

# Exciton-polariton behaviour in bulk and polycrystalline ZnO

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We report detailed reflectance studies of the exciton-polariton structure of thin film polycrystalline ZnO and comparison with bulk crystal behaviour. Near-normal incidence reflectance spectra of these samples are fitted using a two-band dielectric response function. Our data show that the reflectance data in polycrystalline ZnO differ substantially from the bulk material, with Fabry-Perot oscillations at energies below the transverse A exciton and above the longitudinal B exciton in the films. In the strong interaction regime between these energies no evidence is seen of the normally rapid oscillations associated with the anomalous waves. We demonstrate that the strong interaction of the damped exciton with the photon leads to polaritons in this region with substantial damping such that the Fabry-Perot modes are eliminated. Good qualitative agreement is achieved between the model and data. The importance of the polariton model in understanding the reflectance data of polycrystalline material is clearly seen.

Keywords: exciton, polariton, thin film, ZnO.

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## Introduction:

ZnO is receiving renewed attention for wide band-gap device applications due to a number of advantages it presents in comparison with GaN for example, e.g. larger exciton binding energy (60 meV), availability of large area substrates for homo-epitaxy etc. [1-3]. ZnO received a great deal of attention in the 1950's-70's, when the fundamental optical and electronic properties were studied by various authors [4-6]. In many respects it was an important system for studying the exciton-polariton concept for a two-band system [6,7].

Recent studies have concentrated on the properties of thin films, given the device-oriented motivation for these investigations. We have studied the reflectance spectra from polycrystalline ZnO samples grown on sapphire using pulsed laser deposition (PLD) and those from bulk single crystal material. We have used a two band polariton model with suitable boundary conditions (both electro-magnetic (EM) and additional boundary conditions (ABC)) in a thin layer to fit the experimental data [8].

## Experimental details and results

A ceramic polycrystalline ZnO target (99.99%) and a KrF excimer laser ( $\lambda=248$  nm) with laser energy density of  $1.7 \text{ J/cm}^2$  at a pulsed repetition rate of 10 Hz and pulse duration of 26 ns were used for the ablation process. The target to substrate distance was  $\sim 4$  cm. The ZnO films were deposited on (0001) sapphire substrates at an oxygen (99.99%) pressure of 0.3 mbar (225 mTorr) and the substrate temperature was maintained at  $400^\circ\text{C}$  during growth. The film thickness was measured to be in the 150-

200 nm range for all films. Some samples were further annealed in O<sub>2</sub> (0.3 mbar) at temperatures of 400°C and 500°C respectively in the growth chamber immediately after deposition. These samples are polycrystalline and the grain structure is columnar with c-axis orientation [9]. The single crystal material was obtained from the Eagle-Picher Corporation [10]. Details of the reflectance measurements are given in [11]. No observable change is seen with different polarisations of the incident radiation.

Fig. 1 shows the experimental reflectance data for the PLD samples at 17 K. In Fig. 1(a) the excitonic features are only weakly observable, and some evidence is seen of oscillatory structure at higher and lower energies. The A- and B-exciton features (region II) are much clearer in the two annealed samples, Figs. 1(b) and 1(c), and also show clear oscillations at both low and high energies (regions I and III). We believe, on the basis of the results to be discussed below, that these oscillations are Fabry-Perot (FP) oscillations due to multiple reflections in the thin film. Previous Raman and AFM measurements on these samples indicate that the unannealed sample has the smallest grain size and the largest surface roughness (standard deviation of ~10 nm) and that the grain size increases and the roughness decreases (to a value of ~3 nm) in the annealed samples [9]. The decrease in the intensity of excitonic features with decreasing grain size is a consequence of electric fields due to charge trapping at grain boundaries [11]. We believe that the variation in visibility of the FP fringes in regions I and III among the PLD samples is due to scattering at the surface (with varying surface roughnesses depending on annealing), which reduces the coherence between the waves from the front and back surfaces of the sample [12]. FP oscillations of this sort have been seen for single exciton resonances in single crystal CdSe platelets [13]. In our samples no

evidence is seen of the short period oscillations characteristic of anomalous wave interference. We wish to examine the reasons for the absence of this structure.

