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Luminescence properties of mechanically milled and laser irradiated ZnO

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Abstract

The effect of mechanical milling on the luminescence properties of ZnO microcrystalline samples has been studied by means of cathodoluminescence in a scanning electron microscope. The samples consisted of pressed pellets of commercially available ZnO powder which were ball milled to investigate the possibility of nanocrystalline ZnO formation. Changes observed in the relative intensities of the characteristic ultraviolet and green band of ZnO are discussed in terms of defects generated during milling. The effect of nano- and picosecond pulsed laser irradiation on the particle size and luminescence of the milled samples has been also investigated.

1. Introduction

ZnO has been extensively studied in the past mainly because of its high luminescent efficiency and non-ohmic properties [1–3]. Now, ZnO is being intensely investigated for different applications. As an ultraviolet laser material it has unique properties because, besides the high luminescent efficiency, excitons in this material have a large binding energy (about 60 meV) enabling photoluminescence and lasing at room temperature [4–6]. Also the fabrication of flat panel displays appears to be a potential application of ZnO powders, with different particle sizes, which have been already used for field emission displays (FED) and vacuum fluorescent displays (VFD) [7–9]. However, there is still much controversy on the origin of the luminescence properties of bulk ZnO (see [10, 11] and references therein). This problem is even more difficult in the case of micro- and nanoparticles, where the influence of surface and quantum size effects on the band structure of the material plays an important role [9, 12]. Consequently the study of the properties of small (from tens of nanometres down to few nanometres) particles has gained importance. Several synthesis methods of ZnO nanoparticles or nanocrystalline films, such as sputtering [13], pulsed laser deposition [14], epitaxial techniques [15, 16] and various chemical routes [17], have been developed. Mechanical attrition appears also to be a suitable method for obtaining semiconductor nanocrystals [18, 19] although some problems related to mechanical damage during processing remain unsolved [20, 21].

The main advantages of mechanical milling to produce nanocrystals are the low cost and performance feasibility, including the possibility of obtaining large amounts of material (from milligrams to grams) avoiding chemical contaminations from the reagents used in other synthesis methods. One of the drawbacks is the high density of defects introduced as a consequence of the severe mechanical damage.

The aim of this work is the study of the influence of ball milling, and of various laser treatments, on the luminescence of ZnO. The cathodoluminescence (CL) technique is used to monitor changes in the electronic structure associated with defects as well as particle size.

2. Experimental method

Milling of commercially available (Merck) ZnO powder was performed in a centrifugal ball mill (Retsch S100) with 20 mm diameter agatha balls. Milling time was varied from 20 to 60 h. After CL measurements the milled powder was aged at room temperature for 2 months and subsequently milled again for times up to 60 h. For the scanning electron microscopy and laser irradiation experiments, powders were compacted under a compressive load of 5 tonne to form disc shaped samples.

Topography images were recorded in a Leica 440 scanning electron microscope (SEM) operating in emissive mode. The experimental setup for the CL measurements, implemented in a Hitachi S2500 SEM, has been described elsewhere [22]. Spectra were recorded at liquid nitrogen temperature using a CCD Hamamatsu PMA-11.

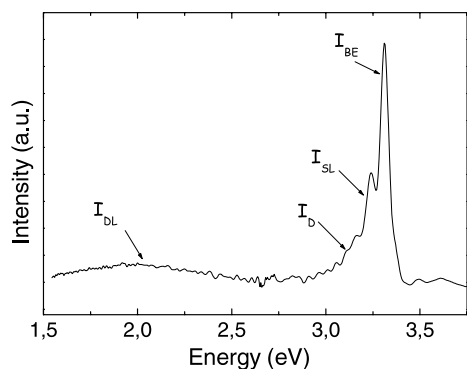


Figure 1. CL spectrum obtained from ZnO raw powders at liquid nitrogen temperature.

The irradiation experiments were carried out using laser pulses at 583 nm with a duration of 30 ps and 6 ns full width at half maximum (FWHM), performing both single and multiple laser pulse exposures over regions about $300\ \mu\text{m}$ in size, leading to fluences typically in the $10\text{--}100\ \text{mJ cm}^{-2}$ range.

