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Nanoparticles of ZnO obtained by mechanical milling

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Abstract

Structural and optical characterization of mechanically milled ZnO powders are presented in this paper. It is shown that the application of mechanical milling is a very effective and simple technique to produce nanocrystalline powders, with the possibility of obtaining large quantities of materials. The milled powders are analyzed by X-ray diffraction, positron annihilation spectroscopy, scanning electron microscopy (SEM) and photoluminescence spectroscopy (PL). As milling proceeds, a clear reduction of grain size and homogenization are observed.
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1. Introduction

Zinc oxide and zinc-oxide-based powders have been widely studied recently because of their unique optical and electrical/electronic properties and thus they can be used in many demanding technological applications [1], such as low-voltage varistors [2,3]. In order to obtain high-quality zinc oxide powders with fine particle size, narrow size distribution and special morphology, various preparation techniques have been used to synthesize ultrafine zinc oxide powders [4,5], including precipitation, sol–gel, microemulsion, etc.

In general, nanocrystalline semiconductors with dimension less than 100 nm represent a relatively new class of materials. Their short-range structures are essentially the same as bulk semiconductors but their optical and electronic properties are dramatically different. In particular, they have been intensively studied because of their quantum size effects, photo catalysis, nonlinear optical properties and photoconductivity. They can be prepared in the form of dispersed colloids or trapped or stabilized within micelles, polymers, zeolites or glasses. Mechanical milling has proved to be an effective and simple technique to produce nanocrystalline powders and the possibility of obtained large quantities of materials. In this work, we present preliminary studies on mechanically milled ZnO powders together with its structural and optical characterization. The milled powders were analyzed by X-ray diffraction, positron annihilation spectroscopy and optical measurements (photoluminescence). In addition, the evolution of annihilation parameters with milling time and annealing temperature is analyzed and related with the kind of mechanically induced defect involved. The effect of grain size on the optical properties of ZnO is discussed in terms of the deformation and defects generated during the milling.

2. Experimental procedure

Commercially obtained ZnO powder (sized $\cong$500 nm, purity 99%) was milled in a steel cylinder (8 cm^3) with one steel ball (diameter 12 mm) with a ball to powder weight ratio of 14. The mechanical milling was performed in a horizontal oscillatory mill (Retsch MM2) operating at 25 Hz, during different milling times. As milling proceeds, a clearly reduction of grain size was observed. The milled powder was compacted under uniaxial pressure of 1.7 GPa into disk-shaped pellets (diameter 8 mm).

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Structural characterization was made through X-ray diffraction, scanning electron microscopy (SEM) and positron annihilation lifetime spectroscopy (PALS). The optical characterization was performed with photoluminescence spectroscopy (PL).

X-ray diffraction patterns were obtained with a Philips PW1710 diffractometer using CuK_{α} radiation. These were fitted by the Rietveld method with Thompson–Cox–Hastings pseudo-Voigt profiles to determine the lattice parameter, volume fraction and full width at half maximum.

The morphology, dispersivity and defective structure of particles and agglomerates of zinc oxide powders in different stages of milling were investigated by SEM. The SEM images were obtained with a Jeol, model JSM6300.

Positron annihilation lifetime measurements were collected in a conventional fast–fast coincidence system with two plastic detectors. The time resolution (FWHM) was 260 ps. The radioactive source, $^{22}NaCl$ (10 μCi), was deposited onto a kapton foil (1.42 g/cm^3) and sandwiched between two sample specimens. The source contribution and the response function were evaluated from a reference sample (Hf metal) using the RESOLUTION code [6]. The lifetime spectra ($2–3\times10^6$ counts) were acquired at room temperature and analysed with the POSITRONFIT program [6].

Low-temperature unpolarized photoluminescence experiments were performed in the samples in a backscattering geometry by placing the samples inside a helium close-cycle cryostat and using the 325.2-nm line of a He–Cd laser at power level of 30 mW. The emitted light was analysed by a Jobin–Yvon HR460 spectrometer using a GaAs PMT detector optimized for the UV-VIS range.

