Title	Effects of free electrons and quantum confinement in ultrathin ZnO films : a comparison between undoped and Al-doped ZnO
Author(s)	Li, X. D.; Chen, Tupei; Liu, P.; Liu, Y.; Leong, K. C.
Citation	Li, X. D., Chen, T., Liu, P., Liu, Y., & Leong, K. C. (2013). Effects of free electrons and quantum confinement in ultrathin ZnO films: a comparison between undoped and Al-doped ZnO. Optics express, 21(12), 14131-14138.
Date	2013
URL	http://hdl.handle.net/10220/11859
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Effects of free electrons and quantum confinement in ultrathin ZnO films: a comparison between undoped and Al-doped ZnO

X.D. Li,[1] T. P. Chen,[1,*] P. Liu,[1] Y. Liu,[2] and K. C. Leong[3]

[1]*School of Electrical and Electronic Engineering, Nanyang Technological University, 639798 Singapore*
[2]*State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology, Chengdu 610054, China*
[3]*GLOBALFOUNDRIES Singapore Pte Ltd, 738406 Singapore*
[*]*echentp@ntu.edu.sg*

Abstract: Band gaps and exciton binding energies of undoped and Al-doped ZnO thin films were determined from optical absorption measurement based on the Elliott's exciton absorption theory. As compared to the undoped films, the doped films exhibit a band gap expansion and a reduction in the exciton binding energies due to the free electron screening effect, which suppresses the excitonic absorption and results in a blue shift of the absorption edge. The undoped and doped films show the same quantum size dependence, i.e. both the exciton binding energies and band gap energies increase with decreasing grain size of the oxides.

OCIS codes: (310.6860) Thin films, optical properties; (310.6188) Spectral properties; (300.1030) Absorption; (260.7190) Ultraviolet.

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Zinc oxide (ZnO), which has a direct wide band gap (~3.4 eV) and large exciton binding energy (~60 meV), has attracted much attention because of its promising applications in optoelectronics [1, 2]. Nominally undoped ZnO is an n-type semiconductor with carrier concentration of $10^{16} – 10^{17}$ cm^{-3} due to the presence of intrinsic or extrinsic defects, which were generally attributed to native defects, such as the Zn-on-O antisite, the Zn interstitial, and the O vacancy [2]. Al-doped ZnO (ZnO:Al or AZO) has recently emerged as an important transparent conductive oxide (TCO), which can be used as transparent electrodes for optoelectronic devices such as thin film solar cells and flat-panel display. AZO is also an n-type semiconductor; its carrier concentration is usually in the range of 10^{19} - 10^{21} cm^{-3} [3]. With such high concentration of free electrons, excitonic absorptions could be significantly supressed by the free-electron screening [4, 5]; in addition, when the carrier concentration in the oxide exceeds the Mott critical density (10^{18}–10^{19} cm^{-3} in ZnO), a semiconductor-to-metal transition occurs and conduction band filling with free electrons shifts the onset of band-edge absorption towards higher energies (Burstein-Moss shift) [6, 7]. The suppression of excitonic absorptions and Burstein-Moss shift due to high concentration of free electrons could significantly alter the optical properties, in particular, the absorption spectrum in the region near the band gap energy. The situation is further complicated as carrier concentration has a strong dependence on the film thickness [6, 8]. On the other hand, it has been reported that quantum confinement effect has a significant impact on the optical properties of ZnO thin films [9]. Quantum confinement effect on the optical properties is insignificant for thicker film (e.g. >100 nm). However, for optical devices with ultra-thin films (e.g. <50 nm), it could be very significant. The quantum confinement effect is mainly related to the small sizes (a few nanometers) of the grains in ZnO thin films. In a confined semiconductor nanostructure, the confinement can lead to an increase in both the band gap energy [10, 11] and exciton binding energy [12]. Although the undoped and Al-doped ZnO thin films could have the same or very similar structural properties, whether they exhibit the same quantum confinement behaviours remains a question as their carrier concentrations are different.

In this work, a comparison of the free-electron screening effect and quantum confinement effect between the undoped ZnO and AZO is conducted. The undoped ZnO thin films show strong excitonic absorptions at room temperatures; while the excitonic absorptions are greatly suppressed in AZO. As compared to the undoped ZnO, the AZO films exhibit an expansion in the band gap and a reduction in the exciton binding energies due to the free electron screening effect. On the other hand, the undoped ZnO and AZO thin films show the same quantum size dependence as a result of quantum confinement effect, i.e. both the exciton binding energies and band gap energies increase with decreasing grain size of the oxides. The quantum confinement effect on the optical properties is very significant for the ultra-thin films, e.g., as compared to the undoped ZnO film with the thickness of 90 nm, the undoped ZnO film with

the thickness of 20 nm shows an increase of ~40% in the absorption coefficient at 3.6 eV, an increase of ~35 meV in the exciton binding energy and an increase of ~0.1 eV in the bandgap energy. Therefore, it is important to consider the quantum confinement effect on the optical properties when an ultra-thin ZnO film is used in optoelectronic and photonic applications.

