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RESEARCH ARTICLE

TEMPERATURE AND POLARISATION DEPENDENT REFLECTIVITY OF THE C FREE EXCITON OF A-PLANE ORIENTED ZNO EPILAYERS GROWN BY PLASMA-ASSISTED MOLECULAR BEAM EPITAXY.

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Abstract

The photoluminescence (PL) and reflectivity (Ref) properties of a-plane oriented ZnO epilayers, grown by molecular beam epitaxy (MBE) on r-plane oriented sapphire substrate, have been investigated. At low temperature donor-bound exciton (DX) emission (3.355-3.383eV) and the C free excitonic transitions (3.427-3.436eV) were identified through polarization dependent photoluminescence and reflectivity measurements. The DX plays a major role in PL spectra at low temperature, while the free exciton transition (FX) gradually dominates the spectrum with increasing temperatures. In the π polarisation, first the temperature-dependent variations of the PL spectra and of the integrated intensity of the C-free exciton were studied. The activation energy of the C-free exciton was calculated to be 59 meV from the temperature dependent quenching of the integral intensities. Then, the temperature dependence of the reflectivity peak energy position of the C-free exciton, was plotted and fitted. Our results substantiated the excitonic nature of the PL emission of the a-plane ZnO thin film, in the π polarisation (E∥c) axis.

Introduction:-

Zinc oxide (ZnO) is a versatile functional material. Its direct wide band gap (3.37 eV) at room temperature and high exciton binding energy (60 meV) had lead to extensive research on ZnO (John Wiley et al., 2011; Ümit Özgur et al., 2010). In the UV region laser devices operating at room temperature (C. Y. Liu et al., 2014) have been studied. Several studies of bulk ZnO were published in the literature (Robert Triboulet, 2014; C. Klingshirn, 2007) and layers were obtained by different growth method (S.H. Parka et al., 2007; Kyung Ho Kim et al., 20014). Since the presence of an internal electric field parallel with the c-axis in the wurtzite structures, has been confirmed experimentally in ZnO/MgZnO quantum well structures (J.-M. Chauveau et al., 2013), growth of quantum wells ZnO has attracted much more people (J. M. Chauveau et al., 2013; G. Tabares et al., 2015). In fact this inherent internal electric field acts to reduce the binding energy of the free excitons in ZnO-based quantum well structures which is detrimental to the performance of room temperature devices based in such a system. In a-plan ZnO-based quantum well structures, the c-axis of the substrate is in the plane of the ZnO epilayer and thus is perpendicular to the direction of confinement in the quantum wells. In other words the induced electric fields will have no effect on the exciton binding energy in the quantum wells. Recently, the transport of indirect excitons in ZnO quantum wells (G. Tabares et al., 2015; Y.Y. Kuznetsova et al., 2015) and the light polarization sensitive photodetectors as a function of the substrate as studied with m and r-plane homoepitaxial ZnO/ZnMgO quantum wells. However though the principal challenge for realizing ZnO optoelectronic devices is the lack of high-conductivity p-type ZnO, a good understanding of the properties of the material is essential for tailoring the material for specific applications and for developing the devices. Photoluminescence (PL) analysis is a very conventional and effective tool for characterizing and evaluating luminescent materials but reflectivity measurement is the most effective tool to determine the peak energy exciton position. The optical properties of ZnO thin films grown by using different methods have been extensively studied (Ü. Özgüret al., 2005; P. Muret et al., 2012; Feng Li et al., 2013). However, the temperature and polarisation dependent reflectivity of the C free exciton of ZnO epilayers grown by plasma-assisted Molecular Beam Epitaxy, have not received adequate attention. In fact the free-exciton transitions from the conduction band to the three valence bands or vice versa are usually denoted by A also referred to as the heavy hole, B also referred to as the light hole, and C also referred to as crystal-field split band with the higher energy position. The A free exciton energy position is lower than the B one. The three excitons are allowed in the σ polarization $E \perp c$ and $k \perp c$, but the C exciton is quite weak. The C exciton is strongly allowed in the π polarization $E \parallel c$ and $k \perp c$. However, the A exciton is forbidden and the B exciton is only weakly observable in this geometry. In the α polarization $E \perp c$ and $k \parallel c$ all three transitions are clearly observable.

