Magnetism as a tool for band-gap narrowing of zinc oxide films prepared by sol–gel method

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Abstract

sp–d exchange interaction was used to narrow the room-temperature band gap of zinc oxide films prepared by sol–gel method. Zinc oxide was doped with manganese ions by adding manganese chloride to the precursor and post-annealing in hydrogen. Films with different concentrations of manganese were prepared. Exchange interaction was established between the manganese ions in the lattice by introducing oxygen vacancies. The magnetic moment was found to increase with the concentration of manganese. For low concentrations of manganese, the band gap of the doped semiconductor was found to be wider than that of undoped ZnO films, in agreement with Vegard's law. High concentrations of dopant resulted in a narrowing of the band gap. We ascribe the narrowing of the band gap to conduction band-edge Zeeman shifting.

Introduction

Wide band-gap semiconductors, such as TiO22 and ZnO, are used in catalysis and water splitting because they are cheap, chemically stable and corrosion resistant [1]. Yet, photocatalytic efficiency could be significantly enhanced if they were engineered to absorb in the visible and near infrared range. The particular problem is to narrow the band gap without compromising on cost and chemical stability. An approach that has been attempted is the acceptor–donor pair chemical codoping, with the acceptor being nitrogen or carbon [2–5]. Yet, *p*-type doping of oxide semiconductors is very difficult to achieve and, when achieved, leads to films with highly questionable chemical stability. A different approach is based on defect engineering. A large amount of lattice defects, usually oxygen vacancies (VOO's), can be introduced at the surface of the semiconductor oxide by hydrogenation at high temperature [6–8]. If the number of surface defects is large, so is the number of mid-gap states, which eventually will form a continuous band that overlaps with either the conduction or valence band, hence resulting in band-gap narrowing. Unfortunately, the enhancement of photoactivity in these so-called black oxides was found to be disappointingly weak and most likely to be ascribed to improved carrier density. While the induced defect states effectively narrow the optical band gap, they act as efficient recombination centers for photogenerated carriers that will never reach the electrodes.

The introduction of a magnetic order represents an original approach toward narrowing the band gap. *sp–d* exchange interaction in *n*-type semiconductors widens the conduction band because of Zeeman splitting, hence narrowing the band gap. The concept has been well demonstrated in low-temperature magnetic semiconductors, such as bulk Cd1−x1−xZnyyMnxxTe [9, 10] and Zn1−x1−xMnxxSe [11]. All these compounds are not magnetic at room temperature; therefore, a large magnetic field must be applied to align the spin of the 3*d* magnetic dopants. Yet, important

progresses have been made in the last years in the synthesis of room-temperature-diluted magnetic semiconductors, in particular oxide semiconductors [12]. Yang and Nie [13] have reported a significant redshift in the band gap of Co-doped ZnO, and even more interesting, Xu et al. [14] reported a significant enhancement of the photocatalytic properties under visible light as compared to pure ZnO when methyl orange was used as a test contaminant. Similarly, our group has reported redshift of the band gap due to *sp–d* exchange interaction in Mn-substituted ZnO at room temperature [15]. Mn-substituted ZnO is a convenient testbed system to study the effect of exchange interaction on the energy band structure of ZnO because Mn replaces Zn in the lattice with the same valence; hence, it does not change the carrier concentration while introducing a magnetic moment [16]. So far this strategy for narrowing the band gap has been pursued in thin films grown by using high vacuum-based deposition techniques, whereas sol–gel methods would be more cost-effective for applications.

We here report a narrowing of the band gap in ZnO prepared by sol–gel method at room temperature. Films with different concentration of Mn were prepared. A concentration of Mn up to 12 at.% was successfully substituted in the ZnO lattice. Exchange interaction was established between the Mn ions through the mediation of oxygen vacancies introduced through thermal annealing in H22 atmosphere. We measured a redshift in the photoluminescence band-edge peak in films with high concentration of Mn.

