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Cation substitution in ZnO obtained by mechanical milling

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Abstract

In this work we present a structural and optical characterization of M-doped ZnO (M: Cd, Mg) powders obtained by mechanical milling. The mixing of the oxides is followed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). As milling proceed a clear reduction of grain size and homogenization are observed. Photoluminescence (PL) spectra with milling frequency were analyzed in comparison with pure oxide powders and related with the kind of mechanically induced defect involved.

Keywords: Semiconductors; Mechanical alloying; Impurities in semiconductors; Optical spectroscopy; Positron spectroscopies

1. Introduction

Due to its unique optical and electronic properties and its potential use in many demanding technological applications such as blue and ultraviolet light emitter and detector, ZnO has been extensively studied [1–7]. The direct bandgap of this semiconductor ($E_g = 3.2$ eV) can be changed by substitution on the cation site, decreasing (increasing) in the case of Cd (Mg) [1]. The possibility to widen its bandgap has increased the interest in the study of the ternary alloys $Zn_{1-x}Mg_xO$. Although the solubility of Mg is not so high (4%) a variety of preparation methods have been applied. The ternary alloys with up to 36% Mg content was obtained by pulsed laser deposition [2], laser molecular beam epitaxy [3,4], radio frequency magnetron sputtering [5,6] and metalorganic vapour-phase epitaxy (MOVPE) [7].

Mechanical milling is an effective, useful and simple processing technique widely applied to the synthesis of various alloy phases including solid solutions, quasicrystalline, nanocrystalline and crystalline materials. In this work we try to obtained bulk material of the ternary alloys $Zn_{1-x}M_xO$ (M: Cd, Mg) by means of mechanical milling. The structural and optical properties were studied by XRD, SEM and PL.

2. Experimental

The starting materials were commercial ZnO (99.99%), MgO (99.99%) and CdO (99.998%) powders from Alfa Aesar, Johnson Matthey. The samples were prepared by mechanical milling in a Restch PM 400 rotating ball mill. Powders were weight to obtain mixtures of ZnO with 5% of MgO or CdO. The milling was performed in a steel cylinder (12 cm^3) with two steel ball (diameter 10 mm) with ball to powder mass ratio of 32. The powders were milled at 200 and 360 rpm and for different times (1, 5, 10 and 20 h).

The milled powders were characterized by (XRD) with a Philips X'Pert diffractometer using Cu K_α radiation. The grain size and lattice parameters were obtained from the patterns fitted with the Rietveld method [8]. The SEM images were obtained with a Jeol, model JSM6300. The milled powders were then compacted under uniaxial pressure (3.5 GPa) into pellets (diameter 6 mm) in order to perform the photoluminescence measurements.

Low-temperature unpolarized photoluminescence (PL) experiments were performed in a backscattering geometry. Samples were placed inside a helium close-cycle cryostat and the 325.2 nm line of a 30 mW He–Cd laser was used. The emitted light was analyzed by a Jobin-Yvon HR460 spectrometer coupled to a CCD detector.

3. Results and discussion

The effect of milling frequency in the morphology and structure of the milled powders was analyzed at first by means of SEM. Fig. 1 shows the images obtained after 1 h of milling at two different frequencies, 200 and 360 rpm. For both materials the same features are observed. The grain sizes range between 150 and 500 nm. The refinement seems to be more effective at higher frequency since there is larger quantity of smaller particles in samples milled at 360 rpm.

In order to make an optical characterization, PL spectra were taken on those samples already analyzed by SEM. Preliminary

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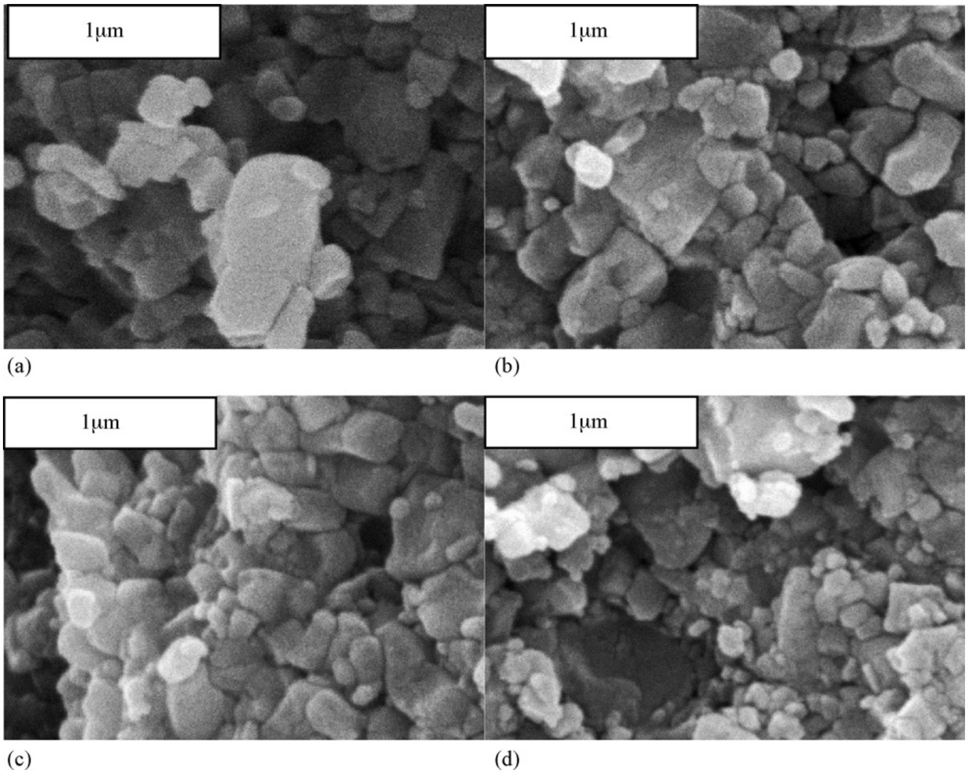