Most of the previous temperature dependence studies of the free exciton energy in Zinc oxide concern c-axis oriented ZnO films (Trilochan Sahoo et al., 2010; Y. M. Lu et al., 2013) and these studies report on the A and B free exciton.

In this communication, we are further by studying temperature and polarization dependent PL and reflectivity of the C free exciton of a-plane oriented ZnO epilayers grown by plasma-assisted Molecular Beam Epitaxy on r-plane sapphire substrates.

Experimental works:-

A 1µm-thick ZnO film was grown in the temperature range of 450-550°C. The growth was performed using solid source Zn and an RF activated plasma as the oxygen source. The growth rate was 0.35µm /h, slightly lower than the optimal growth rate in a c-direction growth. Prior to growth, the r-plane (01-12) sapphire substrates were thermally cleaned and subsequently exposed to oxygen plasma. A streaky RHEED pattern was maintained throughout the growth, albeit with a slight modulation in the [1-100] azimuthal direct. The optical properties of the structures were studied using non-resonant photoluminescence excited with the 325nm line from He-Cd laser. The emitted light was dispersed using a 0.6m monochromator and detected using silicon PMT with conventional lock-in techniques. The sample was mounted in an optical cryostat where the temperature could be varied from 6 to 300K. Reflectivity measurements were excited using a standard mercury bulb.

Results:-

Reflectivity studies were performed on the samples in two polarisations σ and π respectively $E \perp c$ and $E || c$ axis as displayed in Fig.1. While PL measurements were carry out in π ($E || c$) and the spectrum at low temperature is displayed in Fig.2. As showed in these figures, the behaviour of the free excitons as a function of polarisation demonstrates that the selection rules for these transitions are respected. In fact the selection rules for the optical transitions predict large oscillator strength for the A and B excitons in the $E \perp c$ polarisation and large oscillator strength for the C exciton in the $E \parallel c$ polarisation. But when the sample is c-oriented, the oscillator strength of the C exciton is small and it is difficult to measure and to fit the C free exciton energy transition in such structures. The energy measured at the center of the reflectivity peak of A, B, and C free excitons was respectively 3.396eV 3.406eV and 3.436eV as indicated in table.1.

We used a Hopfield model to fit the 10K reflectivity spectra of the C free exciton. The fit parameter are the energy E(eV), the oscillator strength (α), the spectral widening (Γ) and the effective mass (m*) of the excitons. Our result fit curve is displayed in Fig.3 and the values of fit parameters are indicated in table. 2. This value of the energy exciton peak, measured at the maxima of the peak reflectivity, confirm our PL and reflectivity measurements.

At 10 K, the PL spectrum is mainly composed of a strong emission band and two weak emissions respectively labelled D3X, D2X and D1X and located at 3.382, 3.364 and 3.355eV. These emissions are related to bound excitons. Another strong emission band observed at the lower energy of the DX band, in the region of first longitudinal optical phonon replicas (LO), was identified as a defect line (J.M. Chauveau et al., 2007). In high energy side of D3X band, one peak at energy position 3.428eV can be clearly observed. With the low temperature and polarisation reflectivity measurements, this peak was identified as the C-free exciton (C-FX).