Experimental

For the synthesis of the films, the precursor zinc acetate dihydrate [Zn (CH33CO22)22 ·· 2H22O] and manganese chloride (MnCl22) were dissolved in ethylene glycol monomethyl ether (EGME). Solutions with different concentrations of dopant MnCl22 were prepared by tuning the molar

ratio between Zn and Mn. The stabilizer monoethanolamine (MEA) was added in 1:1 molar ratio. The obtained solution was stirred at 80∘∘ for 1 h. The sols were then aged for 2 days after sealing. Before spin coating, single-crystal silicon (100) substrates were cleaned by using the RCA standard cleaning procedure [17]. The sols were spin-coated on the substrates at a spinning speed of 3000 rpm for 30 s. After spinning, the samples were left drying at room temperature for 5 min. Subsequently, they were preheated at 200 ∘∘C in air for 10 min to evaporate the solvent and to remove the residual organics. The thickness of the films could be tuned by repeating the procedure from spin coating to preheating. Thicknesses of the order of hundreds of nanometers could be obtained. The samples were annealed in H22 atmosphere at 400 ∘∘C for 1 h in order to improve crystallinity, as well as increase the concentration of oxygen vacancies. As will be explained later, oxygen vacancies are the mediators for spin interaction and are required to introduce a magnetic moment in the films.

The crystal structure of the films was investigated by X-ray diffractometry using a Philps XPert with Cu Kαα radiation source (λCu=0.154λCu=0.154 nm). The stoichiometry of the films was checked by energy-dispersive X-ray spectroscopy (EDS). The magnetization versus field (MH) loops of the grown films were measured at 300 K by a vibrating sample magnetometer (VSM). Photoluminescence (PL) measurements were carried out by using the fourth harmonic of a Nb:yttrium–aluminum–garnet laser (λ=266λ=266 nm) as the excitation source and a 0.5-m spectrometer equipped with a 150-ln/mm grating and an intensified CCD camera (PI-MAX2) as light emission detector.

Results and discussion

Figure 1 shows the XRD patterns of three different samples, namely pure ZnO, 2 at.% Mn–ZnO and 12 at.% Mn–ZnO. The reported concentration of Mn is the real one, as measured by EDS.

The intensity of each pattern was normalized to the respective maximum value for better comparison. For all samples, we could only detect the (002) peak from the ZnO wurtzite structure, besides those corresponding to silicon (100). We could not detect any other diffraction peak from ZnO, which indicates that the films are texturized along the *c*-axis. We could not detect any peak corresponding to MnxxOyy, which suggests good substitution of Mn in Zn sites in the lattice.

The (002) peak slightly shifts to lower angle as the concentration of Mn increases. This is the expected behavior for Mn-substituted ZnO since the radius of Mn2+2+ (0.066 nm) is slightly larger than that of Zn2+2+ (0.060 nm), which must lead to an expansion of the lattice if Mn replaces Zn. The full-width at half-maximum (FWHM) of the (002) peak does not significantly change with the Mn concentration, for the maximum concentration of 12 at.% considered here, and it corresponds to a grain size of ∼∼20 nm as calculated by Debye–Scherrer formula.

Figure 2 shows the magnetization loops of the pure and Mn-substituted ZnO thin films. A magnetic moment different from zero exists in pure ZnO. This is a common observation, which other authors have ascribed to clustering of oxygen vacancies [18]. The magnetic moment increases with the concentration of Mn, as expected. It must be noticed that ferromagnetism in diluted magnetic oxides is not due to direct exchange interaction but formation of bound magnetic polarons [19]. Magnetic polarons are localized regions in the material where Mn ions can exchange moment through the mediation of oxygen vacancies. Not all the Mn is ferromagnetically coupled, and therefore, the overall magnetic moment does not have a trivial linear dependence on the concentration of Mn.

Figure 3 shows the PL measurements carried out at room temperature. Only the range of wavelength between 330 and 500 nm has been plotted after normalization to the maximum intensity. We focused on this range to emphasize the correlation between the band gap and the magnetic order of the films. A small and very broad emission peak exists in the visible range. This is a common observation for ZnO and is due to recombination of defect acceptors (Zn vacancies or Zn interstitial) with oxygen vacancy donors [20, 21].