The undoped ZnO and AZO thin films were deposited on quartz substrates by RF magnetron sputtering of a pure ZnO target (99.99% purity) and an AZO target (2% Al_2O_3, 99.99% purity), respectively, under the same deposition condition. The chamber was pumped down to 7×10^{-6} Torr prior to the deposition process. The sputtering deposition was carried out at room temperature in argon ambient with the background pressure of 9×10^{-3} Torr, and the RF power was maintained at 80 W. The pure argon environment was to ensure that the influence of oxygen on the structural and optical properties of the deposited films is minimized [13, 14]. The thicknesses of the as-deposited films for both the undoped ZnO and AZO were 20, 40, 90 and 185 nm, as determined by spectroscopic ellipsometry (Woollam VB-250). The crystalline structures of the thin films were characterized by X-ray diffraction (XRD) (Siemens D5005) using Cu Kα radiation (40kV, 40mA) in the θ–2θ geometry; and the film surface morphology was investigated by using scanning electron microscope (SEM) (LEO 1550 Gemini). Optical absorbance measurement was carried out with an UV-Vis spectrophotometer (Perkin-Elmer 950) in the wavelength range of 250-800 nm.
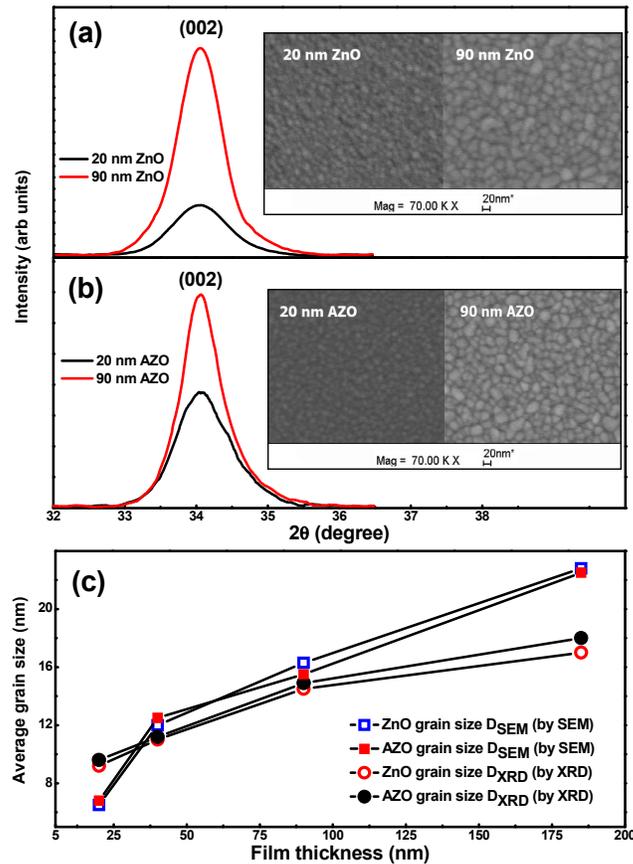

Fig. 1. XRD measurements and SEM images of the undoped ZnO (a) and AZO films (b) with the thicknesses of 20 nm and 90 nm; and c) average grain sizes of the undoped ZnO and AZO films estimated from the XRD and SEM measurements as a function of film thickness.