In order to support our peak assignment in the low- temperature PL spectrum, the temperature and polarisation dependence of the PL spectra from the a-plane ZnO measured in the range of 6 to 300K are depicted in Fig.4. With increasing measurement temperature, the peak energy of the luminescence emission gradually shifted towards lower energy from 3.428 eV at 6K to 3.351eV at 300K. The low-temperature PL of the ZnO thin film was observed to be dominated by bound exciton emission, while at room temperature, the emission was due to free exciton recombination. This peak becomes stronger and stronger and the intensity of the PL emission was reduced significantly with temperature increasing to 300 K. Such shifting of the emission energy to lower energy and such a reduction of the PL intensity is observed in semiconductors due to temperature-dependent band gap narrowing and enhancement of non-radiative recombination (R. Pässler et al., 1999). But, gradually as the temperature increases, the determination of the peak position probably induces some error resulting from temperature broadening.

Fig. 5 exhibits the temperature dependence of integral PL intensities for C-FX band (scatter). One can clearly see that at high temperature, the PL intensity represents the exponentially decrease due to thermally activated nonradiative recombination mechanism. The dependence of the integral PL intensities on the temperature for C-FX band was fitted by the following formula:

$$\mathrm{I} = \mathrm{I_0} + \mathrm{A}\exp\left(-\frac{\mathrm{E_a}}{\mathrm{K_B T}}\right) \qquad (1)$$

where I_0 is the emission intensity at temperature T=0K, E_a is the activation energy in the thermal quenching process, and K_B is the Boltzmann constant, T is a thermodynamic temperature and A is a constant. From the plots (scatters), the thermal activation energy is estimated to be 59meV for C-FX band. This value agrees well with the free exciton binding energy of ZnO (60 meV) (Z. K. Tang et al., 1998; A. F. Kohan et al., 2000).

So, to substantiate the excitonic nature of the PL emission of the a-plane ZnO thin film, in the π polarisation (E∥c) axis, we studied the variation of the reflectivity peak position energy with temperature. We plotted the variation of the C free exciton reflectivity peak energy exciton from 6 to 300K, as shown in Fig. 6. The figure shows that the peak energy varied non-linearly with temperature. The observed curve energies were fitted numerically using the Pässler formula for the variation of the energy exciton with temperature.

$$\mathrm{E_{FX}(T)} = \mathrm{E_{FX}(0)} - \frac{\alpha\theta}{\left(\exp\left(\frac{\theta}{\mathrm{T}}\right)-1\right)} \qquad (2)$$

where, $E_{FX}(T)$ is the free exciton energy, α is a constant related to the average phonon frequency and θ is taken usually to represent the Einstein temperature θ_E. This expression is equivalent to the Bose–Einstein model function proposed by Viña et al (1984). The result fit gave for C-free energy the $E_{FX}(0)$, α and θ values listed in table.3. The close fitting of the free exciton energies to the Bose–Einstein model function indicates the excitonic nature of the so called C-free exciton peak of the a-plane ZnO thin film. The values of α and θ also suggest that the band gap and its temperature variation are sensitive to free excitons, which, in turn, depend on growth method and the growth parameters. Our results correspond also to one of the first fit of the temperature dependent reflectivity of C free exciton in a-plane ZnO epilayer.

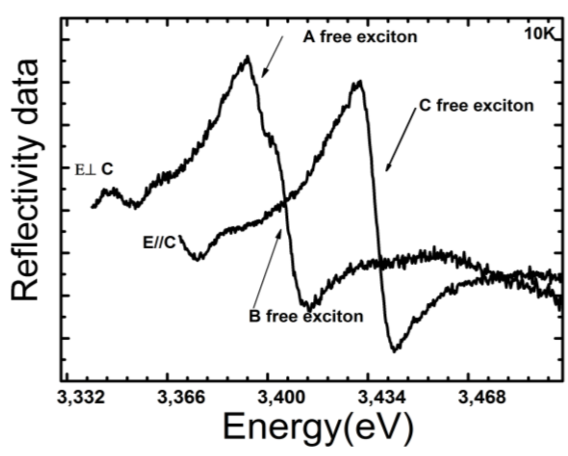

Fig.1: Reflectivity spectra of ZnO thin films a-plane. The spectra are shown in both polarizations. The A and B free exciton are seen in the E⊥c polarisation and the C free exciton in E∥c polarisation. For clarity the spectra are vertically displaced.

