行政院國家科學委員會專題研究計畫 期中進度報告

雷射技術及時析光譜研究奈米光電材料與結構之研究(第 2 年)
期中進度報告(精簡版)

計 畫 類 別 ：個別型
計 畫 編 號 ：NSC 96-2628-E-009-018-MY3
執 行 期 間 ：97 年 08 月 01 日至 98 年 07 月 31 日
執 行 單 位 ：國立交通大學光電工程學系(所)

計 畫 主 持 人 ：謝文峰

處 理 方 式 ：期中報告不提供公開查詢

中 華 民 國 98 年 06 月 07 日

行政院國家科學委員會補助專題研究計畫□ 成 果 報 告 X期中進度報告

雷射技術及時析光譜研究奈米光電材料與結構之研究(2/3)

計畫類別：X 個別型計畫　　□ 整合型計畫
計畫編號：NSC 96-2628-E-009 -018 -MY3

執行期間： 96年08月01日至 99年07月31日

計畫主持人：謝文峰
共同主持人：
計畫參與人員：吳靜娜、許智章、歐伯濟、陳厚仁、黃宗櫃。
成果報告類型(依經費核定清單規定繳交)：X精簡報告　□完整報告

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中　華　民　國 98 年 6 月 6 日

行政院國家科學委員會專題研究計畫成果報告

雷射技術及時析光譜研究奈米光電材料與結構之研究(2/3)

計畫編號：NSC 96-2628-E-009 -018 -MY3

執行期限：97 年 8 月 1 日至 98 年 7 月 31 日

主持人：謝文峰教授　　國立交通大學光電工程系

一、中文摘要

我們利用倍頻飛秒鈦藍寶石雷射為光源，以Z掃描法研究由雷射MBE成長的氧化鋅薄膜。由於近激子共振，我們觀察到相當大的雙光子吸收(TPA)增強效應，在390 nm波長激發下，約為3000 cm/GW，這個數值為我們以前報導的在近紅外區雙光子近激子共振數值的6.5倍，並為以532 nm 波長量測塊材的結果之710倍。除此之外，在接近激子共振之情快下，由線性吸收和非線性吸收所貢獻之自由載子吸收變得很重要。

關鍵詞：非線性光學、半導體材料、非線性光學材料、超快量測。

Abstract

Nonlinear optical absorption of ZnO thin film grown by the laser molecular beam epitaxy was investigated by the Z-scan method using a frequency-doubled femtosecond Ti:sapphire laser. Due to near-exciton resonance, an enormous enhancement of two photon absorption (TPA) is about 3000 cm/GW at 390 nm which is about 6.5 times larger than the previously reported at two-photon exciton resonance in near-IR regime and 710 times larger than that of ZnO bulk measured at 532 nm. Besides, the free-carrier absorption resulting from linear absorption and TPA becomes essential when the excitation approaches the exciton resonance.

Keywords: Nonlinear optics, Semiconductor materials, Nonlinear optical materials, Ultrafast measurements.

二、緣由與目的

ZnO, a kind of II-VI compound semiconductor, has been a potential candidate of ultraviolet (UV) photonic devices due to its wide bandgap of 3.37 eV and a relative large exciton binding energy (E_b) of about 60 meV at room temperature (RT), which is much higher than that of ZnSe (20 meV) and GaN (27 meV). The high exciton binding energy permits excitonic recombination even at RT that can be a potential candidate for UV laser diode [1]. Besides, research on the photoluminescence (PL) properties of ZnO nanostructures has shown that, under high excitation conditions, exciton-exciton scattering as well as the recombination of electron-hole plasma is the key process leading to stimulated emission and lasing [2]. These studies demonstrated the potential of using ZnO to fabricate RT UV laser [3]. Because of these potential applications, extensive research efforts have been made on the basic physical properties of ZnO. A comprehensive review on the synthesis, mechanical, chemical, thermal and optical properties of ZnO may be found in Ref. [4].

