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ZnO gap states investigated using magnetic circular dichroism

Minju Ying^{1,2}, Wala Dizayee^{1,4}, Z X Mei³, X L Du³, A Mark Fox¹ and Gillian A Gehring¹

¹ Department of Physics and Astronomy, University of Sheffield, Sheffield, S3 7RH, UK

² Key Laboratory of Beam Technology and Material Modification of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, People's Republic of China

³ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

⁴ Department of Science, Salahaddin University, Erbil, Iraq

E-mail: mjying@bnu.edu.cn and g.gehring@sheffield.ac.uk

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Abstract

We investigate gap states in a series of nonmagnetic ZnO films grown by molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) using magnetic circular dichroism. This technique is shown to be sensitive enough to investigate defect states in thin films of disordered wide-gap semiconductors by differentiating between a loss of transmission due to scattering and absorption. The method is first applied to Zn- and O-terminated films grown by MBE. The O-terminated film shows a broad peak centred at ~ 2.4 eV which corresponds to the green PL signal, whereas the Zn-terminated film shows a magnetic circular dichroism (MCD) signal that increases slowly with energy. The method was then extended to PLD films. Oxygen vacancy states in both MBE and PLD-grown films were identified, and the introduction of low concentrations of Al was shown to quench the MCD signal at low energy by neutralising the paramagnetic oxygen vacancies. In PLD-grown ZnAlO we observed a negative MCD that increased in magnitude as the energy approached the band edge indicating a much more pronounced spin-split impurity and conduction band. These examples illustrate the versatility of the MCD technique in identifying gap states in a variety of different types of ZnO samples.

Keywords: magnetic circular dichroism, ZnO, polar surfaces

(Some figures may appear in colour only in the online journal)

1. Introduction

Many of the useful properties of wide band gap semiconductors depends on the density and character of the states in the gap. Magnetic circular dichroism (MCD) is a very powerful tool that can be used for investigating the presence of gap states in these materials. Its use in characterising magnetic materials is well known but in this paper we show its power to investigate nonmagnetic films. ZnO is a highly versatile technologically important material because it is transparent in the visible region as the band gap is 3.4 eV at room temperature and because the exciton states are particularly strongly bound; it can also be doped readily [1].

Many of the useful properties depend on the states in the energy gap; some of these are intrinsic to pure ZnO and are due to vacancies, interstitials, anti-site ions, grain boundaries and surfaces; others are due to the dopants that have been introduced intentionally. In such a wide band semiconductor the mobile carriers all originate from gaps states and the defect states also scatter the mobile carriers thus limiting the mobility [2]. ZnO naturally grows oxygen deficient and hence is n-type. Its many uses include as a component with a p-type semiconductor in light emitting diodes, photodiodes and in thin film transistors. It is piezoelectric and thin films of pure ZnO have been found to be ferromagnetic when the grain size is small [3].

ZnO is a polar material and it is known that there are a number of differences between samples that are grown with an O-polar or a Zn-polar exposed surface. These include the density of structural defects, tendency to absorb impurities and optically active states associated particularly with the O-polar surface [4–7]. There are many applications of polar films of ZnO in heterojunctions [8], for catalysis [9] and for enhanced piezoelectricity [10]. For these reasons it is particularly interesting to investigate the effect of O- or Zn-termination on the gap states on these films.

The number of applications increases dramatically when we consider doped ZnO. The conductivity increases rapidly when it is doped with Al (AZO) or Ga ions and it is regarded as a cheaper and more bio-compatible replacement for indium tin oxide ITO [11] in LED's [12], thermoelectric devices [13], photocurrent detectors [14, 15]. The band gap of pure ZnO is below that of ITO but it increases after doping with Al [16].

Doping with transition metals and other dopants has been found to enhance the magnetism that is observed in pure ZnO and has produced many reports of ferromagnetism at room temperature. It has been shown that this requires oxygen vacancies but is also increased by increasing the number of carriers for example by co-doping with Al [17–19]. Recently there is increased interest in using pure ZnO, ZnMgO, InGaZnO and ZnCoO to obtain resistive switching [20–23]. This effect relies on oxygen vacancies [21, 23] and so a technique that measures the energy states of the associated with oxygen vacancies is particularly useful. In addition the piezoelectricity of ZnO may be enhanced very significantly by the addition of vanadium.

The states in the gap play an important role, particularly those due to oxygen vacancies, and in pure ZnO these can be measured with photoluminescence (PL). However this technique is not always available because the PL is quenched by dopant transition metal or Al ions [24, 25]. It is also very difficult to measure the direct absorption from the gap states as it is usually masked by scattering from the surfaces and crystalline imperfections. In this paper we demonstrate the power of magnetic circular dichroism (MCD) to detect the weakly absorbing gap states in thin films of ZnO. The technique measures the fractional difference in absorption for left and right circularly polarised light making it essentially insensitive to scattering and hence it is applicable to samples of doped ZnO that have quenched luminescence. MCD is also only sensitive to paramagnetic gap states and hence it is complementary to PL where signals are also detected from singlet states.