(a) (b)

(c) (d)

Fig. 1. SEM images for 1 h milled samples: (top) ZnO:Cd, (bottom) ZnO:Mg; (a) and (c) at 200 rpm and (b) and (d) at 360 rpm.

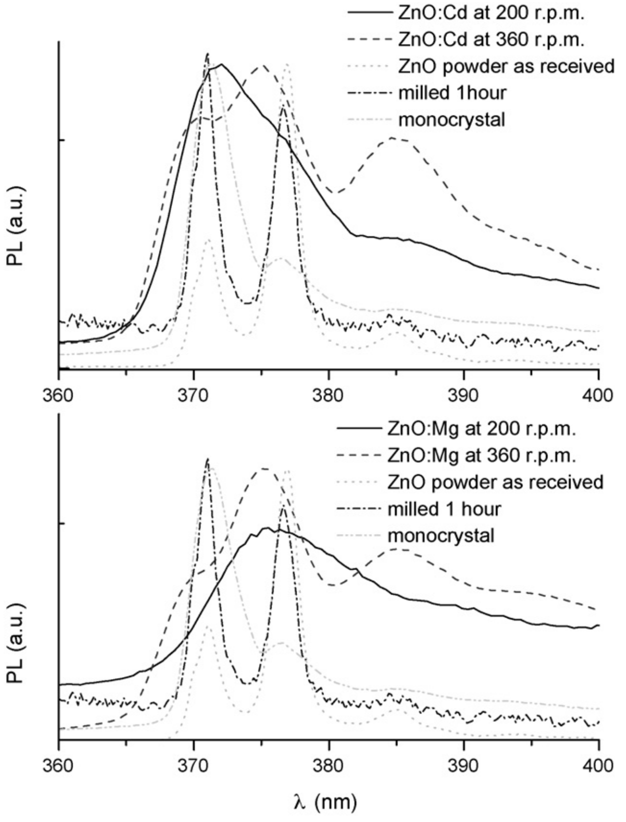

Fig. 2. PL spectra for 1 h milled samples at different milling times: (top) ZnO:Cd, (bottom) ZnO:Mg; ($T = 20$ K, He–Cd laser excitation).

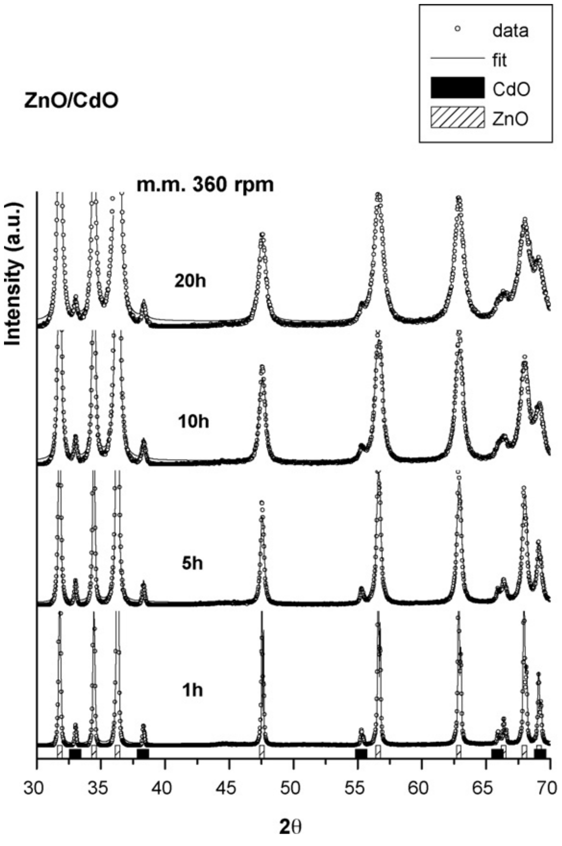

Fig. 3. XRD patterns for ZnO:Cd milled at 360 rpm during 1, 5 and 10 h. Continuous lines represent the fitting results.