In addition to the application in UV photonic devices, the nonlinear optical properties of

ZnO such as the second-harmonic generation (SHG) and the third-harmonic radiation [5-7] are also attractive and have been investigated. The nonlinear refraction and the two photon absorption (TPA), belonging to the third order nonlinearity, have been measured by the Z-scan method with nanosecond and picosecond visible light [8] and femtosecond near-IR [9]. The nonlinear processes induced by TPA-excited charge carriers [10] and the multi-photon absorption (including two photon and three photon absorption) induced PL emission of ZnO under intense femtosecond excitation [11] had been reported. With the different effects on photonic devices, enhancement of optical nonlinearity on ZnO was also studied in various situations such as at two-photon exciton resonance [9] and at distinct interfacial state [12].

The exciton could enhance the nonlinear absorption when the excitation photon energy equals to the exciton transition energy as reported in GaN thin film [13]. Because of the larger exciton binding energy of ZnO than that of GaN, one would expect observing similar resonant behaviors in ZnO thin film at RT. Although we have observed two-photon resonance to exciton by enhancing TPA coefficient [9], the nonlinear properties in near UV regime are seldom reported. For this reason, in this paper we focus on the optical nonlinear absorption of ZnO thin film near resonant to its band-gap by using the Z-scan method. Due to the near-resonant excitation, enhancement of TPA and high-order nonlinearity such as free carrier absorption (FCA) was observed.

三、研究方法與步驟

Our ZnO film was grown on a fused silica substrate by laser molecular beam epitaxy (MBE). To obtain the

linear optical absorption coefficients α at different wavelengths, we first measured the transmittance and reflectance spectra using a Lambda 950 spectrometer (PerkinElmer Inc). The schematic setup of the standard degenerate Z-scan measurement is shown in Fig. 1. A commercial Ti:sapphire laser (Tsunami, Spectra-Physics Inc.) with 100 fs pulsewidth and 82MHz repetition rate was used as the excitation source. After frequency doubling (SpectraPhysics No. 3980) the near-IR wavelength was converted into UV wavelength from 390 nm to 420 nm with pulse width ~ 200 fs. The input irradiances I_0, the on-axis irradiance at focus (i.e., z = 0), can be estimated by knowing the incident average power, the pulse width, and the beam waist w_0, which is obtained from the Rayleigh range z_0 by fitting the Z-scan trace [14].

The incident light was then chopped by a chopper before it was divided into two beams by a beam splitter. The reflected beam was detected by a photodiode as the reference. The transmitted beam, being the excitation light, was focused into the sample by a 4x objective lens with focal-length of ~ 20 mm and detected by another photodiode. The tested sample was mounted on a step-motor and moving along the Z-axis. The electric signals from the two photodiodes were connected to a lock-in amplifier (Stanford Research SR830) to enhance the signal-to-noise ratio. The nonlinear absorption coefficient can be obtained when the aperture was completely opened to obtain the open aperture z-scan trace (S = 1). Besides, the FCA, an effective fifth-order nonlinearity, in which the free carriers were generated by TPA, can be investigated by an irradiance-dependent Z-scan measurement. A wavelength-dependent Z-scan will be also presented for the resonance behaviors.

四、結果與討論

The transmission and the reflection (in the inset) spectra of ZnO thin film were shown in Fig. 2(a) illustrate obvious interference fringes. By the fitting to these fringes [15], we can acquire the thickness L of the ZnO thin film to be ~ 4.3 μm. Besides, an extra peak at 380 nm in the reflection spectrum results from the exciton resonant emission that matches with our previously reported PL spectrum [9]. By using the equation: $T = (1-R)^2 exp(-\alpha_0 L)$, where T is the transmittance and R is the reflectance, we obtained the linear absorption coefficients α_0 between 420 nm and 390 nm ranging from 5147cm^{-1} to 7338cm^{-1}. Figure 2(b) is a plot of $(\alpha_0 h\nu)^2$ versus photon energy $h\nu$. By extrapolating the curve to the relation [16]: $\alpha_0 h\nu = A(h\nu - E_g)^{1/2}$, to intercept the abscissa (dashed line), we got the band gap energy E_g ~ 3.24 eV, where A is a constant. The obtained band gap energy seems to a little bit deviate from the theoretical value that may be due to defect induced long-range band tailing, which extends the absorption tens of nanometers to below 420 nm in Fig. 2(b).

