deposition

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A study of thermo-optical coefficient (dn/dT) of GaN using spectroscopic ellipsometry is made, and a large thermo-optical nonlinearity near band edge, which increases with increasing temperature, has been observed. Kramers–Kronig transformation has been used to verify our results and a qualitative consistency has been obtained. © *1998 American Institute of Physics.*
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The Group III nitride-based semiconductors have become the most promising material for short-wavelength light-emitting diodes and lasers which are crucial for high density optical read and write technologies,[1] and also have a potential for application to optical nonlinear devices.[2] Optical bistability and related nonlinear phenomena have been well studied in several semiconductors like small band gap materials, such as, InSb,[3] InAs,[4] and CdHgTe,[5] and in bulk GaAs, and GaAs quantum wells.[6] These materials exhibit large nonlinearities of electronic origin at photon energies close to the band gap energy. Thermally induced refractive index changes in semiconductors have also gained increasing interest. Optical bistability has been achieved in this way under band gap resonant conditions in Si,[7] GaAs,[8] ZnSe,[9] and ZnS.[10]

In order to predict accurately the performance of a candidate material for optothermal nonlinear devices, a knowledge of the thermo-optical coefficient (dn/dT) is needed. In this letter, we present the results of the nonlinearity of GaN epilayer grown by metalorganic chemical-vapor deposition (MOCVD), near the absorption edge caused by thermally induced refractive index changes. It is found that this material is having a very large thermo-optical coefficient compared to other semiconductors. Spectroscopic ellipsometry (SE) has been used to determine the refractive indices of GaN layer over a broad wavelength range for different measurement temperatures. The measured parameters of SE, Δ, and Ψ, are extremely sensitive to overlayers on the surface of the material, such as a natural oxide layer or a rough layer, which is a major drawback in the accurate determination of optical constants of studied materials. Fortunately, GaN has a very good chemical stability which makes the oxide layer negligible, and with MOCVD growth technique, a very flat surface can be obtained.

The sample used in the experiment is a 2.4-μm-thick undoped GaN epitaxial layer grown on a mirror polished sapphire (0001) substrate with a low temperature grown 30-nm-thick GaN buffer layer by MOCVD.[11] The material is semi-insulator, and the full width at half maximum of the double crystal x-ray rocking curve is 200 arcsec. The low temperature (4.2 K) photoluminescence was found to be dominated by free A-exciton and B-exciton emissions lines.[11] The thickness of the epilayer is measured by scanning electron microscope. During the SE measurement, the sample has been kept at constant temperature by placing it on a hot plate and the temperature is measured with an W–Re thermocouple. A drop of oil has been used between the contact point of the sample and the probe to have a good thermal contact, since oil has greater thermal mass and heat transfer capability than that of air.

Due to high refractive index of GaN, the interface of GaN with air has a reflection coefficient of about 40%, and the same with sapphire is about 20%, so these interfaces form a Fabry-Perot etalon. When a light beam radiates the sample, the interference effects will be observed. Figure 1 shows the SE data Ψ for two different measurement temperatures, 25 and 160 °C, where shift in the absorption edge and fringes are clearly observed. The SE measurement parameter Ψ is expressed by:[12]

$$\tan \Psi = |R_p|/|R_s|,$$

where,

$$R_i = 1 - \frac{(1-|r_1^i|^2)(1-|r_2^i|^2)}{1+2r_1^i r_2^i \cos \beta + |r_1^i|^2 |r_2^i|^2}, \qquad (1)$$

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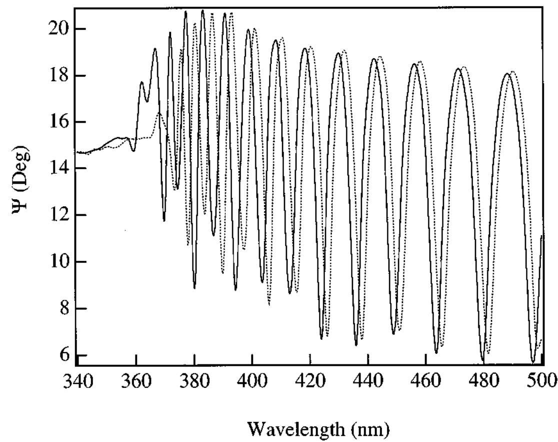

FIG. 1. Solid and dotted lines show the values of Ψ for 25 °C and 100 °C, respectively.

with $i=s,p$. r_1^i and r_2^i are the reflectances at the air/GaN and GaN/sapphire interface, respectively, and β represents the phase difference given by,

$$\beta=\frac{4\pi l(n^2-\sin^2\phi)^{1/2}}{\lambda}, \tag{2}$$

here λ is the wavelength of monochromatic light in air, l and n are the thickness and refractive index of the GaN layer, respectively, and ϕ is the angle of the incidence which is set at 50° in our experiment. The oscillations of the curve arises from the cosine term in Eq. (1).

