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Effects of mechanical roll-milling on electronic and optical properties of ZnO nanoparticles

U Olgun* & M Gülfen

Department of Chemistry, Faculty of Arts and Sciences, Sakarya University, Sakarya, Turkey

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In this study, UV-*vis* absorption spectroscopy, electrical conductivity, band gap energy, particle size and morphology of prepared ZnO nanoparticles were examined after roll-milling process. A roll-milling process works with two rolls rotating at reverse directions and the ZnO powder goes through a narrow gap between these two cylindrical metal rolls. The roll-milling process was applied to the ZnO powder in several times by reducing the gap between the rotating cylinders. It was seen that the white color of the ZnO particles turned into yellow color. The UV-*vis* spectroscopy measurements showed that the absorption band of the ZnO particles shifted to the low energy wavelengths upon the roll-milling process. The band gap energy of the ZnO decreased from 3.10 eV to 2.68 eV. Also, it was observed that the electrical conductivity increased from 0.19 to 42.47 S/cm. Furthermore, the SEM and AFM measurements showed that the particle size of the ZnO decreased significantly and the particle morphology changed after the roll-milling process. It is concluded that the property changes in spectroscopy, electrical conductivity and band gap energy is due to the reduced particle size and the increase of the number of deformation defects in crystalline structure of ZnO particles.

Keywords: ZnO nanoparticles, Roll-milling, Band gap energy, Electrical conductivity

Zinc oxide (ZnO) is an important semiconductive ceramic material widely used in various applications ranging from electronic to medical, such as optoelectronic devices, piezoelectronic transducers, chemical sensors, cosmetics and pharmaceutical lotions. Also, there are many experimental studies in the literature about the functionality and the properties of ZnO containing powders, thin films and additives[1-4]. Özgür, *et al.*[5] reviewed the wide range of properties of ZnO particles. ZnO has two main crystalline forms, which are hexagonal wurtzite and cubic zinc blende. These structures have no inversion symmetry and this unique lattice property results in the piezoelectricity. The piezoelectric properties of ZnO particles were examined by different researchers[3,4,6]. Also, ZnO exhibits semiconducting properties with a wide band gap energy of about 3.30-3.40 eV[7-9]. It has a high-excition binding energy of 60 meV and a high electron mobility of 100 $cm^2/V{\cdot}s$[10-12]. In recent years, ZnO material is widely utilized in various technological applications in optoelectronic devices, piezoelectronic transducers, chemical sensors, field-effect transistors, light-emitting diodes, ultraviolet lasers, photodetectors, solar cells, and surface acoustic wave devices[1,2,4,8].

The roll-milling process is often used in material forming purposes to reduce the thickness of metals, alloys and polymers[13]. The roll-milling is a low cost and practical technique and it is an environmental friendly process. The mechanochemical processing of semiconductive ceramic powders has not been investigated in detail by using the roll-milling method in the previous literature. The possible effects of mechanical force on ZnO powder were studied by using various techniques. For example, Broitman *et al.*[14] applied mechanical force to ZnO piezoelectric ceramic material and they showed changes in the charge distributions in lattice structures. Previously, it was found that the B_4 phase of ZnO could transform into the B_1 (cubic NaCl) structure at a pressure of 9 GPa[8,15]. Here, in this work, the possible effects of the roll-milling process on the ZnO ceramic powders have been examined in detail. In the present work, the UV-*vis.* absorption spectra, the band gap energy, the electrical conductivity and the particle size of ZnO were investigated after the roll-milling process. The measurements showed that the roll-milling of ZnO with high anisotropic forces resulted in strongly deformed and broken ZnO particles with the low band gap energy and the high electrical conductivity.

*Corresponding author (E-mail: uolgun@sakarya.edu.tr)

Experimental Procedure

Roll-milling process

Previously, the roll-milling system for the preparation of nanocomposite materials has been studied[13,16]. By using the similar roll-milling process, the ZnO particles encapsulated into copper pipe goes through a narrow gap between two rotating cylindrical stainless steel rolls. Cavalline brand roll-mill machine was used for the preparation of ZnO nanoparticles. Figure 1a shows the roll-milling system. 3 g ZnO powder was filled into Cu pipe and the capsule was prepared by closing the both ends of the pipe. Then, the ZnO particles were processed several times by reducing the gap between the rotating cylinders. After the roll-milling process, the prepared long copper stripe was cut and the ZnO sample was taken out. The roll-milled ZnO powder was used for the experimental measurements.