The normalized transmittance of the open aperture z-scan trances for the sample at different input irradiances I_0 under fs-pulse excitation centered at λ =390 nm were shown in Fig. 3(a). Due to large nonlinear absorption, the z-scan traces reveal obvious and symmetric dips around the focal point (z = 0). The normalized transmittance increases from 0.04 to 0.37 as the peak irradiance increases from 0.154 to 0.634 GW/cm^2. Similarly, the intensity dependent normalized transmittances at 420 nm were shown in Fig. 3(b). Under low intensity, a peak instead of a dip was observed due to the saturation of the linear absorption from ZnO defect states that are located in the band tailing region as shown in Fig. 2(b). As the laser intensity increased, the TPA and FCA effects became dominant and dip started to appear again. One would have doubted that why the similar effect were not observed for the excitation wavelength of 390 nm, which is also located within the band tailing region. It may be due to the relatively large nonlinear absorption occurs even at low intensity so that a dip rather than a peak can be seen in Fig. 3(a).

In order to acquire TPA coefficient of the material, the traditional fitting equation for open-aperture Z-scan trace developed by Sheik-Bahae et al. [14] is generally used to fit the normalized transmittance. However, it is only suitable for $|q_0| < 1$, where $q_0 = \beta I_0 L_{eff}$ is equivalent to the strength of nonlinear absorption with $L_{eff} = [1-e^{-\alpha L}]/\alpha_0$ and β being the nonlinear absorption coefficient. In our situation, when the pump wavelength was used close to band gap energy, the nonlinear absorption is too strong to guarantee $|q_0| < 1$. Therefore, we obtained the Rayleigh range z_0, so as the corresponding beam waist w_0 ($z_0 = \pi w_0/\lambda$ with λ being the excitation wavelength), no longer being a constant. Using the resultant w_0 to calculate the peak irradiance would lead to large errors in the calculation of nonlinear absorption coefficient, which runs away from the linearly increase of I_0, shown as square symbols in Fig. 4(a). Therefore, the modified model considering the higher order nonlinear absorption [17] has to be used to analyze our results.

Similar to nonlinear refraction [18], the free carrier absorption (FCA) resulting from two-photon excitation behaves as an effective fifth-order nonlinear absorption [19]. As a result, when a Gaussian beam propagates through a thin sample with a physical length L, the optical loss can be described by

$$\frac{dI}{dz'} = -(\alpha_0 + \beta_0 I + \sigma_a N)I, \qquad (1)$$

where z' accounts for coordinate within the sample, α_0 is again the linear absorption coefficient, σ_a is the

cross-section of free carrier absorption, β_0 is the TPA coefficient, and N is the carrier density. In our measurements, the excitation wavelength (390 to 420 nm) is in the band tailing region near the band edge of ZnO; therefore, the contribution of linear absorption for free carrier generation should be considered [20]. Thus, the photo-generated carrier concentration can be expressed by

$$\frac{dN}{dt} = \frac{\alpha_0 I}{h\omega} + \frac{\beta_0 I^2}{2h\omega}. \quad (2)$$

Integrating Eq. (2) to obtain

$$N \cong \frac{\alpha_0 I}{h\omega}\tau_a + \frac{\beta_0 I^2}{2h\omega}\tau_a, \quad (3)$$

where τ_a is the lifetime of free carrier. When the pulse duration of laser τ_p is shorter than τ_a, τ_a in Eq. (3) should be replaced by τ_p. By substitution Eq. (3) into Eq. (1) to rewrite

$$\frac{dI}{dz'} = -[\alpha_0 + (\beta_0 + \frac{\sigma_a \alpha_0 \tau_p}{h\omega})I + (\frac{\sigma_a \beta_0 \tau_p}{2h\omega})I^2]I = -[\alpha_0 + \beta_{eff} I]I. \quad (4)$$

The effective TPA coefficients β_{eff} can be expressed as $\beta_{eff} = \beta + DI$. Here, the effective third order nonlinearity β can be expressed as

$$\beta = \beta_0 + \beta_1, \quad (5)$$

$\beta_1 = \frac{\sigma_a \alpha_0 \tau_p}{h\omega}$ represents the contribution of FCA induced by the linear absorption, and the effective fifth-order nonlinearity can be expressed as

$$D = \frac{\sigma_a \beta_0 \tau_p}{2h\omega}. \quad (6)$$

And $\beta_2 = DI$ represents the contribution of FCA induced by TPA.