Table 1
Results from Rietveld analysis

Sample	Milling time (h)	f (m%)	Grain size (nm)	Lattice parameters (Å)
ZnO	–	–	–	$a = 3.2499$, $c = 5.2066$
ZnO:Cd	1	2.6	114	$a = 3.2502$, $c = 5.2065$
	5	2.3	77	$a = 3.2490$, $c = 5.2041$
	10	1.9	45	$a = 3.2496$, $c = 5.2056$
	20	1.8	33	$a = 3.2513$, $c = 5.2096$
ZnO:Mg	1	11.7	103	$a = 3.2507$, $c = 5.2082$
	5	10.3	32	$a = 3.2486$, $c = 5.2055$
	10	10.1	34	$a = 3.2490$, $c = 5.2062$
	20	9.7	31	$a = 3.2509$, $c = 5.2083$

The starting lattice parameters for pure ZnO are $a = 3.2499$ Å, $c = 5.2066$ Å and its starting grain size 123 nm.

PL results are shown in Fig. 2. Also, included are the results obtained for pure ZnO powder, ZnO powder milled 1 h and a ZnO single crystal sample for comparison. These spectra indicate that milling at 360 rpm reveals the typical features in the excitonic region for the ZnO PL spectrum [8]. However, the presence of several recombination mechanisms (shallow donors and acceptors) is indicated by the broadening of the PL signal for the ZnO:Cd, ZnO:Mg powder samples compared with the ZnO powder sample.

The powders were then milled at 360 rpm during 1, 5, 10 and 20 h in order to obtain progressive cation incorporation in the oxide. Figs. 3 and 4 show the XRD patterns of ZnO:Cd and ZnO:Mg powders, respectively. The diffractograms show the reflection lines corresponding to hexagonal ZnO (*P*63*mc*) together with the ones corresponding to cubic (*Fm*3*m*) CdO or MgO. As milling proceeds, the relative intensities of the additional oxides (CdO or MgO) decrease with respect to the ZnO intensities peak. Also a reduction of grain size is produced as can be verified by the broadening of the peaks. Table 1 displays the main results from a Rietveld analysis.

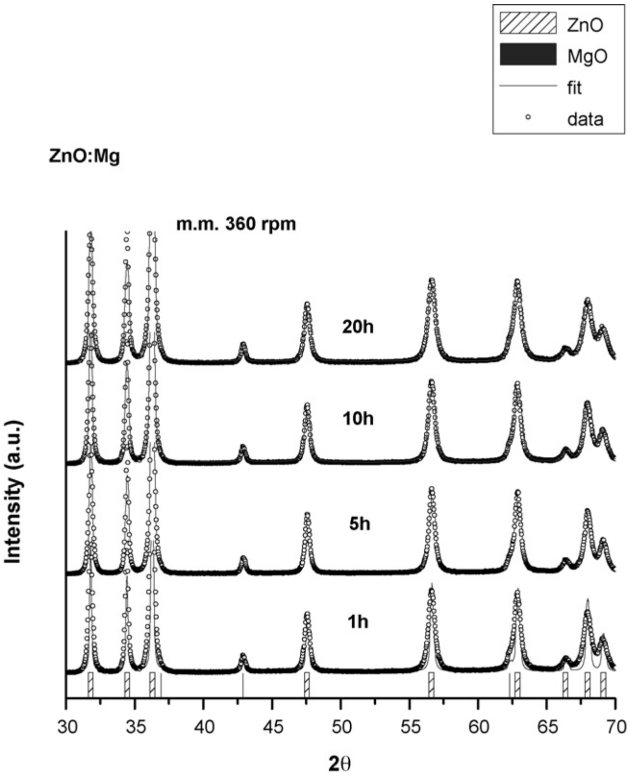

Fig. 4. XRD patterns for ZnO:Mg milled at 360 rpm during 1, 5 and 10 h. Continuous lines represent the fitting results.

The lattice parameters for both samples with the first milling step show a small increase with respect to the corresponding ones of pure ZnO ($a = 3.2499$ Å, $c = 5.2066$ Å) due to the introduction of point defects by mechanical work. With increasing milling time, these parameters slightly decrease. It is expected that ZnO lattice properties do not drastically change with the addition of Cd or Mg since their ionic radii are rather similar (0.60, 0.57, 0.90 for Zn, Mg and Cd, respectively) [1,6]. The typical grain size reduction with milling occurred from the initial value of 100 nm to around 30 for both samples. Similar grain size reduction was observed in pure milled ZnO [8–10]. The decreasing fraction of the minor oxides with milling time is also shown in Table 1.

4. Conclusion

Nanometer sized oxide powders were obtained by mechanical milling. The complete mixture of the ZnO–CdO and ZnO–MgO was not obtained for the present frequencies and milling times. However, the cation impurities in ZnO produced a different signal in the PL spectra not just due to mechanical induced defects. Millings at prolonged periods of time are in progress with the aim of obtain the ternary alloys.

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