Characterization

The UV-*vis.* absorption spectra of the ZnO powders were measured by using the solid phase absorption measurement technique on a Shimadzu UV-*vis*. 2600 PC model spectrophotometer with ISR-2600-Plus attachment. For the electrical conductivity measurements, the ZnO powder samples were compressed into the discs (12.5 mm radius with thickness of about 0.5 mm) under a pressure of 10,000 kg/cm^2. The electrical resistivities of the prepared discs were measured by using the four-point resistivity system (Lucas Pro4). The morphological changes for the ZnO samples were examined by using the scanning electron microscopy (SEM) and the atomic force microscopy (AFM) methods. The measurements were recorded on a JOEL-JSM 6060LV model SEM and a NTEGRA P9 model AFM instruments.

Results and Discussion

Roll-milling of ZnO

Roll-milling method was applied to the ZnO particles for the enhancement of its optical and electronic properties. The simple roll-milling process is shown in Fig. 1a. In the roll-milling process, multi-directional forces (non-isotropic pressure) (Fig. 1b) can be applied to the material, whereas in the classical compressing process one directional force (isotropic pressure) (Fig. 1c) is applied. ZnO is a piezoelectric material and it is widely used in many different industrial applications. In this study, the ZnO particles were filled into the copper capsule and then it was processed in the roll-milling system in several times by increasing the effective pressure. It was seen that the white color of the ZnO particles changed to the yellow color after the roll-milling. This change in the color of the ZnO particles indicates the improvement of the light absorption properties in the visible region. In order to understand the effects of the roll-milling, the UV-*vis.* absorption spectra, the band gap energy, the electrical conductivity and the particle morphology of the ZnO sample were investigated in detail.

SEM and AFM analyses

The particle size and the morphology changes were examined by using scanning electron microscopy (SEM) and atomic force microscopy (AFM) methods. The SEM images of the starting ZnO powder are provided in Figs 2a and 2b.The SEM images of the ZnO samples after the roll-milling are given in Figs 2c and 2d. The starting ZnO powder exhibited needle, rod and triangle-plate like particle morphologies. However, after the roll-milling process, these shapes of particles disappeared and the round shape ZnO particles were observed. Also, the particle size decreased significantly after the roll-milling. In addition, the large agglomerations between the ZnO particles were observed after the roll-milling process. Due to the high pressure and the shear forces, the agglomerations occurred between the broken particles with high surface defects.

AFM technique was also used to investigate the surface morphology of the ZnO particles before and after the roll-milling process. The observed AFM images of the ZnO particles are given in Fig. 3. The images clearly showed the formation of the particle aggregations in the roll-milled ZnO sample. Also, more homogeneous particles were observed on the surface of the ZnO particles after the roll-milling process.

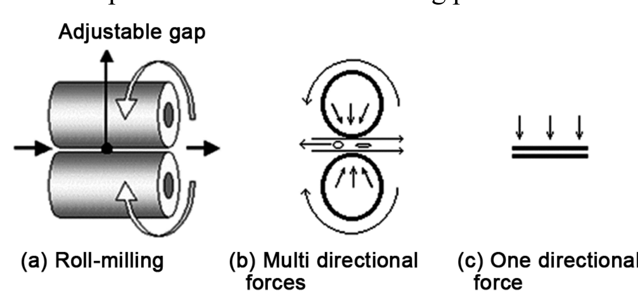

Fig. 1 — (a) Roll-milling system, (b) multi-directional forces in roll-milling (non-isotropic pressure) and (c) one directional force in compressing (isotropic pressure)

