Effective mass in diluted magnetic semiconductors: Zn_{0.98}Ti_{0.02}O by means of magneto-optics

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Abstract
Thin film samples of Ti-doped ZnO were grown on sapphire (0001) substrates by pulsed laser deposition (PLD). The magnetic moments were measured by SQUID magnetometry and the films were ferromagnetic at room temperature. The Faraday rotations and magnetic circular dichroisms (MCD) were measured as a function of energy at the range of 1.5-4 eV, and carrier concentrations were obtained from Hall effect measurement. The samples exhibited a band-edge shift, which varied with carrier concentration. Effective-mass of carriers were obtained by the Burstein-Moss effect and the band-gap shrinkage.

Keywords: diluted magnetic semiconductor, magnetic circular dichroism, effective-mass, Burstein-Moss effect, band-gap shrinkage

1. Introduction
ZnO is a semiconductor with a direct-transition semiconductor and wide band-gap (3.4 eV at room temperature). Therefore, ZnO-based DMS would be useful for short-wavelength magneto-optical (MO) applications [1]. Diluted magnetic semiconductors (DMSs) are also known as semi-magnetic semiconductors, in which rare earth or transition metal ions replace a considerable number of the native ions in the semiconductor’s lattice [2, 3]. The MCD spectrum can identify the origin of ferromagnetism, because the ferromagnetic metals often show a monotonic MCD spectrum, thus the relationship between the MCD and absorption spectra is apparent.

There have also been earlier reports that no MO effects exist in Ti doped samples [4] and although a signal was obtained, no hysteresis loop was shown at low temperature [5]. However, Neal et al. [6] observed a strong MCD signal and the MCD ferromagnetic hysteresis loop at the band edge even at room temperature. On the other side, increasing carrier density on the heavily doped semiconductors cases the band-edge shift [7-9].

2. Preparation of target for PLD
The Zn_{0.98}Ti_{0.02}O target was prepared by mixing appropriate amounts of Johnson Matthey 99.999% purity powders of ZnO and TiO_2 in the following way.

3. The PLD system
The PLD system is consisted of three main parts:
a) The laser,
b) The optical system,
c) The deposition chamber.
The laser used in this work was a Lambda Physik
LEXTRA 200 excimer laser operating at a wavelength of 308 nm (XeCl). The laser produced a pulse with energy per pulse up to 400 mJ, and of duration 28 ns. The laser was operated at a frequency of 10 Hz.

The optical arrangement consisted of a quartz lens of focal length 40 cm (for transmission UV wavelength) mounted on a horizontal rail; this focused the beam, through an optical window in the PLD chamber, onto the surface of the target inside the chamber. The laser beam was incident on the rotating target at 45° to the target normal and created a spot size of about 3 mm² (see figure 1). The target-substrate distance was fixed at 3.5 cm for all the films. Before deposition, the substrates were carefully cleaned with ethanol and those were then fixed onto the substrate holder using two small steel clamps.

4. Samples and measurements

The samples studied were thin films grown on sapphire (0001) substrates at 450 °C by PLD; the oxygen pressure in the deposition chamber was 10 mTorr. Magnetization measurements were made with a quantum design SQUID magnetometer and the thickness of the films was measured with a Dektak profilometer and lay in the range 60−1250 nm. The magneto-optic spectra were taken with a Xe lamp and monochromator with a photoelastic modulator.

Table 1 shows thicknesses, carrier densities and saturation magnetic moments of the investigated samples.

5. Results

Figure 2 shows the MCD spectra of some of the samples measured in a field of 0.9 T. Figure 3 also shows the effect of carrier density on magnetic moment, which is fully explained by A J Behan et al. [14] and Xu et al. [15]. We note that the position occupied by a donor atom depends on several factors, such as donor concentration, deposition temperature, deposition chamber pressure and the laser ablation energy and also the cooling rate after deposition. However, we tried to ensure that the preparation conditions were the same for all samples.

On the other hand, by considering the band-gap energy, we could see that the variations of the carrier density cause the MCD peaks to appear at different energy values for these samples.

6. Effective mass

The influence of increasing carrier density on the band-gap widening and narrowing of heavily doped semiconductors has been observed in a number of earlier papers [7-9,16,17]. These earlier reports are in general agreement with two phenomena, firstly, the Burstein-Moss effect and secondly the band-gap shrinkage [8, 9].

The Burstein-Moss effect expresses the fact that the dopant atoms become ionized and their electrons occupy the bottom of the conduction band, and causes the band-gap to become larger than in the undoped semiconductor crystal [9]. Band-gap narrowing occurs when a semiconductor is in the metallic-like phase. Since it could be observed when the carrier concentration has almost satisfied the Mott condition [18], the metal-insulator transition occurs for \( n_C \sim 0.25 \) [14] and leads to a critical concentration, \( n_C \sim 3 \times 10^{19} \text{cm}^{-3} \) [8]; this effect is associated with different many-body effects on the conduction and valence bands [9].