In our work we apply the MCD technique to compare the gap states in polar ZnO films grown by MBE and thin films grown by pulsed laser deposition (PLD) with and without Al doping. None of the films were magnetic, but we show here that MCD can be used to detect the energies of the defect states arising from oxygen vacancies and extended defects such as grain boundaries in both types of film. The PL spectra of polar films have been studied extensively [3] and so in this case we can compare the results for MCD and PL directly. By contrast, the application to the films doped with Al allows identification of the gap states in samples where no corresponding PL data

is available [25]. These examples show the versatility of MCD in detecting gap states in ZnO.

In section 2 we describe the principles of the MCD applied to ZnO and also to the sapphire substrate since the signal from the substrate needs to be subtracted to obtain the signal from the film. The preparation of the samples and the optical techniques are described in section 3 and the results are given in section 4 with the conclusions in section 5.

2. MCD spectra in ZnO

Pure ZnO has a full valance band and an empty conduction band but in this paper we are concerned with the defect states that exist commonly, particularly oxygen vacancies. The lowest energy state of a neutral oxygen vacancy has two trapped electrons in a spin singlet; this is a deep donor and there is also a spin triplet that is still inside the energy gap [19], however in the interior of the grains the majority of the vacancies are in the singly ionised, paramagnetic state [26]. In all cases the energies are broad because of the lattice relaxation and the proximity of depletion regions near to the grain boundaries. In addition there are extended defect states associated with the depletion layer in the grain boundaries which will become spin polarised in an applied magnetic field and can accept additional electrons. In what follows we describe the MCD spectra expected from these different types of defect together with the contribution from shallow Al donors that are deliberately introduced into the samples. These can only bind a single electron.

An applied magnetic field will split all of the electronic states in the material by energies of the order of $\mu_B|B|$. If there are partially occupied levels this will result in an induced magnetisation due to the induced unequal populations of the states. (The whole sample is very likely to be diamagnetic because this defect induced paramagnetism is so small.) The spin orbit coupling produces an unequal orbital polarisation as a result of spin polarisation. The intensities of the absorption observed along a direction parallel to the direction of the field will be polarised σ_+ or σ_- due to this unequal orbital population which affects the oscillator strength for $\Delta m = \pm 1$ in electric dipole transitions [27]. Historically this type of MCD spectrum is known as ‘paramagnetic’ and the MCD spectrum follows that of the absorption spectrum modulated by the strength of the Zeeman splittings and the spin orbit interaction in the electronic states that are involved in the transition. In a nonmagnetic material in an induction of 1.8 T, as used in our experiments, at room temperature the population imbalances are small, of the order of 10^{-3} , so this MCD signal is weak but observable.

There is another type of MCD signal known as ‘diamagnetic’ which can occur in materials with and without partially filled shells. This signal results from the differences in energies of the σ_+ and σ_- transitions because of the Zeeman effect [27]. A diamagnetic MCD signal is dispersive over an energy range of $\mu_B|B|$; for the induction used in these experiments, 1.8 T, this corresponds to an energy of the order of 10^{-4} eV. This energy is much smaller than the resolution of our apparatus which is about 10^{-2} eV and hence it is not observed in our

measurements. This type of spectrum may be observed using a large value of $|B|$ and is the only MCD signal that accompanies a transition between completely full and empty levels. This is shown in figure 1(a) for a transition to an ionised donor state for example an ionised Al donor and in figure 1(b) for a transition from the singlet state of a neutral oxygen vacancy to the conduction band we call these ‘silent’ transitions because they contribute to the absorption but not to the MCD that we can observe.

In the other transitions shown in figure 1 the spin of the electron making a transition is determined by the spin of an electron in the initial or final state. In figure 1 all the polarisable states are shown with spin up; there will be equivalent transitions for all the starting configurations with spin down and the MCD is given by the, small, population differences between these two types of initial state. These are the type of transition that give rise to the observed MCD spectrum. Figure 1(c) shows excitation from the oxygen vacancy triplet state to the conduction band to give the partially ionised state. Figures 1(d)–(f) show possible transitions that can occur from a single occupied defect state. The ionisation of this state is shown in figure 1(d); this would be seen in our experiments for a single occupied oxygen vacancy but not for an Al donor because in that case the energy, 0.01 eV, is below our limit of detection. The processes shown in figures 1(e) and (f) involve an electron being excited out of the valance band into a partially ordered oxygen vacancy state to form either the spin singlet (e) or the spin triplet state (f).