The magnetic order has a clear effect on the position of the near band-edge emission peak. Substituting Mn in paramagnetic state into ZnO is expected to broaden the band gap, according to Vegard's law [22]. This is because MnO has a larger band gap than ZnO (4.2 and 3.3 eV, respectively). On the contrary, if Mn forms a ferromagnetic phase, *sp–d* exchange interaction tends to narrow the band gap as a consequence of the downshifting of the conduction band edge due to Zeeman effect [9–11]. In Mn-substituted ZnO both effects are at play and can prevail according to the amount of Mn that forms bound magnetic polarons. In our samples, for low concentration of Mn the average distance between Mn ions in the crystal is relatively long and most of the Mn is in the paramagnetic state; therefore, the blue shift prevails. As the concentration of Mn increases, more closely spaced Mn ions can form bound magnetic polarons. As a consequence, the magnetic moment increases and the redshift prevails. It must be noticed that the size of the bound magnetic polarons in the absence of externally applied magnetic field is of the order of tens of nm [23], whereas the laser spot size for the PL measurements in Fig. 3 is ~100μ~100μm.

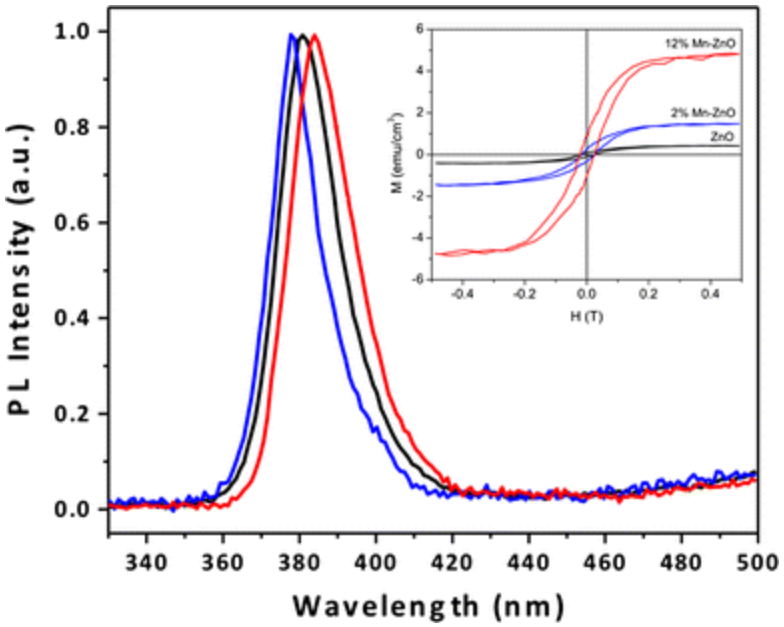
While the effect we observe here has already been reported at room temperature in magnetically diluted oxide semiconductors, it has been reported on either powders or films grown by pulsed

laser deposition [13–15]. To the best of our knowledge, the effect has never been observed before in films prepared by sol–gel methods. Our work suggests that this strategy toward band-gap narrowing of oxide semiconductors can be extended to low-cost thin-film technologies.

Conclusions

We studied the effect of the magnetic order on the optical band gap of ZnO thin films prepared by sol–gel method. Substitution of Mn in the Zn sites was achieved by adding $MnCl_2$ to the zinc oxide precursor and subsequent hydrogenation. As the concentration of Mn increases, so does the magnetic moment. In films with high concentration of Mn, Zeeman effect in the conduction band results in a downshift of the band edge and, consequently, a narrowing of the band gap. The effect was observed at room temperature and can be exploited for band engineering of oxide semiconductors.

Graphical abstract



12 at.% Mn was successfully substituted in ZnO films deposited by sol–gel method. Exchange interaction was established between the Mn ions through the mediation of oxygen vacancies. A narrowing of the band gap of ZnO was achieved by Zeeman shifting of the bottom of the conduction band.

