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Ultrafast electron spin dynamics in ZnO and $Zn_{1-x}Co_xO$ sol-gel thin films

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Abstract. We probe the electron spin dynamics in ZnO and $Zn_{1-x}Co_xO$ sol-gel films with time-resolved Faraday rotation spectroscopy. Dephasing times T_2* on the order of nanoseconds are observed at room temperature due to charge-separated states. In ZnCoO the effective electron Landé g factor rises with increasing Co^{2+} concentration, providing the mean-field electron-Co^{2+} exchange energy $N_0\alpha = +0.25 \pm 0.02$ eV.

Semiconductors are well-suited for ultrafast opto-spintronics. Polarized femtosecond laser pulses may be used to intitialize, manipulate and read out spin states in semiconductor systems ranging from three to zero dimensions. The wide-bandgap semiconductor ZnO possesses both a large bandgap of 3.4 eV and an exciton binding energy of 60 meV. These properties will be strongly beneficial to room-temperature operation of future spintronic devices made of this material. ZnO may also be readily doped with magnetic ions. $Zn_{1-x}Co_xO$ has received extraordinary attention over the past decade, ever since reports of room-temperature ferromagnetism in this material began to appear. Remarkably, the magnitude of the Co^{2+}-electron exchange energy $N_0\alpha$ has never been measured for this diluted magnetic semiconductor.

We use time-resolved Faraday rotation (TRFR) spectroscopy in the ultraviolet to directly probe the transient electron spin dynamics in chemically prepared ZnO and $Zn_{1-x}Co_xO$ sol-gel films [1]. Figure 1 shows TRFR traces of an undoped ZnO sol-gel film, recorded at a temperature of T = 10 K and room temperature, along with traces collected from $Zn_{1-x}Co_xO$ films at various Co^{2+} concentrations.

Surprisingly, TRFR signals not only persist up to room temperature, but the electron spin dephasing time T_2^* increases with rising temperatures, in stark contrast with previous observations for epitaxial ZnO films. Sol-gel films of $Zn_{1-x}Co_xO$ show a similar temperature dependence of T_2^*. The contrast with epitaxial films suggests that the anomalous T_2^* observed in these sol-gel ZnO films arises from their granularity. Hole traps at the surfaces of ZnO nanocrystals slow down electron-hole recombination and hence allow observation of extended electron spin coherence times. We have observed this effect in a previous study on the ultrafast spin dynamics in colloidal ZnO quantum dots [2] and believe that this mechanism is also active in the sol-gel films studied here. We confirmed this hypothesis by probing the carrier recombination dynamics in a regular pump-probe experiment recording differential transmission and comparing the results to the spin dynamics obtained by the TRFR measurements.

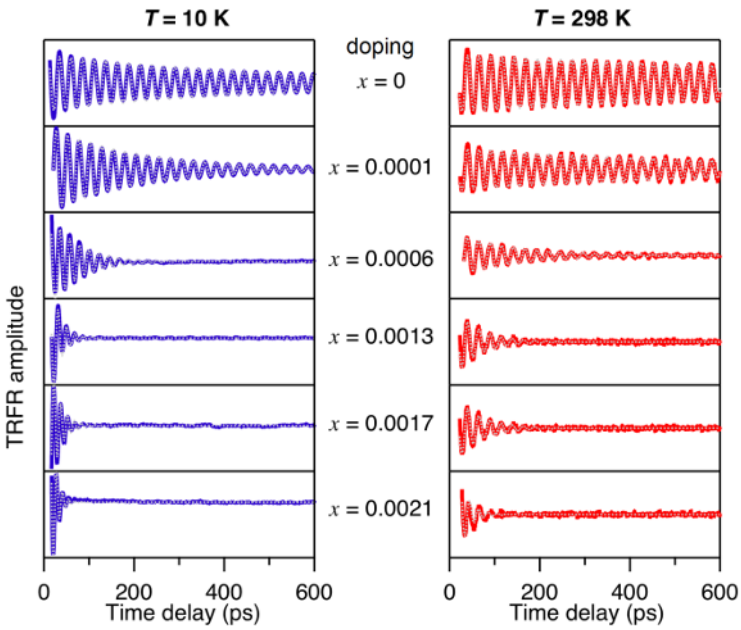

Fig. 1. Time-resolved Faraday rotation curves for ZnO and $Zn_{1-x}Co_xO$ sol-gel thin films, recorded at a temperature of T = 10 K (left) and room temperature (right). Exponentially damped sinusoidal fits are displayed as dotted lines.