Fig. 2 shows a comparison of the reflectance spectra of one PLD sample (Fig. 2(c)) and a single crystal ZnO sample (Fig. 2(b)) at 20 K. For the bulk single crystal reflectance anomalies corresponding to the A- and B-excitons are seen at  $\sim 3.374$  eV and  $\sim 3.390$  eV respectively. We also see evidence of the C-exciton at  $\sim 3.427$  eV. We will neglect the contribution of the C-exciton from this point on [8]. No evidence of the C-exciton is seen in any of the PLD samples.

The bulk sample shows no evidence of the FP oscillations in regions I and III. The excitonic features in region II are substantially quenched for the PLD sample in comparison to the bulk.

In order to describe the reflectance spectra we will use a two band exciton resonance model, with appropriate boundary conditions for a thin film on sapphire or a bulk slab (i.e. semi-infinite) [8]. The transverse modes are found by solving the following equation for  $k^2$ :

$$\frac{k^2 c^2}{\omega^2} = \epsilon_\infty + \frac{\alpha_{0A}}{\epsilon_0} \left( \frac{\omega_{AT}^2}{\omega_{AT}^2 - \omega^2 + \beta_A k^2 - i\omega\Gamma_A} \right) + \frac{\alpha_{0B}}{\epsilon_0} \left( \frac{\omega_{BT}^2}{\omega_{BT}^2 - \omega^2 + \beta_B k^2 - i\omega\Gamma_B} \right) \quad (1)$$

where the symbols have their customary meaning [8]. These solutions are used with suitable EM boundary conditions and ABC's to calculate the reflectance spectra. We have chosen to use the Pekar ABCs, with the excitonic polarisation vanishing for each

band, at each interface. For the bulk sample we also use an exciton dead-layer of variable thickness in the fit [14].

In Fig. 2(a) we show the best fit to the bulk crystal experimental data of Fig. 2(b). The reflectance anomalies are well described by the fit. The fit parameters are given in table I and are similar to those found in Ref. [8].

To fit the reflectance data for the PLD samples firstly we began by fitting the excitonic region (region II) neglecting the thin film nature of the sample. This fit is shown in Fig. 3(a), and it may be seen that region II of the experimental curve (Fig. 3(b)) is well described by this fit, with the parameters given in table I. One may compare the parameters for the PLD sample with those found for the bulk sample in table I. There is a substantial change in the transverse A-B splitting, due to both biaxial strain arising from lattice mismatch with the substrate and grain boundary electric fields [9, 11]. The LT splitting of the B-exciton in the PLD sample is also substantially different to the value in the bulk crystal. The physical origin of such a dramatic difference is not clear, but may also be due to the combination of strain and electric fields in these samples. In particular, it is clearly seen that the exciton damping factors for the A- and B-excitons in the PLD sample are much larger than the values in the bulk sample as expected on the basis of the significantly poorer crystal quality of the PLD material and the small grain sizes. The exciton “dead-layer” thickness in the fit for the PLD sample is zero, while the exciton effective mass is 0.5 times the electron mass. While both these values are different to those found for the bulk sample, the fit is largely insensitive to these parameters given the rather large damping. Visually identical spectra are computed with the bulk values of these quantities.

The oscillations in regions I and III are not reproduced by this fit (Figs. 3(a) and (b)). We have thus used a multi-layer model of an air-ZnO-sapphire (refractive index of sapphire  $\sim 1.8$ ) structure, using identical parameters to those found in fitting the excitonic region, with the ZnO film thickness as an additional variable. Fitting this model to the data we get the curve in Fig. 3(c), with a ZnO layer thickness of 215 nm, in good agreement with the known values of film thickness. The agreement between the experimental data in Fig. 3(b) and the fit in Fig. 3(c) is qualitatively good. The reflectance minimum at  $\sim 3.327$  eV and the reflectance increase at lower energies are reproduced as is the oscillatory behaviour in the 3.4 – 3.45 eV range.