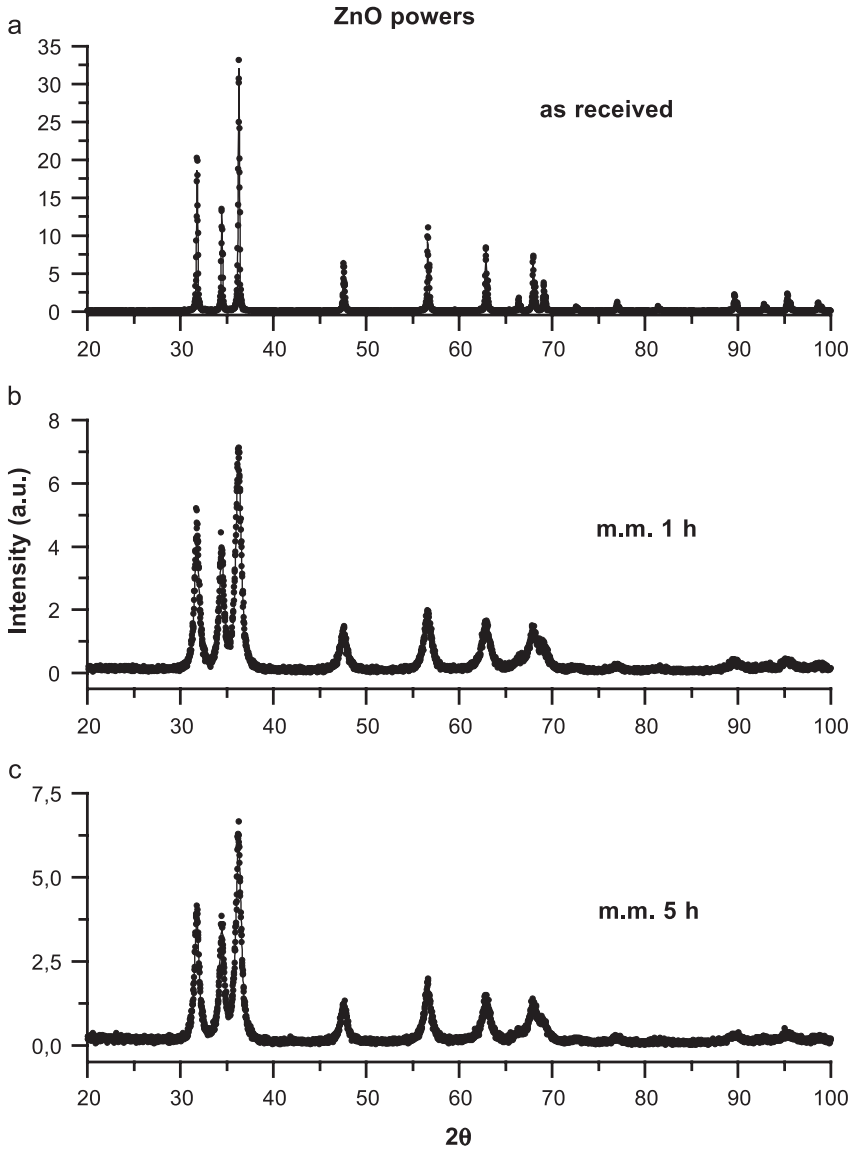

Fig. 1. X-ray diffraction patterns of the three samples: (a) as received; (b) after mechanical milling for 1 h; (c) after mechanical milling for 5 h.

3. Results and discussion

3.1. X-ray diffraction spectra

The XRD patterns for the ZnO powders, as received and after different milling times, are shown in Fig. 1. The diffractograms display the reflection lines of hexagonal ZnO (P 63 mc). With increasing milling time, the corresponding peaks became broader and no major change is observed on the lattice parameters. The considerably broad reflections are mainly a consequence of the small grain size with a small contribution from internal strain induced by the severe mechanical deformation.

In order to quantify these effects, we carried out the whole powder pattern fitting analysis by the Rietveld method. The resulting fitting curves are shown as lines in Fig. 1. The grain sizes and microstrains were calculated according to the integral breadth method [9]. It should be noted that, when measured in this way, crystallite size refers to the mean size of coherently diffracting crystal domains and does not indicate the distribution width or how the crystallites are assembled into particles. The obtained values are shown in Table 1, together with the fitted lattice parameters. From this analysis, it can be seen that the major size reduction is obtained after the first hour of milling. The additional milling does not reduce the grain size, only an increase in the a lattice parameter is observed.

3.2. Scanning electron microscopy

Fig. 2 shows the SEM micrographs of the three samples studied, before and after milling. The direct results that can be deduced from these images are: (a) Various sizes are present in the original sample before milling (Fig. 2a), covering the range between 170 and 500 nm; (b) after 1 h milling (Fig. 3b), the sizes are much more homogeneous and are ranging from 110 until 50 nm and (c) after 5 h milling (Fig. 3c), we cannot distinguish very clearly the different particles due to a kind of accretion produced between them. The size in this case is less than 17 nm.