Solving Eq. (4) integrating it spatially and temporally, using the highly efficient Simpson arithmetic, an analytic expression of nonlinear transmission $T(z)$ were obtained by [17] as:

$$T(z) = \frac{\ln(1+q)}{q} \frac{\ln[(1+p^2)^{1/2} + p]}{p} f(q, p), \quad (7)$$

where

$$f(q, p) = \frac{[\sum_{n=0}^{5} a_n p^n + q\sum_{n=0}^{5} b_n p^n]}{[1 + q\sum_{n=0}^{5} c_n p^n]} \quad (8)$$

q and p are given by $q = q_0/(1+z^2/z_0^2)$ and $p = p_0/(1+ z^2/z_0^2)$, with $q_0 = \beta I_0 L_{eff}$ and $p_0 = (2DI_0^2 L'_{eff})^{1/2}$ being the on-axis peak phase shifts caused by the third and the fifth-order nonlinear absorption processes, respectively, and $L'_{eff} = [1 - e^{-2\alpha_0 L}]/2\alpha_0$. When considering laser pulses having both the temporal and the spatial Gaussian profiles, the coefficients a_n, b_n, and c_n are listed in Table I of Ref. [17].

For the pure TPA ($D = 0$), the nonlinear transmission can be calculated using the following formula:

$$T(z) = \frac{(a_0 + b_0 q)\ln(1+q)}{q(1 + c_0 q)} \quad (9)$$

Therefore, the effective two photon coefficient β_{eff} can be obtained by fitting Eq. (9) to the Z-scan traces. The plots of effective two photon coefficient β_{eff} versus the input intensity at 390-420 nm were shown in Figs. 4(a) and 4(b). Instead of a constant value in the near-IR region [9], β_{eff} increases linearly following the input intensity and the slope increase seriously as the excitation close to the band-edge of ZnO. It suggests that the sample should exhibit FCA, which could be treated as an effective fifth-order nonlinearity arising from TPA-generated carriers [18] other than TPA. As reported [21, 22], the free carriers are generated while the laser pulsewidth is close to the lifetime of free carriers. A TPA assisted excited state absorption has been previously reported for Au nanoparticles using 7 ns pulse duration excitation at 532 nm [23]. Besides, the relative high input intensity and the pump wavelength closing to the band gap of the material can cause material to generate large linear and two photon absorption so that it results in FCA [20]. Although the lifetime of free carrier in ZnO is 2.8 ns [8], which is far longer than our femtosecond pulsewidth (about 200 fs), the peak power is high enough to excite a large number of electrons into conduction band by TPA.

When the excitation wavelength is set close to the bandgap energy of ZnO, the FCA obviously increases. Therefore, the linear relationship between β_{eff} and I_0 display in Figs. 4(a) and the slope decreases evidently as lowering the excitation photon energy. As we further lower excitation energy, we observed $®_{eff}$ deviates from

the expected straight line at the low excitation intensity as shown in Fig. 4(b). This phenomenon might be due to dominant saturation of linear absorption over TPA in the band tailing region near the band edge as seen in Fig. 2(b). The saturation of linear absorption would function as an effective negative TPA coefficient and that will result in the reducing of net value of effective TPA coefficient. As expected, the absorption saturation at 410 nm is more serious than that at 420 nm because it is closer to the bandgap. Using an input irradiance of 0.1 GW/cm2, the magnitude of β_{eff} obtained from the normalized transmittance to be -5419 (cm/GW) and -3118 (cm/GW) at 410 nm and 420 nm, respectively. Therefore, at low intensity, the reduction at 410 nm is greater than that at 420 nm as shown in Fig. 4(b). However, when the excitation intensity increases, the contribution of TPA and FCA became domination and the influence of saturation of linear absorption can be neglected. Therefore, at the higher excitation intensity, the obtained values of β_{eff} in use of center wavelength of 410nm are larger than that using 420nm excitation.