3. Results and discussion

The CL spectra of the raw material consist mainly of the near band edge I_{BE} emission which includes a well resolved component associated with shallow levels (I_{SL}) and a weak emission related to dislocations (I_D) [10, 23]. The spectra shown are reproducible and representative of the average emission of the sample. Since they were recorded from various areas in the sample, the differences in spectral emission from grain boundaries and grain interior [24, 25] are averaged. The well known green–yellow band associated with the presence of several deep levels I_{DL} is also weak, indicating a low density of defects (figure 1). The milling process was found by transmission electron microscopy (TEM) to produce particles with a range of sizes down to about 30–50 nm (figure 2(a)). As observed by high resolution TEM (HRTEM), these particles are composed of grains a few nanometres in size (figure 2(b)). After ball milling a reduction of the total CL intensity as well as spectral changes are observed. In figure 3 the CL spectra of samples prepared with different milling times are shown. For the sake of comparison the spectrum of the raw material is included in all the plots with the intensity normalized to that of the milled sample. The relative intensity of the shallow

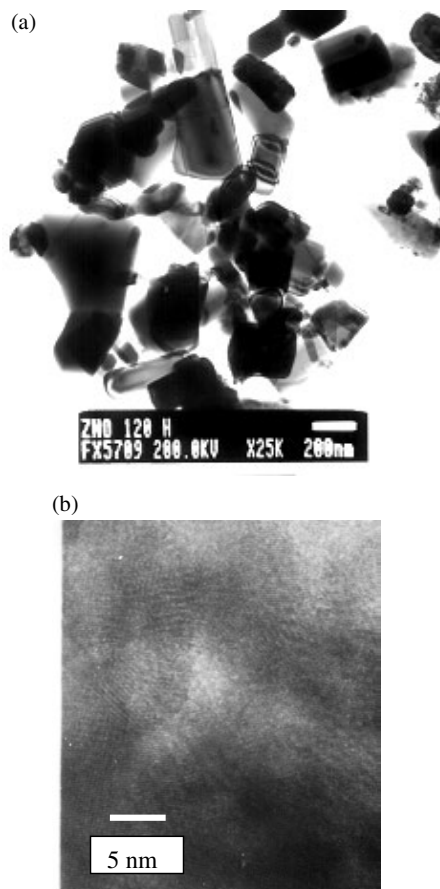


Figure 2. TEM micrographs of ZnO particles from powder milled for 120 h (a). (b) HRTEM image of one of the particles shown in part (a).

levels peak as compared with the band gap emission has been found to increase with the milling time (figures 3(a) and (b)); it has been suggested that this is related to the formation of point defects, mainly vacancies, during plastic deformation. The progressive broadening of this emission with increasing milling time is attributed to an increased dislocation density, since in this region, 3.1 eV, a dislocation related peak has been reported [10]. In the low energy parts of the spectra, milling causes the increase of a broad yellow–orange emission. These results show that the effect of mechanical milling on the deep level luminescence is qualitatively similar to that reported for

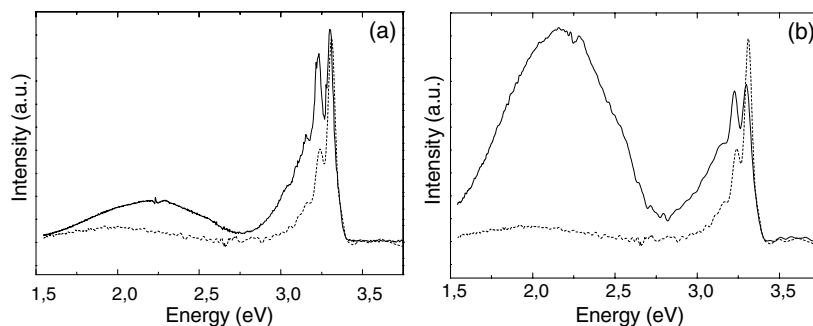


Figure 3. CL spectra from samples milled for 40 h (a) and 60 h (b). For the sake of comparison, the spectrum from the raw material is included in the graphs (dotted curves).