3.3. Positron annihilation spectroscopy

In order to identify the mechanically induced defects, the sample before milling and after 1 h of milling were analysed by positron annihilation lifetime spectroscopy. The lifetime spectra for both samples are decomposed into three exponential decays with a χ^2 close to 1.0. The fitted lifetime parameters for the ZnO samples together with those for the reference sample are listed in Table 2. For ZnO samples, a lifetime of 386 ps with an intensity of 32% was included as source correction in the POSITRONFIT analysis.

For both samples, a lifetime of 2.2 ns with a relative intensity (1.4%) higher than the corresponding one in the reference sample is observed. This fact indicates that larger voids are still present after the compression process leading

Table 1
Lattice parameter (a, b), coherent scattering domain size (L) and average root mean squared strain (ϵ) obtained from the Rietveld refinement (determined from the fit with best agreement factors)

Sample	a (Å)	b (Å)	L (nm)	ϵ (%)
ZnO as received	3.2484	5.2045	113_3	0.000042_3
ZnO m.m. 1 h	3.2505	5.2048	33_1	0.010_1
ZnO m.m. 5 h	3.2518	5.2042	35_2	0.010_1

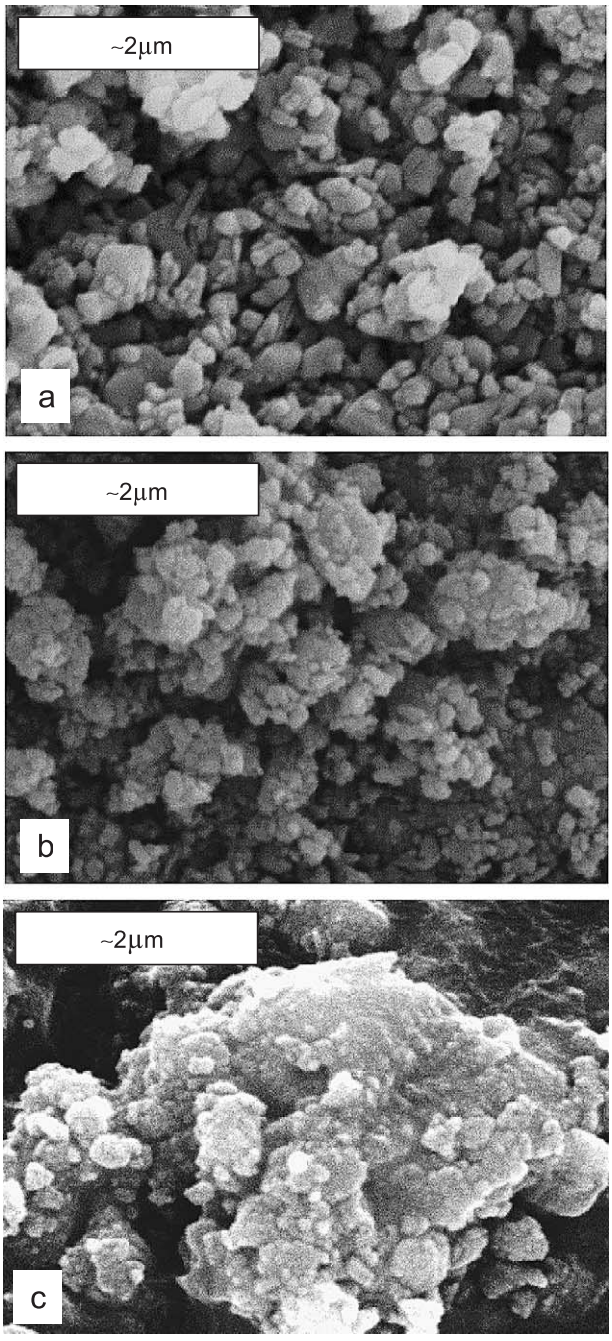

Fig. 2. SEM micrographs of ZnO particles formed in the different milling steps: (a) as received; (b) after mechanical milling for 1 h; (c) after mechanical milling for 5 h.