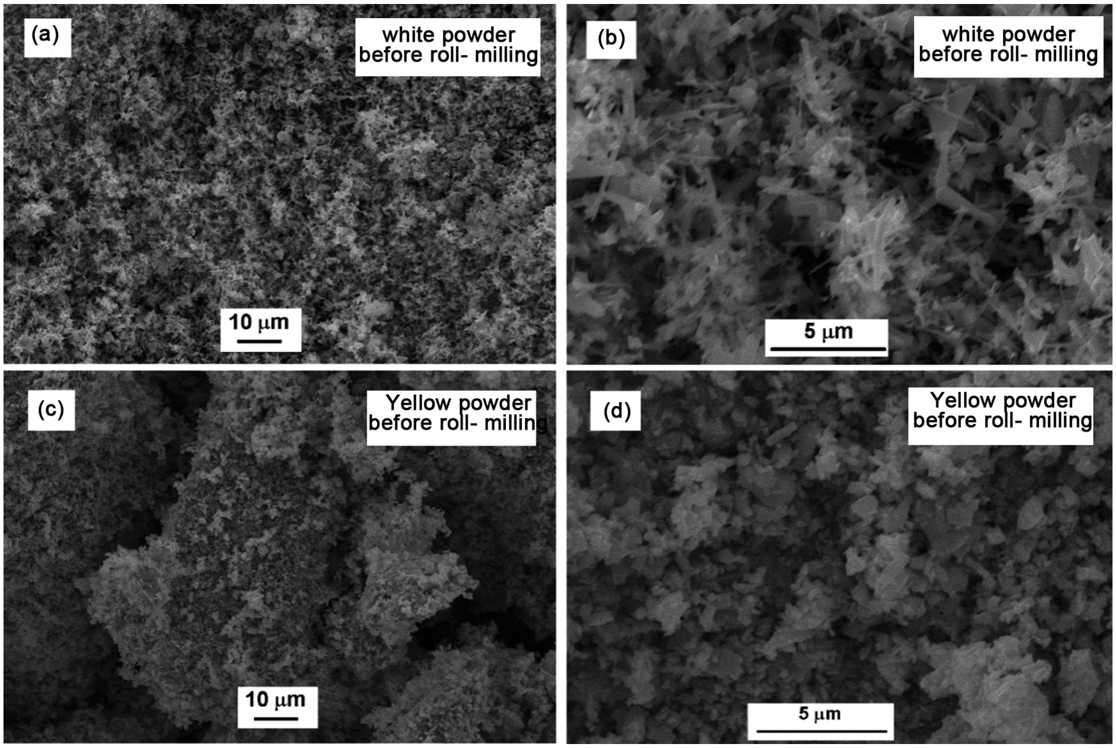

Fig. 2 — SEM images of ZnO particles before and after roll-milling

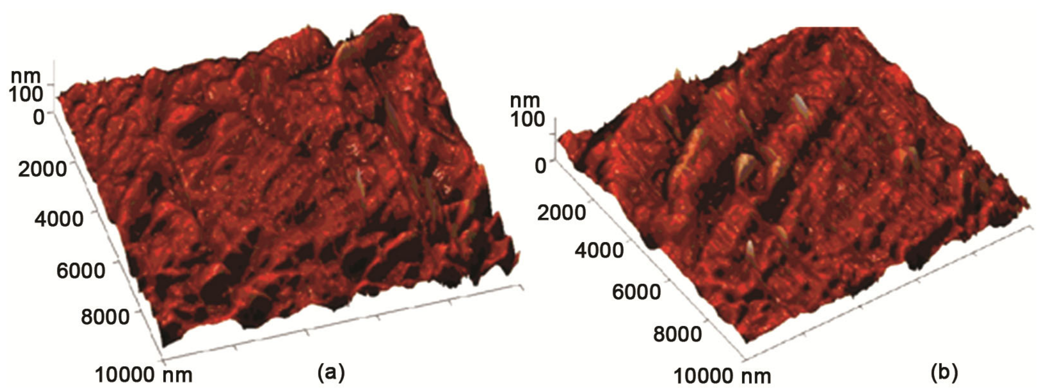

Fig. 3 — AFM images of (a) ZnO and (b) roll milled ZnO particles

XRD analysis

The roll-milled ZnO powder was also examined by XRD method. The obtained XRD pattern was compared with the reference ZnO material as shown in Fig. 4. In addition, the measured 2θ and *d* values for each (*hkl*) planes are given Table 1. The results showed that the main diffraction peaks of the roll-milled ZnO powder shifted to higher 2θ degrees. In Fig. 4, these shifted peaks were labeled as 31.980°, 34.639°,36.460° and 47.740°. At the same time, the *d* values corresponding to the distance between the atomic planes were reduced to smaller numbers after the roll-milling process. The other small diffraction peaks between 50° and 90° were obtained at lower 2θ degrees and slightly higher *d* values for the roll-milled ZnO. These XRD measurements indicated that the crystal structure of the ZnO phase has been affected by the roll-milling process. The atomic planes of the ZnO crystals have slightly decreased in one axis due to the effective pressure during the roll-milling. There are similar observations in the previous literature about the lattice deformations in the crystal structure of ZnO[17].