When ZnO is heavily doped with Al there is another contribution because there is a significant number of degenerate electrons in the conduction and impurity bands. Transitions from the valance band cannot occur to occupied states and hence there is an MCD that is proportional to the difference in the populations of conduction electrons with up and down spin. If the occupations, n_0 , are low then Boltzmann statistics may be used and the $MCD \sim n_0 \mu_B B / k_B T$ and if the conduction electrons are degenerate then $MCD \sim \mu_B B G(E_F) \sim B n_0^{1/3}$.

There are also transitions to extended defect states that exist around grain boundaries and dislocations. There is a conducting layer in the grain boundaries in ZnO and also an increase in the number of singly ionised oxygen defects [26]. The spin splitting of the electronic states in this layer has been proposed as the origin of magnetism in undoped films [13]. The contribution of these layers to the MCD may understood in a similar way to the effects of a spin split conduction band discussed above.

3. Experimental methods

3.1. Samples

We have chosen to apply the technique to two different types of samples. We have studied polar films in order to investigate the types of defect that are introduced by growing the films with a definite polarity. As a contrast films were also studied that had been grown by pulsed laser deposition, a very commonly used technique, with and without doping with aluminium.

Table 1 gives a summary of the samples that are investigated in this paper. In the following sub-sections we describe their fabrication.

3.1.1. MBE-grown ZnO films. Two films of ZnO were grown by molecular beam epitaxy (MBE) in order to investigate the effect of surface termination. A radio-frequency plasma-assisted system (Omni Vac) was used to grow single crystal ZnO films on sapphire substrates which were degreased in trichloroethylene and acetone and rinsed with deionized water before being introduced into the chamber. Elemental Zn was evaporated by Knudsen cells (Veeco), and oxygen generated by rf-plasma system (SVTA) was used as a radical source. The controlled growth of unipolar ZnO films was realized by interface engineering using an MgO buffer layer on α -Al₂O₃ (0001). An ultra-thin MgO with a strained rocksalt structure, with thickness of a few atomic layers (~0.5 nm), resulted in O-polar ZnO films. The Zn-polar ZnO films were grown on a three unit cell thick (~10 nm) relaxed rock salt MgO buffer layer. In both cases an additional ZnO buffer layer, about 10 nm thick, was deposited at low temperatures, 450 °C, before the deposition of the 400 nm thick ZnO epilayer at higher temperature, 650 °C [28].

These films are of n type with electron concentration of about 10^{16}cm^{-3} and electron mobility between $90\text{--}110 \text{cm}^2 \text{Vs}^{-1}$. X ray diffraction characterization reveals that the full width at half maximum of ZnO(002) rocking curve is about 95 arcsec and ZnO(102) is about 446 arcsec. The polarity of the films were confirmed by electron energy-loss spectroscopy (EELS) and convergent beam electron diffraction (CBED) [29, 30].

3.1.2. PLD-grown (ZnAl)O films. Four films of ZnO doped with Al were grown by pulsed laser deposition (PLD), together with an undoped reference sample, see table 1. The targets were made by grinding and sintering of powders mixed with the appropriate ratios. The procedure was repeated three times, grinding for 20 min using pestle and mortar, followed by sequential sintering in a furnace at 400 °C and 600 °C for 12 h. After that the final powder was pressed into a cylindrical pellet followed by the last sintering at 900 °C for 15 h. An XeCl excimer laser (Lambda Physik LEXTRA 200) was used to synthesise the thin films on sapphire substrates. The laser wavelength was 308 nm, which matches to a spectral region in which the materials show strong absorbance. 28 ns pulses were used with a repetition rate of 10 Hz with pulse energies up to 400 mJ. The pressure during the growth is in the range of $1\text{--}3 \times 10^{-5}$ Torr in order to grow oxygen deficient films, and the substrate temperature was 450 °C.

3.2. Optical techniques

The absorption spectra of the films between 1.7 and 4.5 eV were taken by measuring the transmission using chopped light from a xenon lamp and a monochromator with a photo-multiplier tube detector. This was analysed in terms of the intensity lost in the film to give a loss coefficient, α ; this incorporates