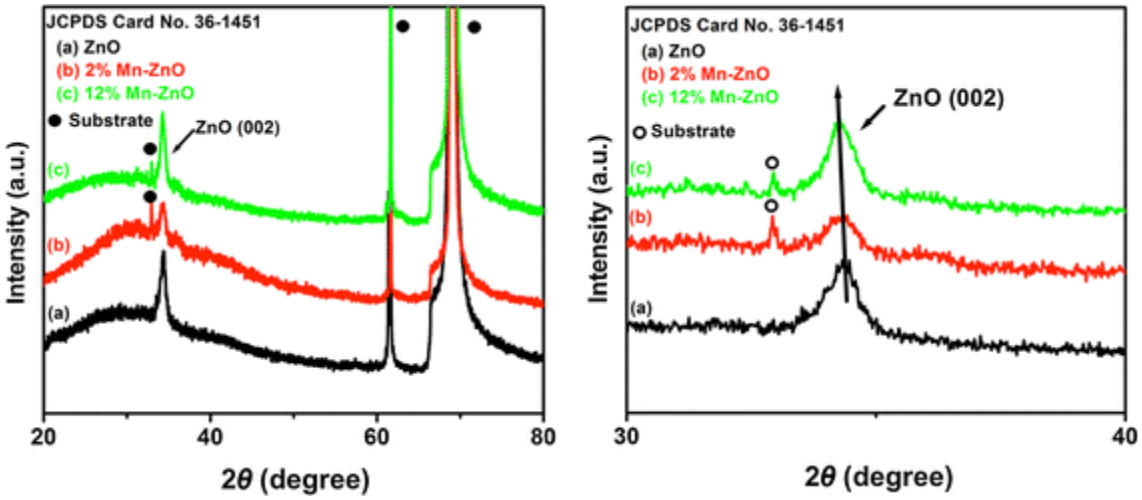


Fig. 1 *Left* XRD spectra of Zn1−x1−xMnxxO films with x=0x=0, 0.02 and 0.12, after annealing in H22 at 400 ∘∘C. *Right* a magnification of the same spectra around the (002) diffraction peaks.

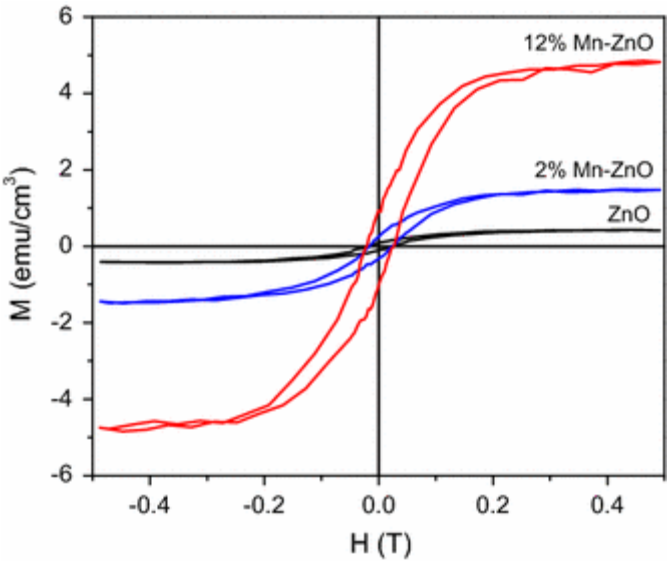


Fig. 2 Magnetic moment versus field at room temperature of Zn1−x1−xMnxxO films with x=0x=0, 0.02 and 0.12.

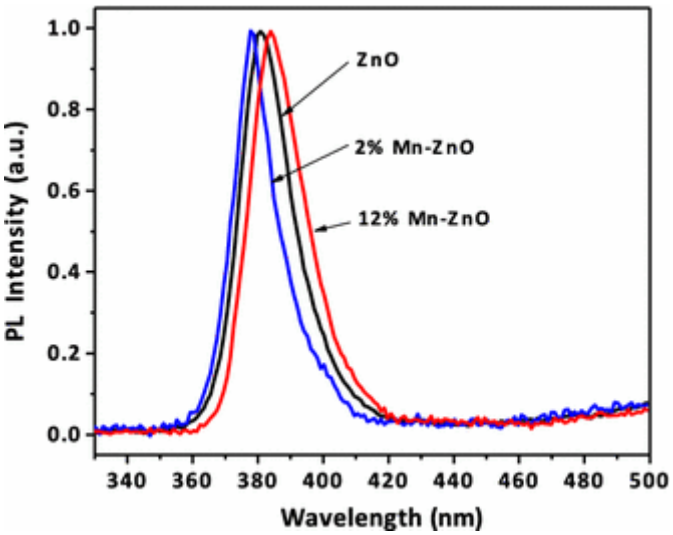


Fig. 3 Photoluminescence spectra at room temperature of Zn1−x1−xMnxxO films with x=0x=0, 0.02 and 0.12

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