UV-vis spectroscopy and band gap energy

The UV-*vis* absorption spectra of the ZnO particles were measured by using the powder reflectance spectrophotometry technique. The UV-*vis* spectra of the ZnO taken before and after the roll-milling process are given in Fig. 5. The ZnO showed a broad maximum absorption band at 200-400 nm wavelengths. However, after the roll-milling process, the onset of the absorption band of the ZnO red shifted to the higher wavelengths (from 400 to 463 nm). Also, it was noted that the molar absorptivity of the ZnO increased in the visible region after the roll-milling. The ZnO has a white color with a broad absorption band in the UV region, and therefore, it is commonly used as UV light absorber in sun blockers[18]. After the roll-milling process, it was found that the color of the ZnO changed to yellow and its light absorptivity has been improved.

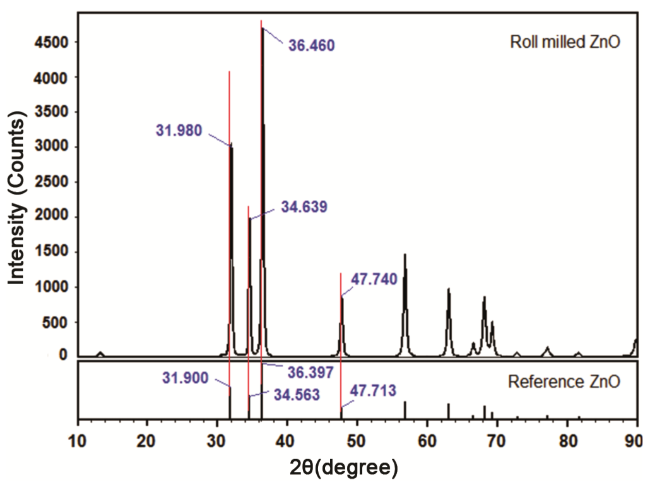

Fig. 4 — XRD patterns of the roll-milled ZnO and the reference ZnO.

Using the UV-*vis* absorption spectra, the optical band gap energies (E_g) of the ZnO were calculated from their low energy absorption edges according to the Planck's equation ($E_g = 1240/\lambda_{onset}$)[19,20]. The E_g values were found as 3.10 eV before the roll-milling and 2.68 eV after the roll-milling. The E_g of ZnO is related to the grain size, carrier concentration, defects and stress state of the material[17,21,22]. The XRD analysis of the roll-milled ZnO (Fig. 4 and Table 1) revealed that the *d* space between the atomic planes of the crystals has been decreased due to the roll-millling. In general, the results showed that the approach of the atomic planes has enhanced the light absorption behavior of ZnO in both UV and visible wavelengths. Consequently, the band gap value of the ZnO powder has also decreased. Furthermore, these results agree with the formation of smaller grains, and large defects in roll-milled ZnO. The UV-*vis* absorption measurements shown in Figs 5 and 6 revealed