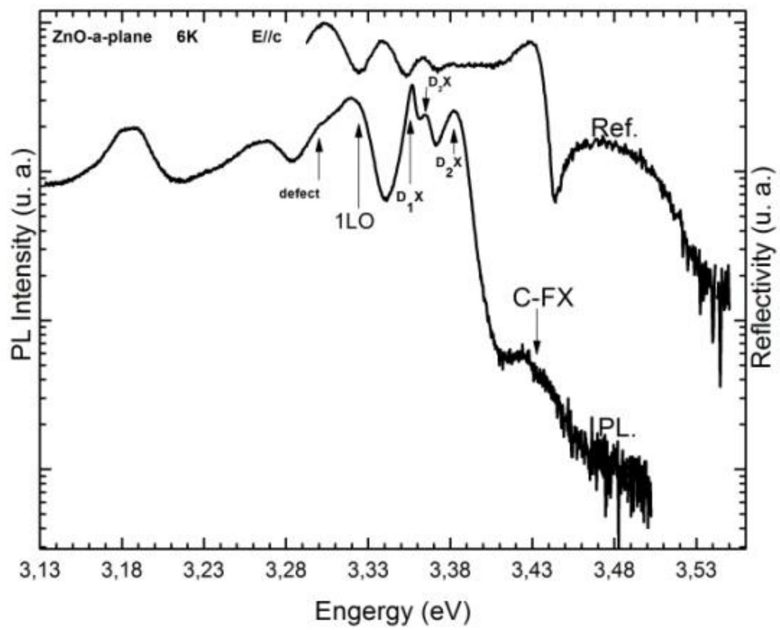

Fig.2: PL and reflectivity spectra at low temperature (6K) of ZnO thin films a-plane. The spectra are shown in π polarization (E ∥ c). For clarity the spectra are vertically displaced.

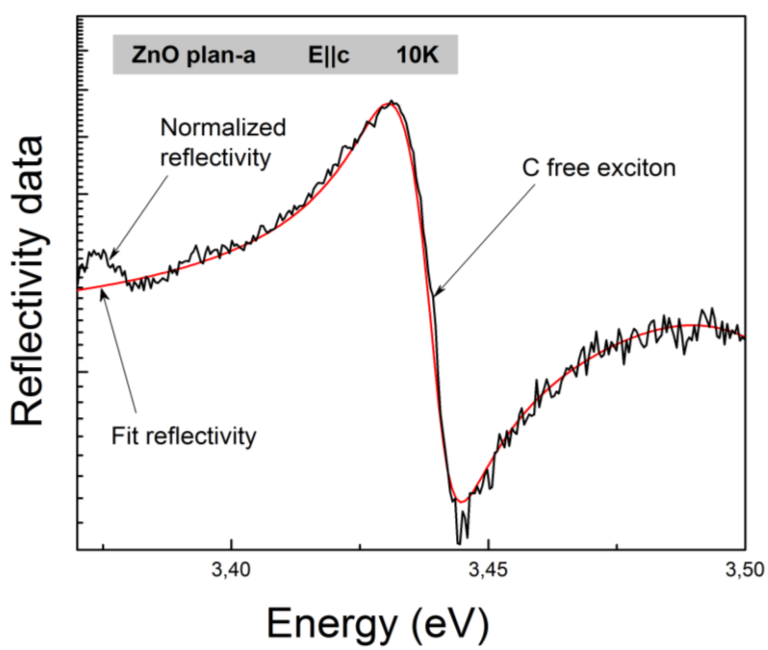

Fig.3: Reflectivity fit using Hopfield model. The 10K normalized reflectivity spectrum of the C-free exciton and its fit are shown respectively solid black and red black line. The parameters used to fit are the peak energy, the strength oscillator (α) the spectral widening (Γ) and the effective masse of the exciton (m*).