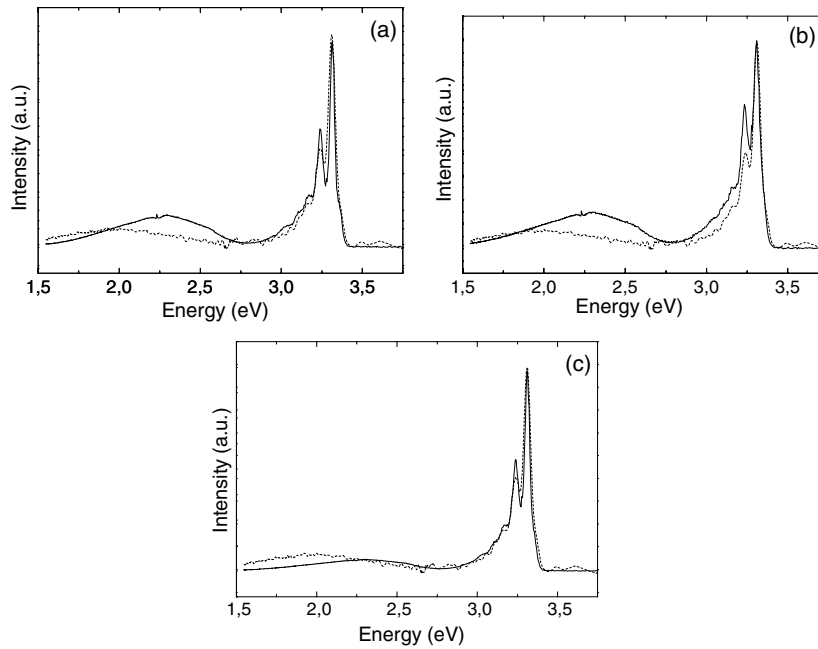


Figure 4. CL spectra from (a) a sample milled for 60 h and then aged over a period of time; and samples additionally milled after ageing (b) 20 h and (c) 60 h. For the sake of comparison, the spectrum from the raw material is included in the graphs (dotted curves).

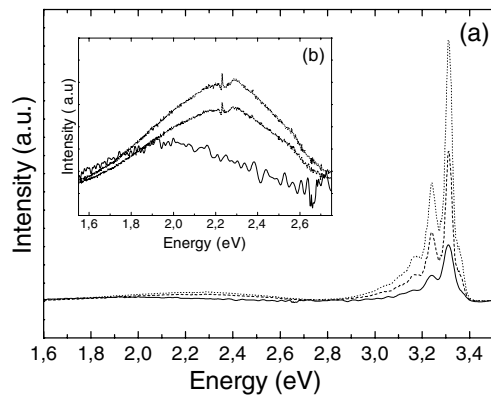


Figure 5. CL spectra from non-irradiated (straight curve), ps pulse irradiated (dashed curve) and ns pulse irradiated (dotted curve) non-milled samples. (a) Near band edge region, (b) deep level region.

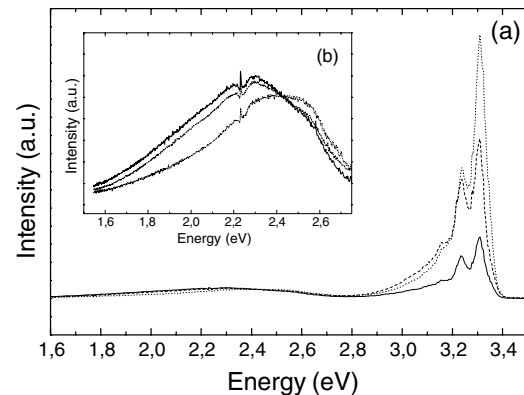


Figure 6. CL spectra from non-irradiated (straight curve), ps pulse irradiated (dashed curve) and ns pulse irradiated (dotted curve) samples milled for 80 h. (a) Near band edge region, (b) deep level region.

plastically deformed ZnO ceramics [23, 26]. In those works plastic deformation was found to produce a strong reduction of the CL emission together with a relative increase of the yellow band. It was concluded in [23] that these effects are not related to the generation of oxygen vacancies but rather were caused by Zn vacancy defects and/or non-radiative centres associated with dislocations. The CL spectra of plastically deformed ZnO did not show the features observed in this work in the near band edge region after ball milling, in particular the increase of both shallow level and dislocation luminescence bands. This is due to the severe mechanical damage produced during ball milling that appears to be associated with a high concentration of point defects contributing to the shallow level band as well as to a high dislocation density causing the increase of the dislocation related band. The appearance of an intense dislocation CL band has been also observed in ball milled silicon [18].

Figure 4(a) shows the CL spectrum of the 60 h milled sample after the ageing period. It is observed that most of the milling induced luminescence changes have recovered. The centres responsible for the yellow band appear to have, to a large extent, annealed out or rearranged which causes the intensity decrease of this band. The same appears to apply for the point defects associated with the dislocation and the corresponding luminescence band. The ball milled material is in a highly stressed state. The relaxation of stresses during ageing would induce rearrangement of defects. Room temperature diffusion of atomic species has been observed after long ageing times in, for instance, ZnSe [27]. In the referenced work it is proposed that, due to the high density of short diffusion paths in material with high density of interfaces, the diffusivity in ball milled samples is enhanced. Figures 4(b) and (c) show the effect of additional milling after the ageing