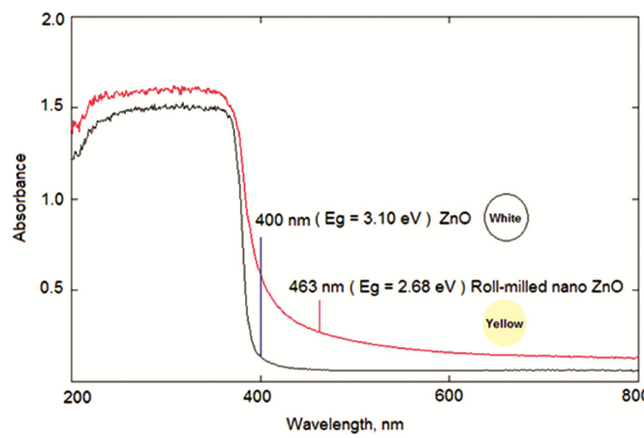

Fig. 5 — UV-*vis* spectra of ZnO before and after roll-milling

Table 1 — XRD data of roll milled ZnO particles and reference ZnO

	Roll milled ZnO particles			Reference ZnO (01-075-0578)				
No	2θ	d(Å)	I%	2θ	d(Å)	I%	hkl	Delta
1	13.259	6.6721	1.4					
2	31.980	2.7963	64.9	31.900	2.8031	56.2	(100)	-0.080
3	34.639	2.5875	41.6	34.563	2.5930	41.2	(002)	-0.076
4	36.460	2.4623	100.0	36.397	2.4665	100.0	(101)	-0.064
5	47.740	1.9036	18.5	47.713	1.9046	21.5	(102)	-0.027
6	56.781	1.6201	30.8	56.791	1.6198	30.9	(110)	0.011
7	63.040	1.4734	20.5	63.075	1.4727	27.2	(103)	0.035
8	66.580	1.4034	4.0	66.601	1.4030	4.1	(200)	0.021
9	68.140	1.3750	17.4	68.180	1.3743	22.7	(112)	0.040
10	69.260	1.3555	10.2	69.320	1.3545	11.2	(201)	0.061
11	72.720	1.2993	1.5	72.819	1.2978	1.8	(004)	0.099
12	77.160	1.2352	2.6	77.222	1.2344	3.5	(202)	0.062

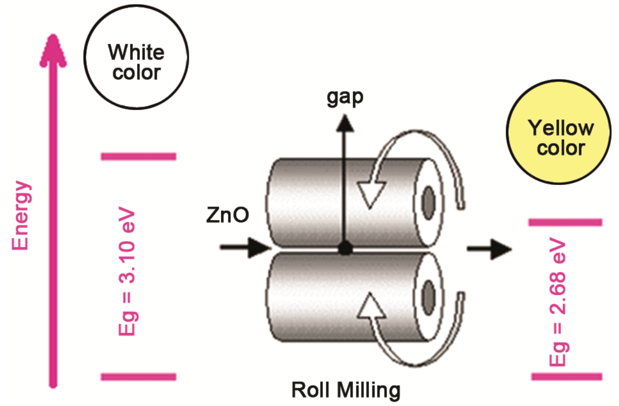

Fig. 6 — Band gap energies of ZnO before and after roll-milling

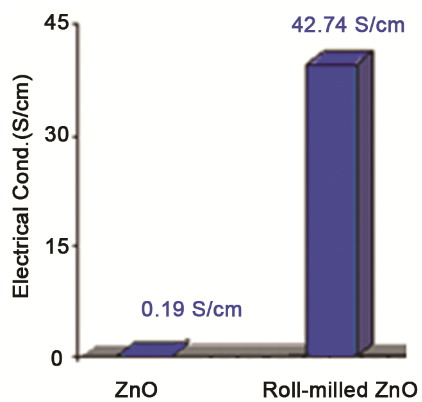

Fig. 7 — Electrical conductivity of ZnO powder before and after roll-milling

that the roll-milling process decreased the optical band gap energy of the ZnO powder.

Electrical conductivity

The ZnO exhibits strong *n*-type conductivity with the electrons moving in the conduction band as the charge carriers. The electrical conductivity of ZnO powder is between 10^{-3} and 1 S/cm depending on the particle size[23]. As a semiconductor material, ZnO also shows piezoelectric material properties[24]. Tenn *et al.*[25] demonstrated the electrical conductivity enhancement of ZnO under high pressure. Here, in this study, the electrical conductivities of the ZnO samples were examined before and after the roll-milling process. The obtained results are demonstrated in Fig. 7, as the bar graphs. It was found that the electrical conductivity of ZnO increased from 0.19 to 42.74 S/cm after the roll-milling process. This corresponds to 225 times increase in the electrical conductivity. This increase can be attributed to the piezoelectric property, the formation of defects and the lattice deformations in ZnO particles under high pressure during the roll-milling process.

Conclusions

The ZnO is widely used in many industrial applications, such as polymers, cosmetics and ceramic composites. Improving the optical and electronic properties of ZnO by the roll-milling process, the high performance ZnO containing materials can be obtained for many different technological applications. In this study, ZnO particles were processed by the roll-milling method. Then, the changes in the UV-*vis* absorption spectrum, the electrical conductivity, the band gap energy and the particle size were examined. After the roll-milling process, the following results were obtained for the ZnO particles: (i) The white color of the ZnO turned into yellow color; (ii) the XRD results indicated the deformations in the ZnO crystal lattice; (iii) the UV-*vis*. spectrum of the ZnO red shifted; (iv) the electrical conductivity of the ZnO increased from 0.19 to 42.47 S/cm; (v) the band gap energy of the ZnO decreased from 3.10 eV to 2.68 eV and (vi) The particle size of the ZnO decreased from micron to submicron range. The roll-milling is an environmental friendly, room temperature process, and it does not contaminate the final product with any toxic chemical. In conclusion, the roll-milling process is a low cost and practical technique to improve the optical and electronic properties of the semiconductive ZnO powder.

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