The basic equation for the interference fringes is[13,14]

$$\beta=m\pi, \tag{3}$$

where m is an even (or odd) integer for maxima and an odd (or even) integer for minima.[13] Therefore, using Eq. (3), the refractive index and thickness of GaN layer can be obtained. In this method the refractive index of the GaN layer can be determined without the necessity of knowing the refractive index of sapphire, since the results are only related with the extreme locations in the interference fringes of SE data Ψ. Owing to absorption, measurement error increases with increasing energy close to band gap energy, and above band gap the interference fringe cannot be clearly seen, which makes it difficult to obtain the refractive index above band gap energy. Figure 2 shows the calculated results of the refractive index for the same three measurement temperatures. The refractive index increases with the increasing temperature, and a large change in refractive index can be observed at photon energies close to the band gap energy. The thickness (2.51 μm) of the GaN also matches closely with that obtained by scanning electron microscopy (SEM). Due to the very small thermal expansion coefficient of GaN ($\Delta a/a = 5.59\times 10^{-6}\ \mathrm{K}^{-1}$), the change in light path length by thermal expansion is one order of magnitude less than the thermo-optical contribution.[15] Therefore, the effect of thermal expansion is neglected in our calculation. Neglecting thermal expansion effect causes an error which can be calculated as following. Let

$$\theta=\lambda\beta, \tag{4}$$

then,

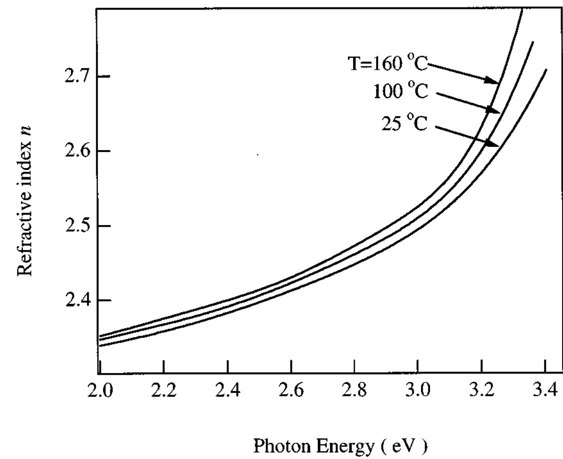

FIG. 2. Refractive index of GaN for different temperatures.

$$\frac{d\vartheta}{dT}=\left(\frac{\partial\vartheta}{\partial n}\frac{dn}{dT}+\frac{\partial\vartheta}{\partial l}\frac{dl}{dT}\right)$$
$$\approx 4\pi nl\left[\left(1+\frac{1}{2}\frac{\sin^2\phi}{n^2}\right)\delta+\left(1-\frac{1}{2}\frac{\sin^2\phi}{n^2}\right)\gamma\right], \tag{5}$$

where δ is the temperature coefficient of the refractive index, $1/n\ dn/dT$, and γ is the thermal expansion coefficient $1/l \times dl/dT$. For a particular SE angle ϕ and a change in measurement temperature ΔT, all the parameters in the above equation can be determined from the shift in the peak position in the Ψ spectra and using Eqs. (3) and (5). The effect of thermal expansion coefficient γ on δ can then easily be obtained which is found to cause an error of around 1%–4% near the band edge and around 20% in the long wavelength region.

Refractive index n is measured for varying temperature conditions in the vicinity of two temperature regions, 25 °C and 100 °C. The derivative of n, $dn(h\nu)/dT$, at the two temperature regions are obtained from the n vs T plots. The temperature dependence of GaN thermo-optical coefficient $dn(h\upsilon)/dT$ in the band edge region is shown in Fig. 3. The value of $dn(h\nu)/dT$ increases with increasing temperature, which results from the shrinkage of band gap with temperature. At room temperature, GaN demonstrates a very large

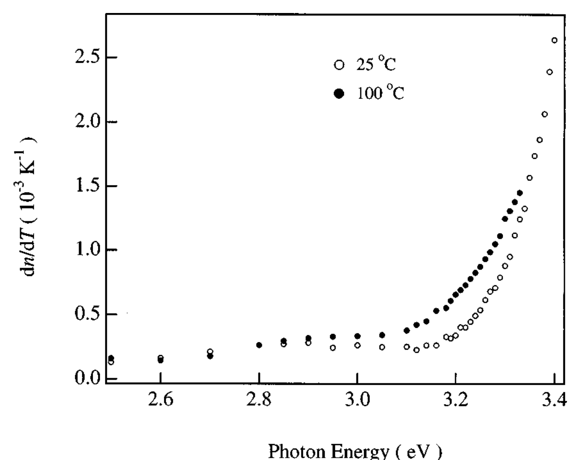

FIG. 3. Thermo-optic coefficient of GaN in the band edge region for different temperatures.