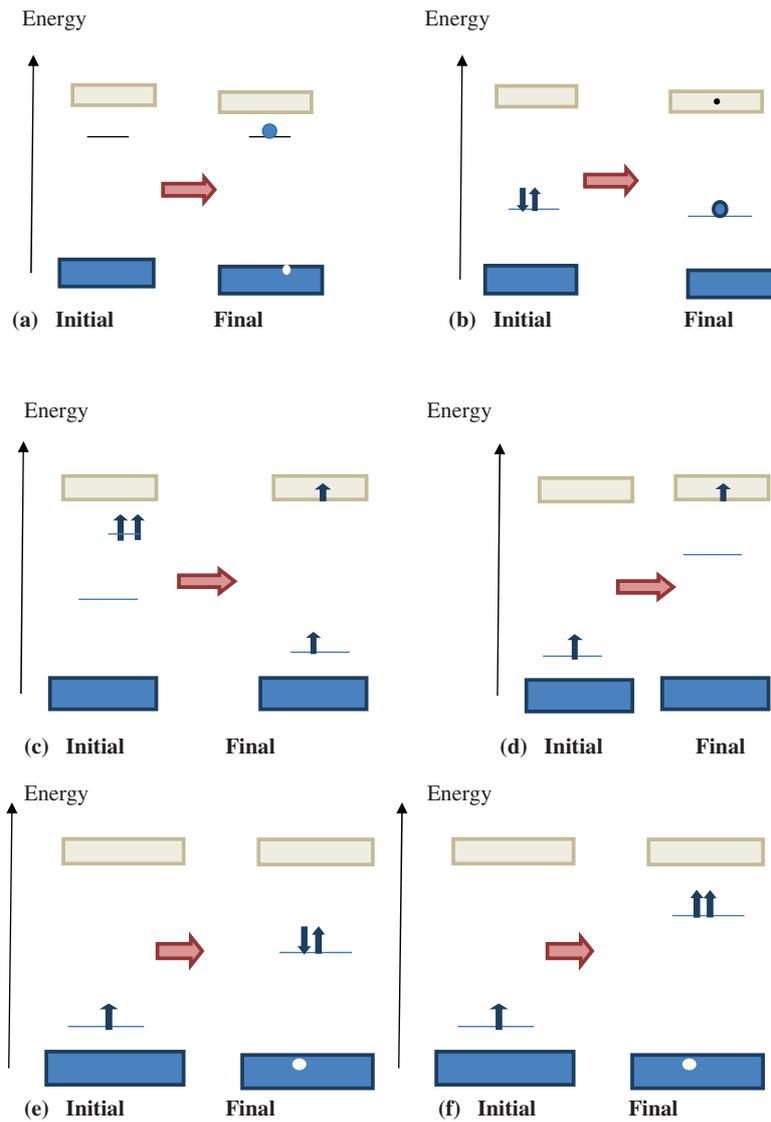


Figure 1. Shows schematically some of the transitions that can occur in ZnO with point defects, (a) and (b) show MCD silent transitions but an MCD signal should be observed for the transitions shown in (c)–(f). (a) shows a transition from the valance band to an ionised Al defect (b) a transition from a neutral oxygen vacancy in a spin singlet to the conduction band (c) a transition to the conduction band from the triplet state of the oxygen vacancy (d) ionisation of a singly occupied defect state (e) a transition from the valance band to the singly occupied oxygen state leading to a defect singlet and (f) an equivalent transition to the oxygen defect triplet.

Table 1. Summary of the samples investigated.

Samples	Growth method	Thickness
O polar ZnO	MBE	400 nm
Zn polar ZnO	MBE	400 nm
ZnO	PLD	155 nm
1% Al doped ZnO	PLD	380 nm
1% Al doped ZnO	PLD	430 nm
1% Al doped ZnO	PLD	660 nm
2% Al doped ZnO	PLD	310 nm

real absorption in the film as well as scattering from the front and back surfaces and also from grain boundaries in the film. MCD spectra were taken in the same energy range using a photoelastic modulator [31, 32]. The measurements were taken at room temperature in an applied magnetic field of 1.8T. The

data from the sapphire substrates was also recorded. Sapphire is transparent and therefore has a very low MCD when measured in degrees/cm. However, as it is so much thicker than the film, its contribution is very important and is subtracted from all our measurements. We find that when the film starts absorbing strongly, so that very low intensities are recorded at the detectors, our data falls to zero in both Faraday and MCD channels. Hence a subtraction of the data from the substrate is not possible. For this reason all the MCD data presented here has been taken where the absorption is sufficiently weak that this does not occur.

4. Experimental results

In this section we show the absorption and MCD spectra of the films. The MCD of the sapphire substrate is also shown.

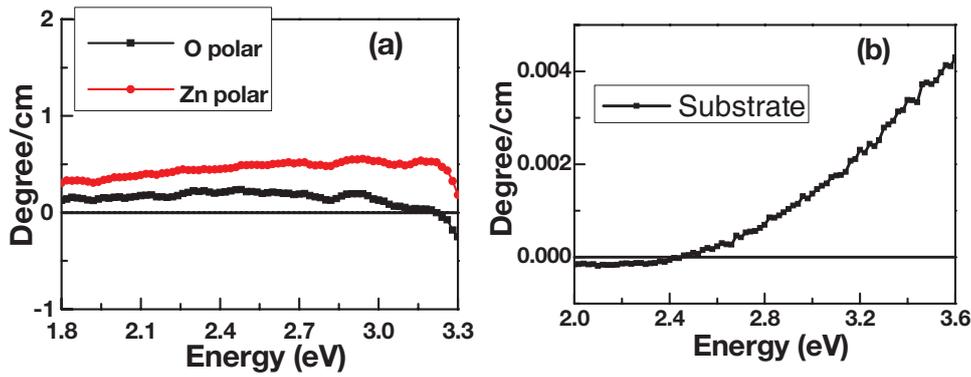


Figure 2. (a) The MCD for O-polar and Zn-polar ZnO films of thickness 400 nm (the signal from the substrate has been subtracted), (b) the MCD of the sapphire substrate.