Figure 1(a) shows the XRD and SEM measurements of the 20 nm and 90 nm undoped ZnO thin films; and Fig. 1(b) shows the same measurements of the 20 nm and 90 nm AZO thin films. The XRD patterns indicate the polycrystalline growth of wurtzite structure along (002) direction. The average sizes of the grains in the oxide thin films can be estimated from the broadening of the Bragg peak in the XRD patterns based on the Scherrer's equation [15]. The estimated grain size D_{XRD} as a function of the film thickness for both undoped ZnO and AZO thin films is shown in Fig. 1(c). The in-plane average grains size D_{SEM} estimated from the SEM images as a function of film thickness for both undoped ZnO and AZO thin films is shown in Fig. 1(c) also. As can be observed in Fig. 1(c), the D_{SEM} is generally comparable with the D_{XRD}.
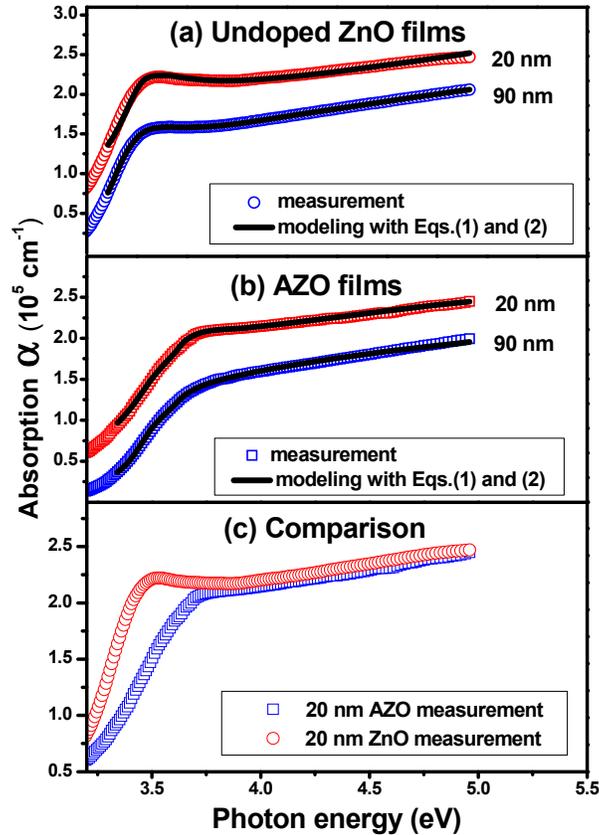

Fig. 2. Absorption spectra of the undoped ZnO (a) and AZO films (b) with the thicknesses of 20 nm and 90 nm; and (c) comparison of the absorption between the undoped ZnO and AZO for the thickness of 20 nm. The modeling based on Eqs. (1) and (2) for the undoped ZnO and AZO films is shown in the figure also.

Figures 2(a) and 2(b) show the absorption spectra in the UV-visible range at room temperature of the undoped ZnO and AZO thin films, respectively, with the thicknesses of 20 nm and 90 nm; and Fig. 2(c) shows the comparison of the absorption between the undoped ZnO and AZO for the thickness of 20 nm. It can be observed from Fig. 2 that there is remarkable difference in the absorption spectrum between the undoped ZnO and AZO thin films and the film thickness has a significant impact on the absorption also. The difference between the undoped ZnO and AZO can be attributed to the large difference in the carrier concentration. As shown in Fig. 2(a) for the undoped ZnO thin films, a broaden absorption

peak is observed at ~3.5 eV, which is attributed to the excitonic absorptions. In contrast, as shown in Fig. 2(b), such peak is not evident in the AZO thin films. This indicates that the abundant free electrons (the carrier concentration in 90 nm AZO is in the order of 10^{18} cm^{-3} as determined from the Hall effect measurement) in the AZO thin films greatly suppress the excitonic absorptions as a result of the free-electron screening effect. It has been known that the three valence bands of wurtzite ZnO result in the formation of the excitons labeled in order of the valence bands as "A", "B", and "C" [16]. The three excitons can be resolved usually at low temperatures; they can merge into a broadened peak at room temperature due to the broadening caused by the exciton-phonon interactions [9], which is the case observed in Fig. 2(a). On the other hand, the dependence of the absorption coefficient on the film thickness can be attributed to the following two factors. As shown in Fig. 1(c), the grain size is smaller for a thinner film. As discussed later, the quantum confinement effect on both the bandgap energies and the exciton binding energies is more significant in a smaller grain. The carrier concentration may be also lower in a thinner film [8]. Thus the free-electron screening effect may be less significant in a thinner film. As such, the excitonic absorption may be more significant in a thinner film, which is indeed observed in Fig. 2.

Excitonic absorption can be described by the Elliott theory [17] for hydrogenic excitons. As exciton absorption can significantly influence a band-edge absorption spectrum, an excitonic theory instead of the traditional Tauc method of linearly extrapolating the absorption edge should be used for more accurate determination of the band gap energies. The discrete states of the exciton lines can be modeled with a broadened Lorentzian line shape [18]

$$\varepsilon(E) = \sum_{\beta=A,B,C} [\sum_{n=1}^{\infty} \frac{A_{0\beta}^{d}}{n^3} \frac{1}{E_{g\beta} - \frac{R_{\beta}}{n^2} - E - i\Gamma_{n,\beta}^{d}}]. \tag{1}$$