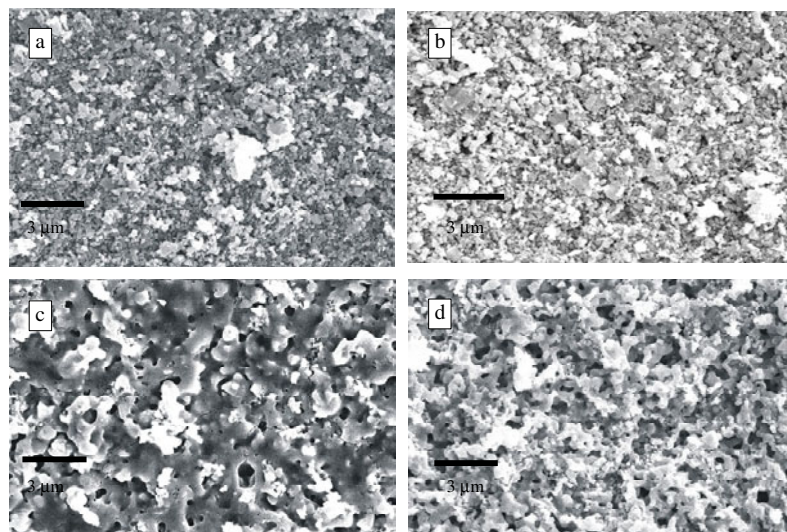


Figure 7. SEM images of non-irradiated (a), (b) and irradiated areas (c), (d) from non-milled (a), (c) and 80 h milled sample (b), (d).

time. Spectral changes appear again during the first steps of milling (figure 4(b)) but after 60 h of this second period of milling, the CL spectrum (figure 4(c)) is qualitatively similar to that of the raw material, although in all milled samples the total CL intensity is lower than in the untreated samples. The series of CL spectra in figures 3 and 4 shows the formation of different radiative defects during milling as well as the two recovery mechanisms: one related to room temperature ageing and the other associated with additional milling. The latter effect is a consequence of the competition between defect creation and recovery which takes place during milling. In fact it has been proposed [28] that during ball milling the dislocation density increases at a first stage but decreases as the grains become very small. Other experimental results (for a review see, for instance, [29]) demonstrate the above-mentioned competition between defect creation and recovery.

Deep level emission includes several components, whose origin is still unclear, the main ones peaking at about 2.58, 2.38 and 2.02 eV (see [30] and references therein). The fact that several defects appear to be involved in this emission makes it difficult to establish the evolution of each component as a function of milling time.

Laser irradiation has been performed with pulses in the nanosecond and picosecond regime. The effect of both types of pulses on the CL spectrum of non-milled material is shown in figure 5. Since the luminescence intensity in the deep level region is relatively weak, low and high energy ranges of the spectrum are represented separately. Irradiation has been found to induce a relative increase of the intensity of the deep level band and a shift of the peak towards the green region. Although it is generally accepted that residual amounts of copper in undoped ZnO are involved in the green luminescence, there is also wide agreement on the role of oxygen vacancies in some of its components [9]. The intensity increase of this component would be related to oxygen loss during irradiation. The effect of irradiation on the high energy spectral region is the relative increase of the band gap luminescence, which is more effective for nanosecond pulses. Figure 6 shows the spectra corresponding to one of the milled samples. The same

qualitative effect of laser irradiation as in the untreated samples but with less pronounced changes is observed. The higher stability of the milled samples could be associated with the high dislocation density generated during milling or with a reduced porosity in the samples prepared from milled powder which would render a higher thermal conductivity.

The effect of laser irradiation is also apparent in the SEM images. Although picosecond irradiations influence the luminescent behaviour of the samples their particle structure, as observed in SEM, is scarcely affected in this irradiation regime; only in the non-milled samples are picosecond irradiated regions slightly visible. On the other hand, nanosecond irradiated regions are readily observed in all the samples. Figure 7 shows irradiated and non-irradiated regions of unmilled and 80 h milling, after ageing. The differences in the melting–solidification process could be associated with the above-mentioned differences in the thermal conductivity of the samples related to different porosity.

4. Conclusions

Mechanical milling of ZnO powders leads to a reduction in particle size to sizes of a few tens of nanometres. The particles are found by TEM to contain nanocrystals with sizes of some nanometres. CL reveals an increase in dislocation related luminescence centres, as well as of shallow electronic levels and of deep centres emitting in the yellow spectral region. Ageing at room temperature leads to partial quenching of the milling induced radiative centres. By increasing milling time a competition between radiative centre creation and recovery is observed. Laser processing allows the modification of the defect structure as revealed by the increase in band edge emission intensity and the shift of the deep level peak position. The laser irradiation effect is lower in milled samples and was found to depend on the duration of the irradiation pulses as well as on the initial conditions of the samples. Annealing effects and melting–solidification features are different for nanosecond and picosecond irradiation.

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