4.1. Films of ZnO grown by MBE

The weak absorption of these films below the energy gap could not be measured accurately as the films were grown on single-side polished substrates and so there was a large scattering below the band edge from the back side of the substrate. Above the gap, 3.34 eV for both films, there was a slightly sharper edge for the O-polar film indicating that it had better crystalline quality than the Zn-polar film. This was not expected as it is usually found that the O-polar films have more defects than the Zn-polar films [4–7].

Figure 2(a) shows the MCD data for the O-polar and Zn-polar ZnO films of thickness 400 nm grown by MBE on sapphire substrates. The scattering from the back surface does not affect the MCD. This data was obtained after subtracting the signal from the substrate which was sapphire with very thin MgO and ZnO buffer layers. The MCD is larger for the Zn-polar film and increases slowly with energy however both spectra are relatively flat. The spectrum from the O-polar films has a weak maximum around 2.4 eV corresponding the prominent ‘green line’ seen in the PL spectrum [24]. Such featureless spectra have been recorded before for defect states [33] and broad PL spectra are seen in ZnO due to lattice relaxation [19, 26].

O-polar and Zn-polar films do have very different PL spectra at low temperatures [4] but these differences have largely disappeared at room temperature [34]. The MCD is sensitive to the defects that have an uncompensated spin as described in section 2 and hence this spectrum is a different weighted average from that obtained from PLD. These spectra are recorded for light that has passed right through the sample and hence have experienced the regions around both interfaces as well as the bulk region. The particular growth conditions necessary to obtain polar films causes different structural defects throughout the films [35, 36].

The MCD is very small for materials with a wide band gap as can be seen for sapphire in figure 2(b) hence the MCD from a layer of MgO layer that is thinner than 10 nm will be negligible compared with that from the ZnO. The ZnO buffer is also much thinner than the films (10 nm compared with 400 nm). Hence we can attribute the signal to the ZnO films. Both films have the same low temperature ZnO buffer and so that cannot be responsible for the observed difference

in the observed MCD of the two films shown in figure 2(a). The larger MCD signal for the Zn-polar samples imply that it has significantly more magnetically active gap states. The processes sketched in figures 1(d)–(f) all have a singly occupied oxygen vacancy state in their initial state and figure 1(c) has the triplet state as an initial state. This data demonstrates that these states all occur in these polar films [26]. The films here are of high quality and this measurement of the MCD indicates the power of this technique. The MCD rises slowly in the energy range $1.8 < E < 3 \text{ eV}$ for the Zn-polar film indicating that the density of defects increases as the band edge is approached. There is a very shallow maximum in the MCD for the O-polar film at 2.5 eV which may be the reverse process seen in PL where there is a broad emission band centred at 2.5 eV with a width of $\sim 0.5 \text{ eV}$ [19, 26]. The MCD drops just as the band edge approaches which may due to transitions to the tail of the conduction band.

4.2. Films of (ZnAl)O by PLD

The results for the absorption and MCD for pure ZnO film and the (ZnAl)O films grown by PLD are given in figures 3(a) and (b). The absorption for pure ZnO rises much more rapidly below the band gap than for the films containing Al indicating much better film quality. The inclusion of Al is known to cause a decrease in the grain size and surface roughening [25, 37]. The band gaps were evaluated from Tauc plots and the values are given in the figure caption. The aluminium forms donor states that are readily ionised at room temperature to give a high density of carriers in the conduction band that cause the absorption edge to shift from 3.5 eV to higher energy, $3.65 \pm 0.05 \text{ eV}$, due to the Burstein Moss effect [4, 7, 37]. In our data we find that the band gap does indeed increase with increasing concentration of Al; however not all our data follows the expected variation with thickness as the energy gap for the film with 1% Al and thickness 430 nm is anomalous and does not lie between the results for the 380 nm and 60 nm films as expected. The energy loss, α , below the band gap is very small $\alpha \sim 0.01\text{--}0.05 \text{ cm}^{-1}$ the largest, 0.05 cm^{-1} , occurs for the film with 2% Al which indicates a degradation in the film quality with Al doping as well as more real absorption.