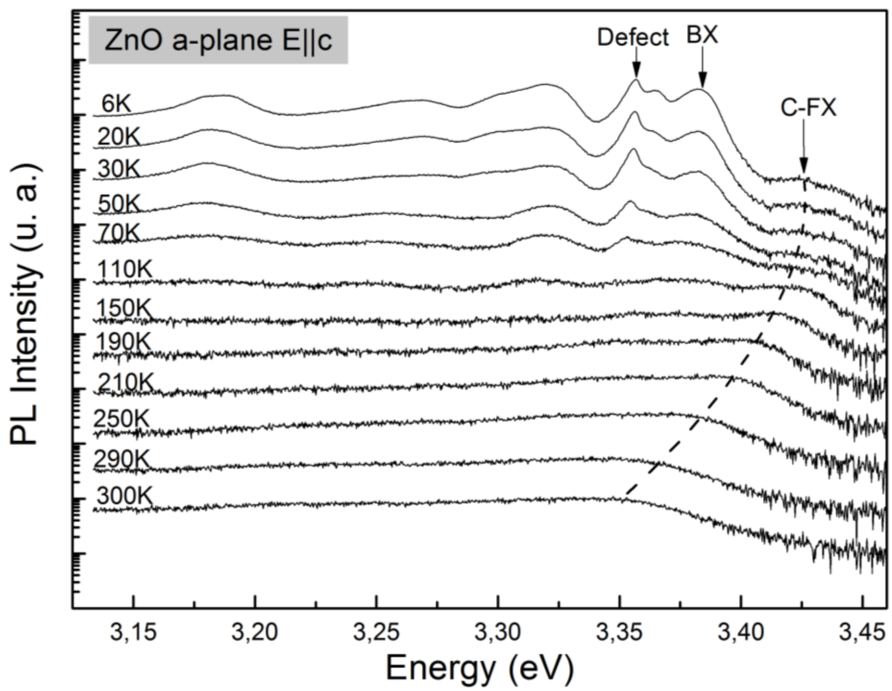

Fig.4: PL spectra at selected temperature from 6 to 300K in the **E||c** polarization. The spectra are vertically displaced.