To acquire the intrinsic TPA coefficient more accurately, we utilized the nonlinear transmission measured at the focal point by setting $z = 0$ in Eq. (7) to obtain the nonlinear transmission $T(0)$ as

$$T(0) = \frac{\ln(1+q_0)}{q_0} \frac{\ln[(1+p_0^2)^{1/2} + p_0]}{p_0} f_0, \qquad (10)$$

and

$$f_0 = \frac{[\sum_{n=0}^{5} a_n p_0^n + q_0 \sum_{n=0}^{5} b_n p_0^n]}{[1 + q_0 \sum_{n=0}^{5} c_n p_0^n]}. \qquad (11)$$

The dependence of the normalized transmission $T(0)$ on the input irradiance I_0 for the pump wavelength 420 nm as an example were obtained from the open aperture Z-scan traces and illustrated by solid squares in Fig. 5. The solid line is the fitting result by using Eq. (10) to extract both parameters β and D, which indicated β = 604 (cm/GW) and D = 0.21 (cm^3/GW^2).

Thus, the cross-section of free carrier absorption σ_a and intrinsic TPA coefficient β_0 can be obtained in use of the Eqs. (5) and (6) and taking the pulse width τ_p to be 200 fs. Using the similar approach, we calculated the coefficients σ_a and β_0 between 390 nm and 420 nm and listed in Table I, in which the value of β_2 is calculated by multiplying D by I_0 = 1.6 GW/cm2. From Table I, we know the contribution of FCA induced by both the linear absorption β_1 and TPA β_2 was puny compared with ®0 due to the small value of σ_a and D. In addition, the increasing tendency of the slope as the excitation wavelength became shorter in Fig. 4 that is consistent with the increase tendency of D at short wavelength in Table I. We also found that the value of σ_a increases when the pump wavelength approaches the band edge.

In order to investigate all the variation of TPA coefficient of ZnO thin film in the region of near-UV and IR, we combined all the data including those excited in near IR region from Ref. [9] in Fig. 6, in which the open squares represent previous measured results and the solid squares represent the data in this work. According to Ref. [9], the enhancement at $(E_g-E_b)/2$ was observed due to the resonance of exciton energy of ZnO as the incoming photon energy at 760 nm. When the pumping wavelength is approached to the exciton resonance, the value of the β_0 coefficient reveals an enhancement about 5 times from 599 (cm/GW) at 420nm to 2975 (cm/GW) at 390 nm. Due to near-exciton resonance, the value of the β_0 coefficient at 390 nm is about 6.5 times larger than the previously reported at two-photon exciton resonance. This near-exciton enhancement behavior have been reported in GaN thin films [13], in which the TPA coefficient reveals an enhancement factor > 100 from the off-resonance region about 15(cm/GW) to 1500 (cm/GW) near resonance. Furthermore, comparing with the results of Ref. [8], in which β_0 = 4.2cm/GW was measured in 1 mm ZnO single crystal at a pump wavelength of 532 nm, we found the TPA coefficient at near exciton resonance of this ZnO thin film is enhanced more than a factor of 710.

五、結論

High-order optical nonlinear absorption of ZnO thin film made by the laser MBE were investigated by the Z-scan method using a frequency-doubled femtosecond Ti:sapphire laser with wavelength near UV. A modified method considering high order nonlinearity was used to calculate various nonlinear coefficients including intrinsic TPA coefficient and FCA cross section by the linear absorption and TPA. It reveals serious large enhancement of TPA coefficient when the photo-excitation energy approaches the excitonic transition energy. The TPA coefficient of about 3000 cm/GW is 6.5 times larger than that measured at two-photon exciton resonance in IR regime and is 710 times larger than that of ZnO bulk measured at 532 nm. Besides, in the near band edge region, the occurring of the FCA due to the enhanced TPA coefficients result in the effective

two photon absorption coefficient become intensity dependent.

六、自我評估

本年度計畫中我們進行兩部分光電物理之研究，分別為氧化(鎂)鋅薄膜與量子點之成長與光電性質研究和光子晶體波導之理論探討等。我們利用雷射濺鍍與 sol-gel 法成功地成長氧化(鎂)鋅薄膜與量子點等。成長之樣品我們分別研究，激子—聲子之交互作用、螢光、受激輻射與雷射現象、拉曼散射等等。在光子晶體波導研究方面，我們以緊束縛原理首次成功地解釋光子晶體波導的偶合與不偶合現象。這一年來共發表 12 篇光電材料相關的 SCI 論文， 以及雷射動力學相關研究 SCI 論文計 3 篇，成果還算不錯。