where ε is the complex dielectric function, $A_{0\beta}^{d}$ is the discrete exciton strength parameter, R_{β} is the exciton binding energy, $\Gamma_{n,\beta}^{d}$ is the broadening parameter of the n th discrete state (since the intensity falls with n^{-3}, only the ground state $n = 1$ is considered in this work), and $E_{g\beta}$ is the band gap energy corresponding to distinct exciton peaks A, B and C. The discrete absorption below the band gap is summed with the continuum absorption above the band gap, which has the form [19]

$$\varepsilon(E) = \sum_{\beta=A,B,C} \frac{A_{0\beta}^{c}(E_{g\beta} - R_{\beta})}{4R_{\beta}(E + i\Gamma_{\beta}^{c})^2} \cdot \ln \frac{(E_{g\beta})^2}{(E_{g\beta})^2 - (E + i\Gamma_{\beta}^{c})^2}. \tag{2}$$

Where $A_{0\beta}^{c}$ is the continuum exciton strength parameter, Γ_{β}^{c} is the broadening parameter. (1) and (2) were used to model both the absorption of the undoped ZnO and AZO thin films, as shown in Figs. 2(a) and 2(b), respectively. The exciton binding energies and the band gap energy at exciton peak C (the largest exciton absorption energy) yielded from the modeling as a function of the grain size are shown in Fig. 3 and Fig. 4, respectively, for both the undoped ZnO and AZO thin films.
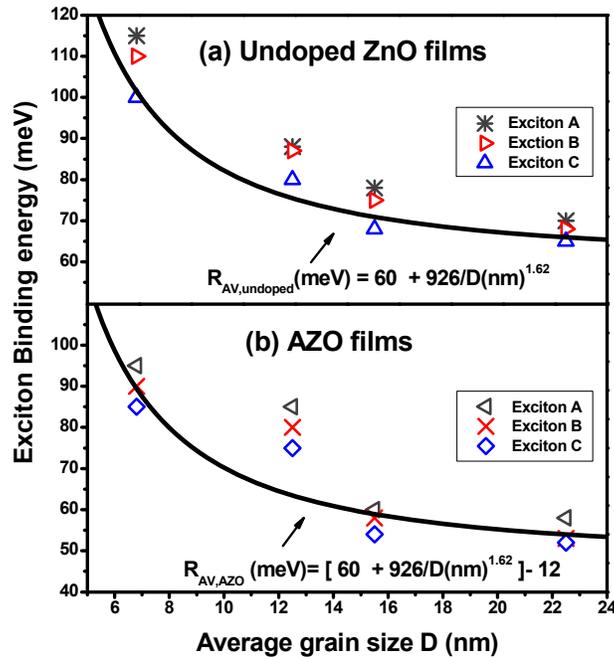
Fig. 3. Exciton binding energies of the undoped ZnO films (a) and the AZO films (b) as a function of the average grain size D (D is determined from the SEM images). The trend lines of the size dependence are for guiding the eyes only.

As can be observed in Fig. 3, the exciton binding energies of the AZO thin films are significantly smaller than that of the undoped ZnO thin films for the same grain size. For example, for the average grain size $D = 15.5$ nm (film thickness = 90 nm), the binding energies of excitons A, B and C of the AZO thin film are lower than that of the undoped ZnO thin film by 18, 17, 14 meV, respectively. One may estimate a screened binding energy with the empirical formula $R_b = R_{b0} - kN^{1/3}$, where R_b is the screened binding energy and R_{b0} is the unscreened binding energy, N is the carrier concentration, and the suggested k value of n-type ZnO is $\sim 1.2 \times 10^{-5}$ meVcm [5, 7]. The 90 nm AZO thin film has an electron concentration in the order of 10^{18} cm^{-3} as determined from the Hall measurement; thus the estimated reduction in the binding energy due to the screening effect is ~12 meV, which is comparable with the above differences in the binding energies between the undoped ZnO and AZO thin films. Note that the carrier concentration of the undoped ZnO thin film with the same thickness is $2 - 3$ orders lower than that of the AZO thin film and thus the screening effect can be ignored for the undoped ZnO thin films. On the other hand, as can be observed in Fig. 4, the band gap energies of the AZO thin films are larger than that of the undoped ZnO thin films for the same grain size. For example, for the average grain size of 15.5 nm, the band gap energy of the AZO thin film is ~50 meV larger than that of the undoped ZnO thin film. The band gap expansion in the AZO films as compared to the undoped ZnO thin films can be explained by the concept of Bursterin-Moss(BM) shift [6, 20]. In the AZO thin films with abundant free electrons in the conduction band, as the direct consequence of Pauli exclusive principle, the filled electron states at the bottom conduction band prevent further electron filling lower energy states, and electron filling can occur only at higher energy states. As a result, the fundamental edge of absorption transitions shifts to a higher energy.
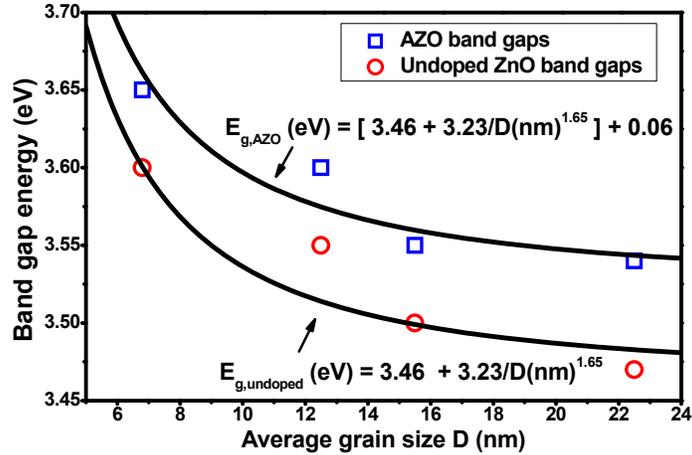
Fig. 4. Band gap energies of the undoped ZnO and AZO films as a function of the average grain size D (D is determined from the SEM images). The trend lines of the size dependence are for guiding the eyes only.