The origin of this behaviour, where FP oscillations are seen at energies below and above the exciton-photon interaction region, while the central excitonic region is well described by a model neglecting the thin film nature of the sample, may be understood as follows. Fig. 4 shows the dispersion of the exciton-polaritons in ZnO and indicates regions I, II and III, as in Figs. 1 and 2. FP oscillations will only be observed if the spatial damping of the propagating modes is sufficiently small that the modes can make two passes through the film. This condition is quantified by requiring that the sample thickness  $d$  is significantly less than  $L$ , where  $L = (n_i k_0)^{-1}$ ,  $n_i$  is the imaginary part of the mode refractive index and  $k_0$  the free space wavevector [15]. The  $L$  values of the photon-like branches in regions I and III, where mixing with the highly damped exciton is minimal, are  $\sim 120,000$  nm and  $\sim 40,000$  nm respectively and  $L \gg 200$  nm. Thus we expect to see oscillatory structure in the reflectance. In region II  $L$  for all modes is  $< 400$  nm due to the large damping of the exciton and the strong exciton-photon mixing. Thus no oscillations would be expected in region II, in agreement with observation.

## Conclusion

We have presented data showing the low temperature reflectance of PLD-grown ZnO and compared it to the behaviour of bulk single crystal material. We see that the experimental data are adequately described by a model based on the interaction of strongly damped excitons with a photon mode. FP oscillations are observed both above and below the strong interaction regime, where the photon-like mode is weakly damped. In the strong interaction regime, where all propagating modes are strongly damped due to mixing, no oscillations are seen. Thus we find that it is important to consider the full polariton picture in interpreting the reflectance spectra of polycrystalline ZnO material.

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Tables:

Table 1: Fit parameters for bulk & PLD samples using two band exciton model. Final column gives literature values for ZnO single crystal.

Parameter	Bulk crystal	PLD sample	Literature value [8]
$\hbar\omega_{AT}$ (transverse A exciton energy, eV)	3.3753	3.3781	3.3758
$\hbar\omega_{BT}$ (transverse B exciton energy, eV)	3.3813	3.3904	3.3810
$\hbar\omega_{AT} - \hbar\omega_{BT}$ (A-B splitting, meV)	6	12.3	5.2
$\Delta_{LT}^A$ (A exciton LT splitting, meV)	2	1.9	1.8
$\Delta_{LT}^B$ (B exciton LT splitting, meV)	11.9	3.6	10.2
$\hbar\Gamma_A$ (A exciton damping, meV)	0.7	6.8	0.7
$\hbar\Gamma_B$ (B exciton damping, meV)	0.7	13.7	0.7
M (multiples of electron mass)	0.87	0.5	0.87
Dead-layer thickness (nm)	4	0	4

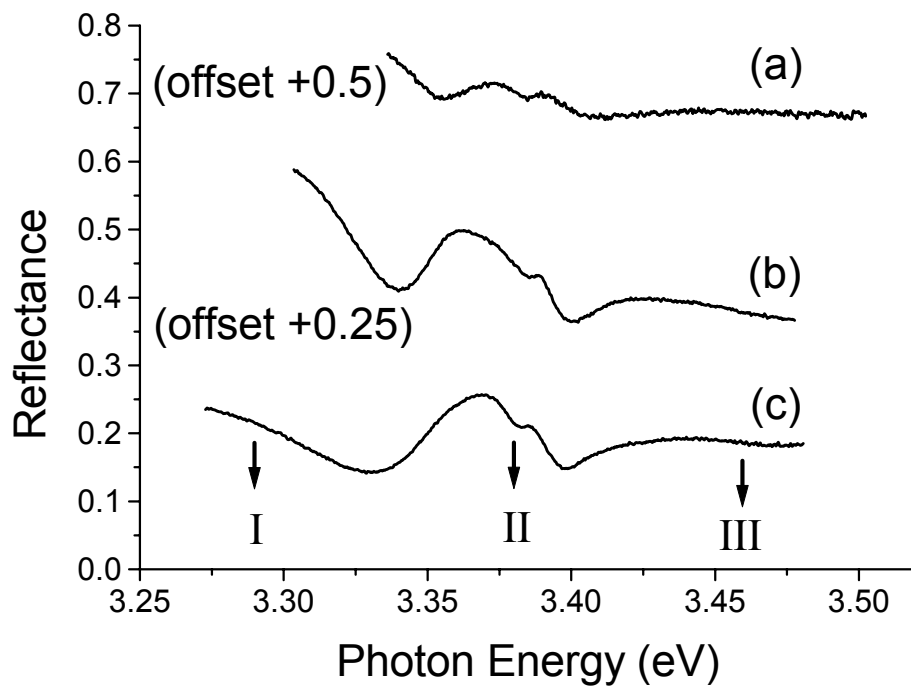
Figure Captions:

Fig. 1: Experimental reflectance data for PLD samples at 17 K: (a) unannealed; (b) annealed 400<sup>0</sup>C, 10 minutes; (c) annealed 500<sup>0</sup>C, 15 minutes.

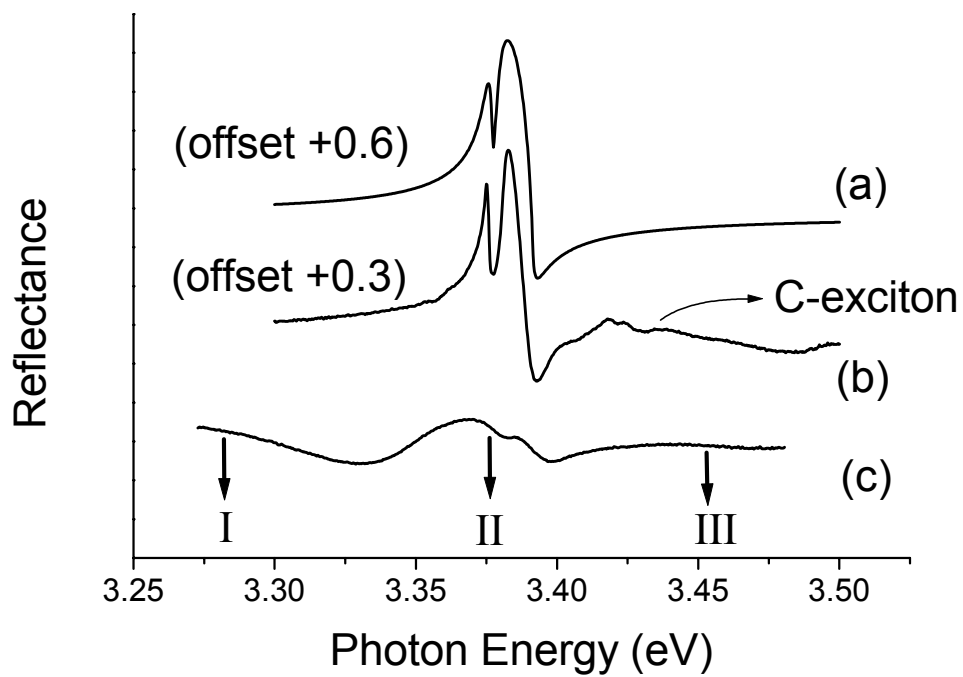
Fig. 2: Comparison of the reflectance spectra (at 17 K) of the PLD sample annealed at 500<sup>0</sup>C (c) and a single crystal bulk ZnO sample (at 20 K) (b). Curve (a) shows the best fit to the experimental data (b) using the model.

Fig. 3: Comparison of the reflectance spectra of the PLD sample annealed at 500<sup>0</sup>C (b) with computed reflectance spectra; without including thin film interference effects (a); including thin film interference effects (c).