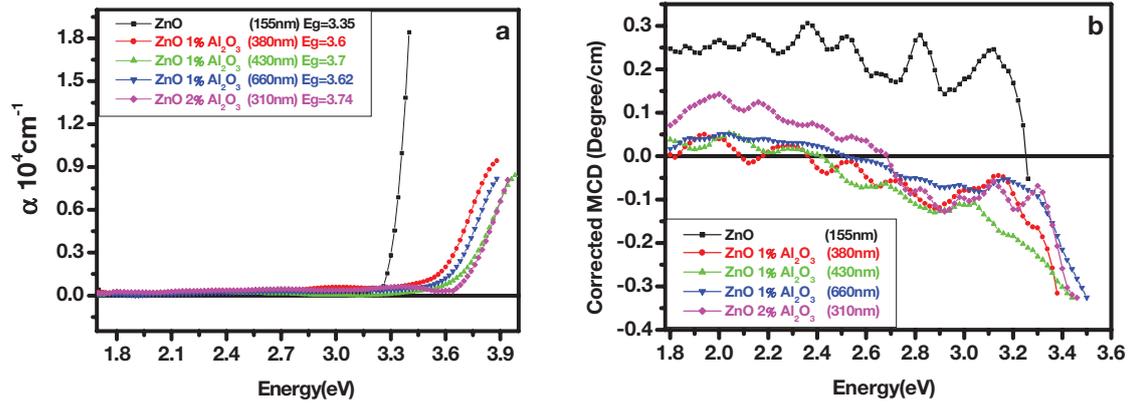


Figure 3. Data for the samples of ZnO and (ZnAl)O grown by PLD. (a) The absorption α , the inset shows the very small loss in the low energy range on an expanded scale. (b) The corrected MCD.

The absolute magnitude of the MCD spectrum per unit thickness, for the pure ZnO film is similar to that of the O-polar film shown in figure 2(a). The measured signal was smaller here because the sample was thinner, 155 nm, compared with 400 nm for the O-polar film the data and is noisier probably due to the intensity fluctuations from the Xe lamp. The MCD is small and positive over the low energy range which is characteristic of a film with oxygen vacancies as was found for the MBE films. There is a small negative region close to the band edge that arises from transitions to the band states split by the applied magnetic field as has been seen in magnetic oxides [14, 15]. This film was thin and so a correction for the relative change in transmitted intensity due to the polar Kerr effect at the interfaces of the film was significant here [38].

The positive contribution to the MCD at low energy seen in pure ZnO has been eliminated in the (ZnAl)O films with 1% doping because the partially occupied oxygen vacancy gap states that caused this signal are now doubly occupied with electrons from the aluminium and hence are nonmagnetic. There is no signal from isolated ionised aluminium donors because these ions now have a closed shell and so are nonmagnetic. The MCD from the transition shown in figure 1(d) is not observed from the neutral Al donor because this has a much smaller energy <0.01 eV than for a singly occupied oxygen vacancy state and so is outside the range of our measurements. This correlates with the result that, although both oxygen vacancies and doped aluminium do provide carriers in magnetic ZnO, the oxygen vacancies are essential for magnetism whereas the aluminium donors only enhance the magnetism when the oxygen vacancies are also present [18].

The negative signal starting at energies above 2.6 eV and continuing to the band edge has become stronger because this depends on a polarised impurity band formed from the partially occupied Al donors. The occupation of the conduction band has been increased by doping with aluminium and the MCD arises from the spin splitting of this band in a magnetic field as described in section 2. There are two competing effects for the film that was doped with 2% of Al. There is now a small positive signal at low energy that arises from the higher density of grain boundaries, due to 2% doping, that are accompanied by an additional concentration of singly ionised

oxygen states [26]. At higher energies the negative signal from the Al impurity band predominates.

These results on ZnO have shown that these films have magnetically polarisable states in the band gap that have an approximately constant density of states. The magnitude of this density of states depends on the imperfections in the films which are larger for PLD grown films than for an O-polar epitaxial film. We showed that the MCD from these states disappeared when they were occupied by an extra electron provided by a small concentration of Al donors; however the concentration of defect states increased faster than the effects of compensation for the more heavily doped film because of the increase of the number of partially ionised oxygen vacancy states associated with the grain boundaries.

Our results for MCD may be compared with the results of PL for films deposited by PLD [25] and ultrasonically assisted chemical vapour deposition with and without the addition of Al [39]. In both cases the inclusion of Al dramatically reduced the intensity of the green PL signal at around 2.2 eV whereas this signal was partially restored for our sample of 2% Al. There was no PLD signal from the defect band detected by MCD at energies above 2.6 eV.