Under these conditions the, band-gap energy is given by;

\[
E_g = E_{g0} + \Delta E_{BM} = \Delta E_g ,
\]

Where \( E_{g0} \) is the undoped semiconductor's band-gap energy, \( \Delta E_{BM} \) is the Burstein-Moss effect shift and \( \Delta E_g \) band-gap shrinkage shift. \( \Delta E_{BM} \) is given by [9]:

\[
\Delta E_{BM} = \frac{\hbar^2 k_F^2}{2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) = \frac{\hbar^2}{2m} \left( 3\pi^2 n_e \right)^{2/3} ,
\]

where \( \frac{1}{m} = \frac{1}{m_e} + \frac{1}{m_h} \), and [8]

\[
\Delta E_g = A(n_e)^{1/3} .
\]

A has different values for the measured value of \( \Delta E_g \) at high \( n_e \). For \( n \sim 10^{20} \text{cm}^{-3} \), \( A \approx 3.6 \times 10^{-8} \text{eVcm} \).

The variations in band-gap occur by increasing carrier...
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Table 1. Thickness, carrier density, the ratio of carrier density \( n_C \) to the donor density \( n_I \) \( (n_C/n_I) \), \( m^*/m \), \( E_g \) and saturation magnetic moment of \( \text{Zn}_0.98\text{Ti}_{0.02}\text{O} \) thin films. Samples marked I are insulator \( (n_C < 3.5 \times 10^{19}) [18] \).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thickness (nm)</th>
<th>Carrier density ( \text{cm}^{-3} )</th>
<th>( m^*/m )</th>
<th>( E_g ) (eV)</th>
<th>( n_C/n_I )</th>
<th>Magnetic moment ( \mu_B / \mu_T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM009</td>
<td>190</td>
<td>8.7E+20</td>
<td>0.77</td>
<td>3.44</td>
<td>1.04</td>
<td>0.04</td>
</tr>
<tr>
<td>AM010</td>
<td>310</td>
<td>9.5E+20</td>
<td>0.77</td>
<td>3.46</td>
<td>1.13</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>AM011 I</td>
<td>70</td>
<td>2.8E+19</td>
<td>0.31</td>
<td>3.46</td>
<td>0.03</td>
<td>0.37</td>
</tr>
<tr>
<td>AM012</td>
<td>400</td>
<td>5.2E+20</td>
<td>0.52</td>
<td>3.50</td>
<td>0.62</td>
<td>0.07</td>
</tr>
<tr>
<td>AM013 I</td>
<td>60</td>
<td>1.8E+19</td>
<td>0.36</td>
<td>3.42</td>
<td>0.02</td>
<td>0.68</td>
</tr>
<tr>
<td>AM014</td>
<td>200</td>
<td>7.2E+20</td>
<td>0.71</td>
<td>3.44</td>
<td>0.86</td>
<td>0.11</td>
</tr>
<tr>
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<td>150</td>
<td>1.3E+21</td>
<td>0.70</td>
<td>3.58</td>
<td>1.55</td>
<td>0.14</td>
</tr>
<tr>
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<td>260</td>
<td>3.1E+19</td>
<td>0.30</td>
<td>3.36</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>AM017</td>
<td>1250</td>
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<td>0.81</td>
<td>3.46</td>
<td>1.31</td>
<td>0.11</td>
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<tr>
<td>AM018</td>
<td>840</td>
<td>9.2E+20</td>
<td>0.75</td>
<td>3.54</td>
<td>1.09</td>
<td>0.02</td>
</tr>
<tr>
<td>AM020</td>
<td>400</td>
<td>1.5E+21</td>
<td>0.85</td>
<td>3.5</td>
<td>1.78</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Figure 3. Magnetic moment as a function of carrier density for \( \text{Zn}_0.98\text{Ti}_{0.02}\text{O} \) thin films at room temperature; the curve is a guide to the eye.

Figure 4. \( m^*/m \) as a function of carrier density, the curve is the best fitted to the data.

density, changing the conduction band, and the valence band from a parabolic to a non-parabolic shape in a direct-transition semiconductor [9].

Since most of our samples are metallic-like with variation carrier density and different observed band gaps in the MCD spectra, we have used relations (1), (2), (3) and calculated the effective masses for the investigated samples. However, for the insulators samples we have ignored the energy shift of the narrowing band-gap as reported by A P Roth et al. [8]. The results are listed in table 1 and also plotted in figure 4.

The obtained results show that in this model the effective mass for a wide band-gap and degenerate thin oxide film first decreases until around \( n_C \sim 6.4 \times 10^{19} \) and then increases with increasing carrier density.

7. Conclusions
By considering the band-gap energy, it can be seen that the MCD peaks all occur at different values for these samples that caused variations carrier density. By using the emerging band-gap in MCD spectrum for the investigated \( \text{Zn}_0.98\text{Ti}_{0.02}\text{O} \) thin film samples produced the effective mass as a function of carrier density.

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References
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