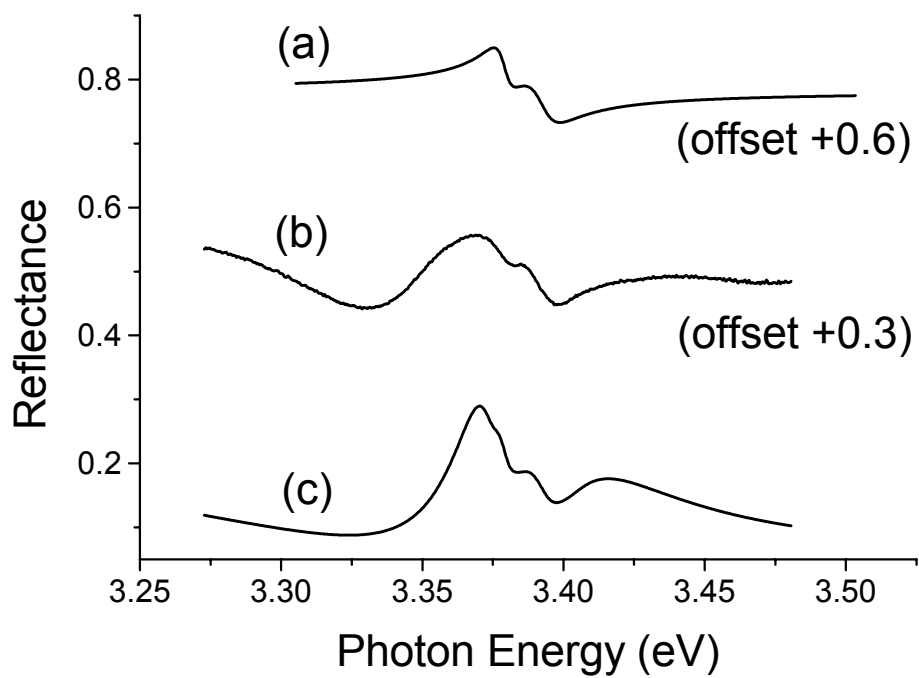
Fig. 4: Dispersion of the exciton-polaritons associated with the A- & B-excitons in ZnO.



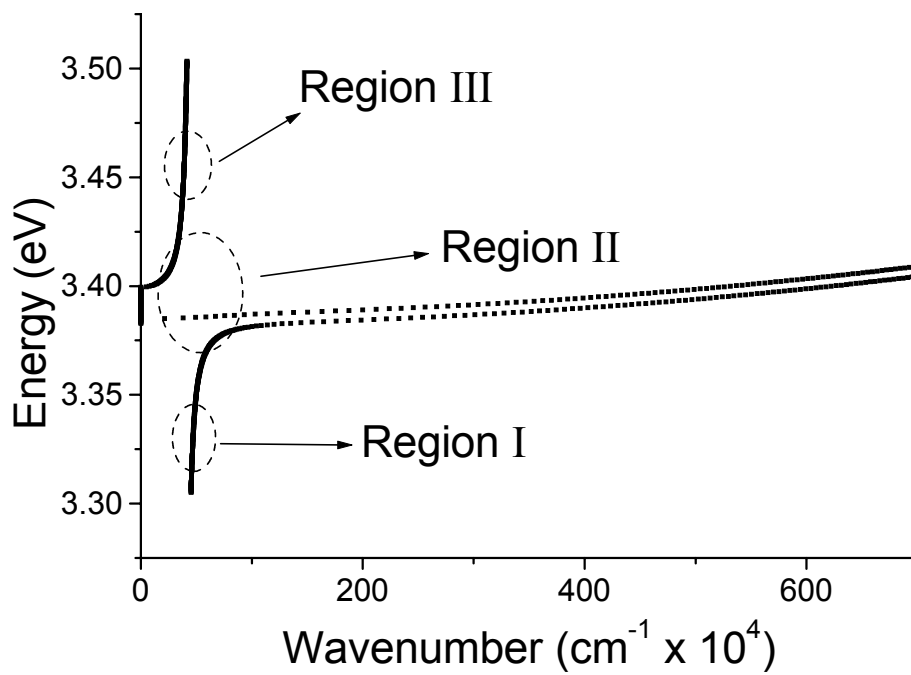
**Figure 1**



**Figure 2**



**Figure 3**



**Figure 4**