4.3. The MCD of the sapphire substrate

We conclude this section with brief remarks on the MCD spectrum of another wide band oxide sapphire, Al_2O_3 , whose MCD spectrum was shown in figure 2(b). The band gap of sapphire is ~ 8.7 eV which is very much wider than ZnO. Hence the MCD (degrees/cm) is much smaller, about 0.004 compared 0.2–0.4 for ZnO. In this case the MCD has detected effects from a very small absorption that would be unlikely to be detectable by direct means. However it is interesting to note that the energy dependence follows the more usual pattern of increasing as the energy is getting closer to the band edge.

5. Conclusions

MCD is known to be a good technique for investigating magnetic materials. In this paper we have shown that it is also useful for detecting and characterising gap states in non-magnetic materials as well even though these effects

are very small. It is a useful complementary tool to photoluminescence because the MCD is only sensitive to the states that are magnetically polarisable whereas the PLD also detects transitions to or from singlet states. Hence a comparison of the two techniques will allow the spin of the deep gap states to be measured. Many of the applications of ZnO involve doped samples and in this case the PL spectrum will be quenched and but measurement of the MCD is still possible.

We then applied the technique first to two different types of polar ZnO-based samples. In this case we could compare our results to the published PL data. We found that the Zn-polar ZnO film contained more spin polarisable gap states than the O-polar one; this was an unexpected result for our films. The energy distribution of the states was slightly different for the two polarities indicating different crystalline imperfections. The broad response in the MCD showed that there are spin polarisable states at a large range of energies.

The MCD of the Zn-polar film was similar to an oxygen-deficient ZnO film grown by PLD. The addition of 1% aluminium quenched the MCD signal at lower energies observed in all three pure ZnO samples due to the electron filling of the polarized gap states. Although there was also an increase in the density of electrons in the band states with higher concentration of aluminium. We also found evidence for the importance of surface states in the thinnest (ZnAl)O samples. The increase in the signal from partially ionised oxygen vacancies in the grain boundaries increased with the concentration of Al. These charged states are clearly an important source of scattering of the mobile carriers and responsible for reducing the mobility as the concentration of Al is increased. We found that films doped with 1% Al had significantly fewer partially ionised oxygen defects. Hence MCD is a powerful technique for determining this important source of scattering mechanisms in ZnO:Al. Many uses of ZnO require oxygen vacancies so the MCD which detects the singly ionised oxygen and any triplet states on oxygen vacancy sites will be a very useful characterisation tool.

The nearly constant density of states in the gap of ZnO is very important for the incorporation of ZnO in organic solar cells and LED's because the localised gap states can couple efficiently to the localised states that occur in the organic materials [38, 40, 41]. Hence this work has shown that this technique can make a contribution to the design of efficient OLED's and organic solar cells.

Finally when we measured the MCD of the sapphire substrates we found an extremely weak positive signal for energies above 2.4 eV which is a long way below the band gap at 8.7 eV. We expected this to be extremely small because the magnetic response of sapphire substrates is diamagnetic and hence any contribution to the susceptibility from polarisable gap states must be overwhelmed by the diamagnetic response of the bulk of the material. The MCD could be measured because the substrate was considerably thicker than our films. However it showed that crystalline imperfections in this insulator also give rise to gap states in the energy range, 2 eV–3.6 eV, covered by our experiment.

We expect that the MCD technique will find similar use in a wide range of other materials that are transparent but weakly absorbing in the visible region.