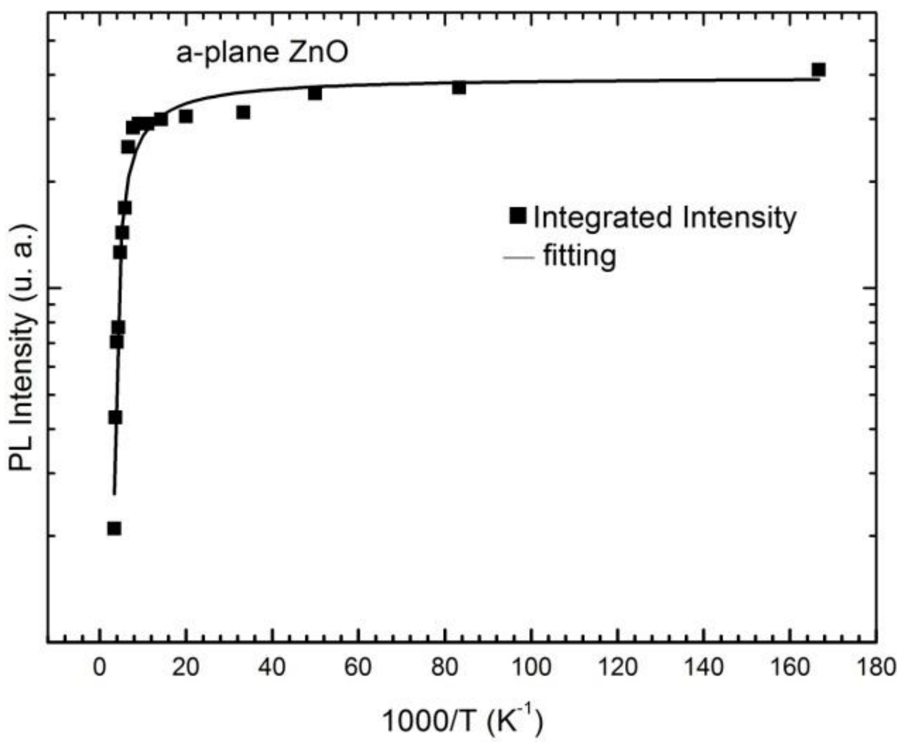

Fig. 5: Arrhenius plot of the integrated intensities of the PL emission as a function of the inverse temperature.

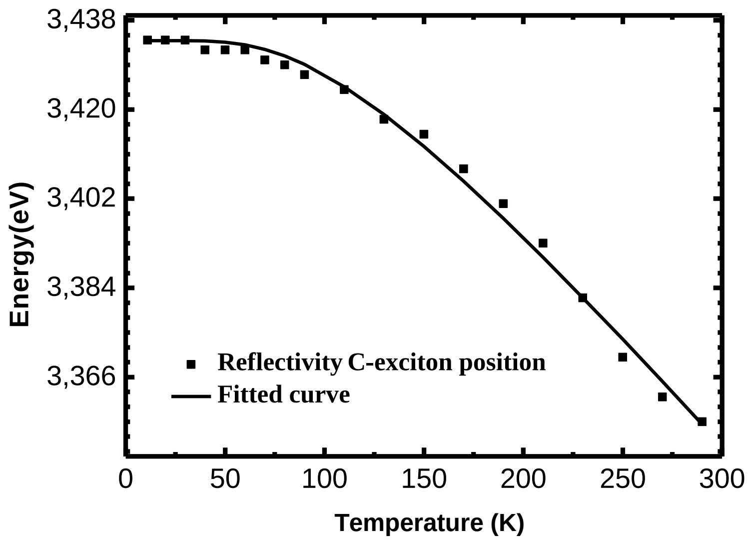

Fig.6: PL peaks position (■) and it fit curve (solid line) (using Eq.1) dependent of temperature. Measurements are realised in the **E||c** polarization.

Table 1: Values of A, B and C free exciton energies measured at the centers of the reflectivity peaks.

A-Free exciton energy(eV)	B-Free exciton energy(eV)	C-Free exciton energy(eV)
3.396	3.406	3.436

Table 2: Reflectivity fit using Hopfield model. The 10K normalized reflectivity spectrum of the C-free excitons and its fit are shown respectively scatter and solid line. The parameters used to fit are the peak energy, the strength oscillator (α) the spectral widening (Γ) and the effective masse of the exciton (m*), where m_0 is the electron mass. The large value of α are probably due to the fact that the C free exciton is fitted together and with the band gap.

Free exciton Energy E(eV)	Oscillator strength α	Spectral widening Γ(meV)	Effective mass m* (Kg)
C 3.430	1.895	8.877	$0.59m_0$

Table 3: Parameter sets obtained by fitting the temperature dependence of the C free exciton peak positions in a-plane ZnO epitaxial film using Eq.(1).

Free exciton	$E_{FX}(0)(eV)$	α (eV/K)	θ (K)
C	3.432	0.00054	368±24

Conclusion:-

In summary, we have investigated the temperature and polarization dependence reflectivity and photoluminescence of undoped a-plane oriented ZnO epilayers grown by plasma-assisted Molecular Beam Epitaxy. Our result indicates that our a-plane oriented ZnO layer is of high optical quality. We have identified the bound exiton and C free exciton transitions at low temperature (10K). The energy positions of the C free exciton, studied in the π polarization (E ∥ c) axis as a function of temperature and the activation energy (59meV) calculated from the temperature-dependent variation of integrated intensities, support our assignment. The PL emission energy and the energy positions of the C free exciton were observed to vary non-linearly with temperature.

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