A strong quantum size effect has been observed in both the undoped ZnO and AZO thin films. Both the exciton binding energies and band gap energies increase with decreasing grain size, as shown in Fig. 3 and Fig. 4, respectively. The increase in the exciton binding energies is due to the confinement of the electron-hole wave-functions in the small dimensions [21]. The confinement enhances the columbic interaction of an exciton, giving rise to an increase in the exciton binding energy [22]. As shown in Fig. 3(a) for the undoped ZnO thin films, the average value ($R_{AV,undoped}$) of the exciton binding energies tends to reach the bulk ZnO value (60 meV) with increasing grain size, and the size dependence of the average value could be roughly described by the trend line of $R_{AV,undoped}(meV) = 60 + 926/D(nm)^{1.62}$. As shown in Fig. 3(b), the same size dependence can be observed for the AZO thin films, but the average value ($R_{AV,AZO}$) of the exciton binding energies of the AZO thin films is lower than that of the undoped ZnO thin films by 12 meV, i.e., $R_{AV,AZO}(meV) = [60 + 926/D(nm)^{1.62}] - 12$. The reduction of 12 meV in the exciton binding energies in the AZO thin films is due to the free-electron screening effect as discussed above. On the other hand, band gap widening as a result of quantum confinement is clearly observed in Fig. 4. The undoped ZnO and AZO thin films show the same size dependence in their band gap energies, but the band gap ($E_{g,AZO}$) of the AZO thin films is larger than the counterpart ($E_{g,undoped}$) of the undoped ZnO thin films by 60 meV, which is due to the BM shift discussed above. $E_{g,undoped}$ and $E_{g,AZO}$ can be approximately described by

$$E_{g,undoped}(eV) = 3.46 + 3.23/D(nm)^{1.65} \text{ and } E_{g,AZO}(eV) = [3.46 + 3.23/D(nm)^{1.65}] + 0.06$$

respectively. The difference of 60 meV in the bandgap energy between the undoped ZnO and AZO thin films can be considered as an average value for different grain sizes. Note that the bulk value of 3.46 eV is larger than the reported value of ~ 3.4 eV [1]. This is due to fact that the bulk value is evaluated based on the largest band gap energy at exciton peak C (corresponding to the largest exciton absorption energy). It has been also found that the oscillator strengths of the excitons in the undoped ZnO thin films increase with decreasing grain size. This can be attributed to the enhancement of electron-hole columbic interaction by a smaller size. This is also one of the reasons to explain the result shown in Fig. 2(a) that the exciton peak in the 20 nm film is stronger than that in the 90 nm film.

In conclusion, both band gap energies and exciton binding energies of ultrathin undoped and Al-doped ZnO (AZO) films with different thicknesses on quartz substrate have been determined from optical absorption measurement based on the Elliott's exciton absorption theory. As compared to the undoped ZnO films, the AZO films exhibit an expansion in the band gap and a reduction in the exciton binding energies due to the free electron screening effect, which significantly suppresses the excitonic absorption and results in a blue shift of the absorption edge. The undoped ZnO and AZO thin films show the same quantum size dependence as a result of quantum confinement effect, i.e. both the exciton binding energies and band gap energies increase with decreasing grain size of the oxide. In addition, the oscillator strengths of the excitons in the undoped ZnO thin films increase with decreasing grain size.

Acknowledgments