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References

- [1] Ozgur U, Alivov Y I, Liu C, Teke A, Reshchikov M A, Dogan S, Avrutin V, Cho S J and Morkoc H 2005 *J. Appl. Phys.* **98** 041301
- [2] Sze S M 2002 *Semiconductor Devices Physics and Technology* 2nd edn (New York: Wiley)
- [3] Straumal B B, Mazilkin A A, Protasova S G, Myatiev A A, Straumal P B, Schutz G, van Aken P A, Goering E and Baretzky B 2009 *Phys. Rev. B* **79** 205206
- [4] Lautenschlaeger S, Sann J, Volbers N, Meyer B K, Hoffmann A, Haboeck U and Wagner M R 2008 *Phys. Rev. B* **77** 144108
- [5] Nakamura T, Yoshimura T, Ashida A and Fujimura N 2014 *Thin Solid Films* **559** 88–91
- [6] Williams J et al 2012 *Appl. Phys. Lett.* **100** 051902
- [7] Oh D C, Kato T, Park S H, Hanada T, Yao T and Kim J J 2008 *Appl. Phys. Lett.* **93** 241907
- [8] Tampo H, Shibata H, Matsubara K, Yamada A, Fons P, Niki S, Yamagata M and Kanie H 2006 *Appl. Phys. Lett.* **89** 132113
- [9] Meyer B and Marx D 2004 *Phys. Rev. B* **69** 235420
- [10] Wang L W 2009 *Mat. Sci. Eng. R* **64** 33–71
- [11] Sernelius B E, Berggren K F, Jin Z C, Hamberg I and Granqvist C G 1988 *Phys. Rev. B* **37** 10244
- [12] Kim H, Piqué A, Horwitz J S, Murata H, Kafafi Z H, Gilmore C M and Chrisey D B 2000 *Thin Solid Films* **377–8** 798–802
- [13] Tsubata T, Ohtaki M, Eguchi K and Arai H 1997 *J. Mater. Chem.* **7** 85–90
- [14] Mahroug S, Boudjadar S, Hamrit S and Guerbous L 2014 *Mater. Lett.* **134** 248–51
- [15] Terasako T, Ogura Y, Fujimoto S, Song H, Makino H, Yagi M, Shirakata S and Yamamoto T 2013 *Thin Solid Films* **549** 12–7
- [16] Yang Y C, Song C, Wang X H, Zeng F and Pan F 2008 *Appl. Phys. Lett.* **92** 012907
- [17] Xu X H, Blythe H J, Ziese M, Behan A J, Neal J R, Mokhtari A, Ibrahim R M, Fox A M and Gehring G A 2006 *New J. Phys.* **8** 135
- [18] Qi S, Jiang F, Fan J, Wu H, Zhang S B, Gehring G A, Zhang Z and Xu X 2011 *Phys. Rev. B* **84** 205204
- [19] Leiter F, Alves H, Pfisterer D, Romanov N G, Homann D M and Meyer B K 2003 *Physica B* **340–342** 201–4
- [20] Chen X, Wu G, Jiang P, Liu W and Bao D 2009 *Appl. Phys. Lett.* **94** 033501
- [21] Chang W Y, Lai Y C, Wu T B, Wang S F, Chen F and Tsai M J 2008 *Appl. Phys. Lett.* **92** 022110

- [22] Kim M S, Hwang Y H, Kim S, Guo Z, Moon D, Choi J M, Seol M L, Bae B S and Choi Y K 2012 *Appl. Phys. Lett.* **101** 243503
- [23] Chen G, Song C, Chen C, Gao S, Zeng F and Pan F 2012 *Adv. Mater.* **24** 3515–20
- [24] Yamamoto S 2012 *J. Appl. Phys.* **111** 094310
- [25] Liu Y D and Lian J S 2007 *Appl. Sur. Sci.* **253** 3727–30
- [26] Ye J D *et al* 2005 *Appl. Phys. A* **81** 759–62
- [27] Scott G B, Lacklison D E, Ralph H I and Page J L 1975 *Phys. Rev. B* **12** 2562
- [28] Liu Z L, He X, Mei Z X, Liang H L, Gu L, Duan X F and Du X L 2014 *J. Phys. D: Appl. Phys.* **47** 105303
- [29] Xu Q Y, Wang Y, Wang Y G, Du X L, Xue Q K and Zhang Z 2004 *Appl. Phys. Lett.* **84** 2067–9
- [30] Wang Y, Xu Q Y, Du X L, Mei Z X, Zeng Z Q, Xue Q K and Zhang Z 2004 *Phys. Lett. A* **320** 322–6
- [31] Sato K 1981 *Japan. J. Appl. Phys.* **20** 2403–10
- [32] Van Drent W P and Suzuki T 1997 *J. Mag. Magn. Mater.* **175** 53–62
- [33] Saji K J and Jayaraj M K 2008 *Phys. Status Solidi a* **205** 1625–30
- [34] Yamamoto A, Moriwaki Y, Hattori K and Yanagi H 2011 *Appl. Phys. Lett.* **98** 061907
- [35] Allen M W, Zemlyanov D Y, Waterhouse G I N, Metson J B, Veal T D, McConville C F and Durbin S M 2011 *Appl. Phys. Lett.* **98** 101906
- [36] Ohshima E, Ogino H, Niiikura I, Maeda K, Sato M, Ito M and Fukuda T 2004 *J. Cryst. Growth* **260** 166–70
- [37] Dong B Z and Fang G J 2007 *J. Appl. Phys.* **101** 033713
- [38] Ying M J, Alqahtani M S, Dizayee W, Griffin J, Buckley A, Fox A M and Gehring G A *Magnetic Circular Dichroism Studies of Amorphous MoOx* to be published
Dizayee W, Ying M, Fox A M and Gehring G A 2015 arXiv:1505.03458
- [39] Sharma B K and Khare N 2010 *J. Phys D: Appl. Phys.* **43** 465402
- [40] Guillén E, Peter LM and Anta J A 2011 *J. Phys. Chem. C* **115** 22622–32
- [41] Bolink H J, Brine H, Coronado E and Sessolo M 2010 *Appl. Mater. Interfaces* **2** 2694–8