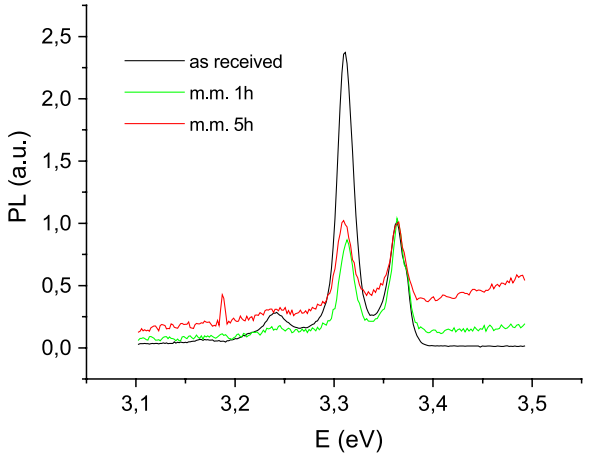

Fig. 3. Normalized photoluminescence spectra of ZnO powders at 15 K.

to the *ortho*-positrium formation and its further annihilation. The first lifetime has a lower value than the bulk lifetime in other oxides (e.g., τ_b=178 ps for TiO_2) [10] and Zn compounds (e.g., τ_b=254 ps for ZnTe, τ_b=223 ps for ZnS) [11] and also in monovacancies of these last compounds. Thus, it may be considered as a mean value of positron annihilation in bulk material and in vacancy type defects. In addition, the *para*-positronium annihilation contributes to this lowest lifetime. The observed intermediate lifetime is sensing positrons trapped at vacancy clusters (nanovoids) or at intersection of interfaces (i.e., triple lines). It is worthwhile to note that annihilation lifetime in divacancies for ZnTe and ZnS were reported [11] to be 336 and 250 ps, respectively. These results are consistent to what is observed in nanocrystalline materials that are usually characterized by three lifetime components τ_1, τ_2 and τ_3 [7,8].

The most noticeable change after 1 h of milling is the increase in the value of the lowest lifetime component. Under mechanical milling, the powders are subjected to severe plastic deformation giving rise to particle and grain refinement. Simultaneously, different kinds of defects, such as vacancies, vacancy clusters, dislocations, etc., are created. In consequence, the observed increment in the value of τ_1 and in the mean lifetime $<\tau>$, are due to the mechanically induced defects.

3.4. Photoluminescence spectroscopy

The obtained spectra of zinc oxide powders using PL spectroscopy are given in Fig. 3, where the three spectra are normalized in order to do an easier comparison. The peak in higher energy present in all samples locates at about 3.36 eV and is due to an exciton bound to a donor level (BE) [12]. Two additional peaks are also observed at lower energies which correspond to the *m*th LO-phonon replicas for *m*=1, 2 [12].

Table 3
Characteristics of the BE peak, for the three samples

Sample	Area	FWHM (eV)	Peak (eV)
ZnO s.m.	2.79	0.01667	3.364
ZnO 1 h	2.69	0.01671	3.365
ZnO 5 h	3.45	0.02542	3.364

These parameters were obtained by adjusting the PL spectrum to three lorentzian shape peaks.

The peak position, area and FWHM for the BE peak are shown in Table 3. It can be observed that only small changes in the parameters are observed for the sample milled during 5 h, which is wider and much less efficient from the point of view of the photoluminescence. As noticed in the PALS results, the mechanical milling produces different kinds of defects in the powders giving place to an increase in the possible recombination mechanisms. The decrease in the PL signal and the broadening in the BE peak are due to the decrease of the active centres responsible of this band and an increase to the nonradiative recombination sites, that are bound to the created defects. However, there is no change in the position of the BE peak, indicating no size quantization effects. Therefore, there is no great quantity of grains with sizes less than 3 Å, the limit for observe these quantization effects [13].

4. Conclusions

Mechanical milling of ZnO powders produces homogenously sized nanoparticles with grain size less than 20 nm. Combined SEM and X-ray diffraction analysis lead to the determination of grain size and microstructure. In addition, the characterization by positron annihilation lifetime spectroscopy confirms the ultrafine structure of the studied powders, but the decrease of the two phonon replicas' emission peaks, in the PL spectra, points out an increase in different kinds of defects. In order to identify the mechanically induced defects, annealing treatments are in progress.

Table 2
Positron lifetime's parameters and the mean lifetime $<\tau> = \sum I_i \tau_i$

Sample	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ns)	I_3 (%)	$<\tau>$ (ps)
ZnO, as received	158_7	38_3	343_6	61_3	2.2_1	1.4_1	300_{25}
ZnO, m.m. 1 h	193_9	37_4	357_8	61_4	2.2_1	1.4_1	320_{34}
Hf metal (reference)	208_4	68_1	386(f)	32_1	1.2_7	0.3_1	269_{12}

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