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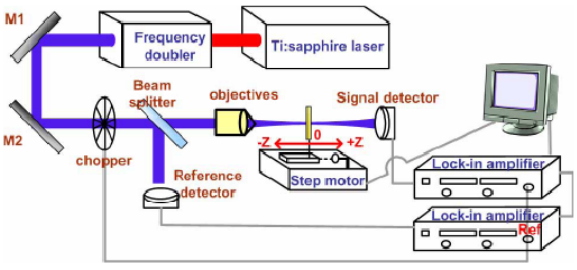

Fig. 1. The Z-scan apparatus with reference detector and lock-in amplifier to minimize background and maximize the signal-to-noise ratio respectively.

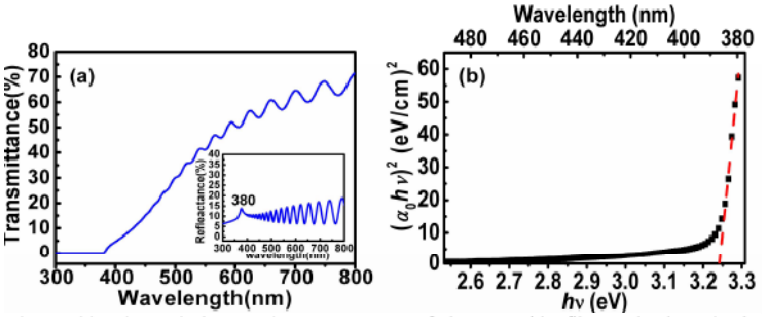

Fig. 2. (a). The optical transmittance spectrum of the ZnO thin film. The inset is the reflectance spectrum. (b) Plot of $(\alpha_0 h\nu)^2$ versus energy.

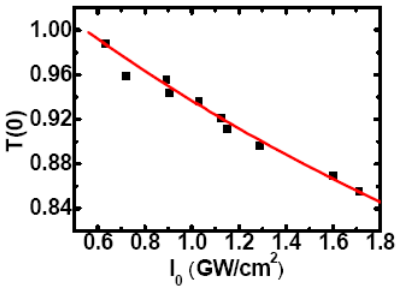

Fig. 5. The nonlinear transmission measurement

at focal point (Z=0) for the pump wavelength 420 nm.

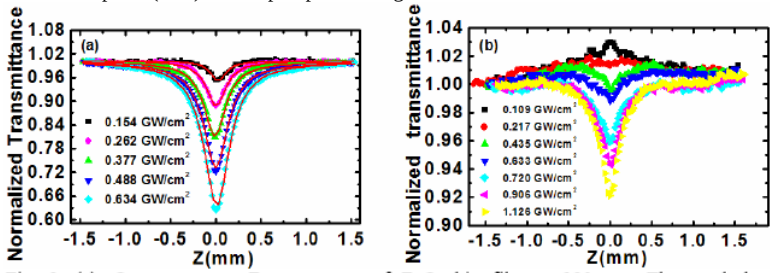

Fig. 3. (a). Open aperture Z-scan traces of ZnO thin film at 390 nm. The symbols are experimental data and the solid lines are theoretically fitting curves by modified theory. (b) .Open aperture z-scan traces of ZnO thin film under different input intensity at 420 nm.

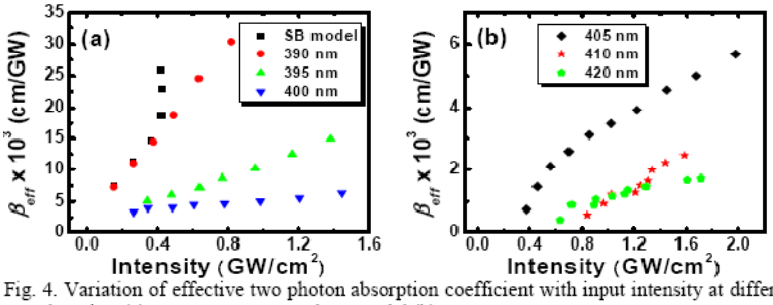

Fig. 4. Variation of effective two photon absorption coefficient with input intensity at different wavelengths. (a) 390 nm-400 nm and SB model (b) 405 nm-420 nm

Figure 4. The carrier lifetime versus peak