We now turn to magnetically doped ZnO. Upon addition of Co^{2+} to the ZnO sol-gel films, an increase in the precession frequency (*i.e.*, an increase in g^*) is observed (Fig. 1). The temperature dependence of g^* is shown in Figure 2. In undoped ZnO, g^* remains nearly constant between T = 10 and 298 K (g^* = 1.98 – 2.00). In $Zn_{1-x}Co_xO$, however, g^* decreases with increasing temperature, approaching that of the undoped ZnO at high temperatures. These experimental results reflect the existence of exchange coupling between the photoexcited electrons and the Co^{2+} dopants. A global fit of the data in Figure 2 yields the electron-Co^{2+} exchange coupling parameter $N_0\alpha = +0.25 \pm 0.02$ eV. The value reported here is independent of complications of earlier attempts using steady-state experimental techniques. Recent *ab initio* calculations on bulk $Zn_{1-x}Co_xO$ have suggested $N_0\alpha = +0.34$ eV, which is in good agreement with our experimentally determined value.

The second striking observation in the TRFR traces of Fig. 1 is that electron spin dephasing is strongly accelerated by introduction of Co^{2+} into the sol-gel ZnO films. With as little as $x = 0.0001$, T_2^* drops from 600 to 250 ps at $T = 10$ K. The accelerated dephasing upon addition of magnetic impurities is due to local fluctuations of the magnetization, which in turn arise from thermal fluctuations of $\langle S_x \rangle$ and from microscopically inhomogeneous spatial distributions of the dopant ions (*i.e.*, a breakdown of the virtual crystal approximation). The resulting linear dependence of $1/T_2^*$ on the Co^{2+} concentration x observed in the experiment (data not shown) has been verified by a model based on these two effects.

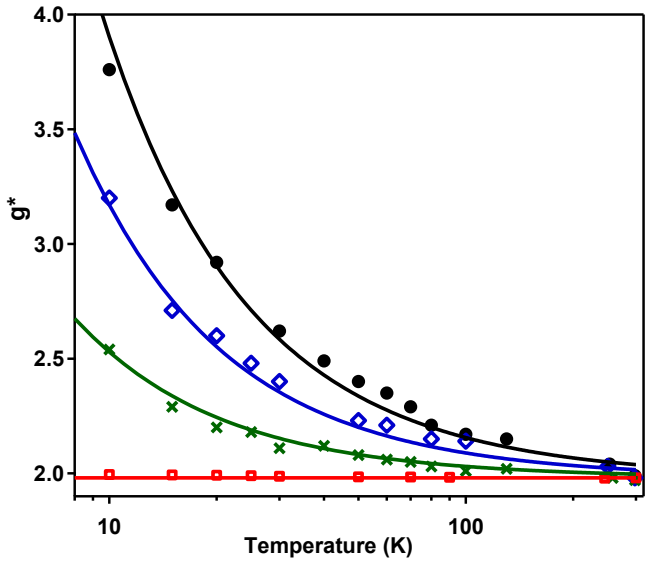

Fig. 2. Temperature dependence of the effective g-factor g^* in $Zn_{1-x}Co_xO$ with $x = 0.0021$ (filled circles), 0.0013 (open diamonds), 0.0006 (crosses), and 0.0000 (undoped ZnO, open squares).

In conclusion, we have prepared ZnO and $Zn_{1-x}Co_xO$ films suitable for optical electron spin generation and detection using rapid solution techniques. Precise control over x marks a promising advance in the development of flexible, low-cost preparative methods for incorporation of oxide diluted magnetic semiconductors into ultraviolet optical microcavities [3] or related opto-electronic and opto-spintronic device structures. In both ZnO and $Zn_{1-x}Co_xO$ sol-gel films, the ensemble electron spin dephasing times T_2^* grow longer at elevated temperatures. This unprecedented property is attributed to inhibition of carrier recombination via thermally activated hole trapping. Through analysis of the electron's effective g factor as a function of Co^{2+} concentration, the mean-field electron-Co^{2+} exchange coupling parameter in $Zn_{1-x}Co_xO$ has been determined to be $N_0\alpha = +0.25 \pm 0.02$ eV.

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