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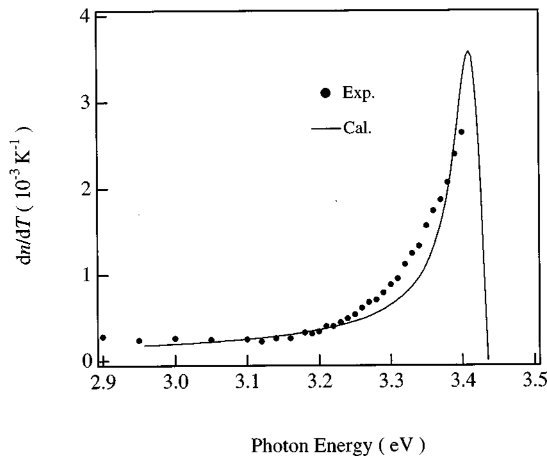

FIG. 4. Photon energy dependence of thermo-optical coefficient of GaN. In the calculation of the solid line, the experimentally obtained absorption coefficients (smoothed and interpolated for calculation) were used.

thermo-optical coefficient (2.6×10^{-3} K^{-1}) at 0.365 μm, compared to other semiconductors for which the thermal dispersive bistability has been reported e.g., Si: 2.4×10^{-4} at 1.06 μm;[7] GaAs: 7×10^{-4} at 0.85 μm;[8] ZnS: 1.4×10^{-4} at 0.514 μm,[10] and ZnSe: 5×10^{-4} at 0.476 μm.[9] Also, at long wavelength (2.5 eV), the value of 5.4×10^{-5} K^{-1} for $(1/n)$ dn/dT obtained is twice as large as that reported by Ejder[16] (5.4×10^{-5} K^{-1}) at long wavelength, measured at below room temperature. An empirical relation was proposed by Moss[17] for the temperature dependence of n in long wavelength region,

$$\frac{dn}{dT}=n\,\frac{1}{4E_g}\,\frac{dE_g}{dT}, \tag{6}$$

where E_g is the band gap energy. Inserting a value of 6.7×10^{-4} eV/K^{-1} (Ref. 18) for dE_g/dT and using $E_g=3.42$ eV,[19] a value of 4.9×10^{-5} K^{-1} is obtained for $(1/n)$ dn/dT, which is close to our experimental result. The large thermo-optical coefficient near the band gap energy may be caused by a steep band gap absorption edge of GaN.

Close to the band gap edge, the nonlinear index is determined by the temperature dependence of the edge itself and the background thermo-optical coefficient is given as follows:[15]

$$\frac{dn}{dT}=\frac{\partial n}{\partial E_g}\,\frac{\partial E_g}{\partial T}+\left(\frac{\partial n}{\partial T}\right)_b. \tag{7}$$

The coefficient $\partial n/\partial E_g$ can be obtained by using a Kramers–Kroning transformation of the band gap edge absorption,[15]

$$\Delta n(h\nu)=\frac{\hbar c}{\pi}\int_0^{\infty}\frac{\alpha(E_g+\Delta E_g)-\alpha(E_g)}{(h\nu')^2+(h\nu)^2}\,d(h\nu'). \tag{8}$$

The measured values of dn/dT may be qualitatively compared to the calculated results of Kramers–Kroning transformation as a consistency check. For this purpose, absorption coefficient, α, of GaN has been taken from Ref. 14. and a rigid shift in the absorption coefficient spectrum with the change of band gap due to increasing temperature has been assumed with $\partial E_g/\partial T$ taken to be 0.67 meV K^{-1}. The experimental (25 °C) and calculated results are shown in Fig. 4. The integral is truncated at $E=2.95$ eV and $E=3.54$ eV since the values of $\Delta\alpha$ outside this region are negligible and; thereby, they will not contribute to the integral. A reasonably good qualitative agreement has been observed.

In summary, the thermo-optical coefficient (dn/dT) of GaN is obtained with SE technique. The experimental results demonstrate very large thermo-optical nonlinearity for this material at the band gap edge which increases with increasing temperature. Using Kramers–Kronig transformation, the theoretical value of dn/dT has been calculated and a good consistency with the experimental results has been obtained.

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