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Band gap engineering of ZnO nanocrystallites prepared via ball-milling

Öğütme ile üretilen ZnO nanokristallerin bant aralığı mühendisliği

***Yazar(lar) (Author(s))**: Telem ŞİMŞEK[1], Abdullah CEYLAN[2], Gülçin Şefiye AŞKIN[3], Şadan ÖZCAN[4]*

ORCID[1]: 0000-0003-4852-2230

ORCID[2]: 0000-0001-5656-0929

ORCID[3]: 0000-0002-5628-639X

ORCID[4]: 0000-0001-7966-1845

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Highlights

- *Ball-milling technique was used to tune the band gap of single-phase wurtzite ZnO nanocrystallites.*
- *UV-visible absorbance measurements and Kubelka-Munk theory were used to calculate the band gap of the ZnO nanocrystallites.*
- *The energy band gap of the samples was successfully tuned in the range of 3.15 - 3.02 eV depending on the nanocrystallite size.*

Graphical Abstract

A sustainable, facile and low-cost room temperature processing method, mechanical milling was employed to produce ZnO nanocrystallites with the size in the range of 24.9 – 22.0 nm. The energy band gap of the samples was successfully tuned from 3.15 to 3.02 eV depending on the nanocrystallite size.

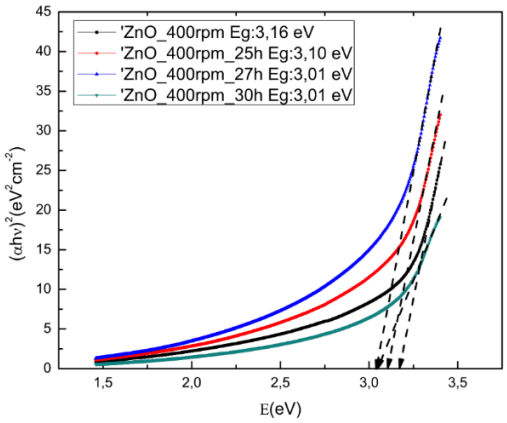

Figure. Kubelka-Munk function vs energy of the excitation source for milled samples with different durations

Aim

The crystallite size dependence of energy band gap of ZnO nanocrystallites fabricated by milling technique was investigated.

Design & Methodology

ZnO nanocrystallites were produced by wet-milling of Zn dust in the presence of distilled water followed by dry milling and structural analyses were performed by using XRD and TEM. The band gap of the samples was determined by using UV-visible absorbance measurements and Kubelka-Munk theory.

Originality

A sustainable, facile and low-cost room temperature processing method, mechanical milling was employed to produce the band gap engineered ZnO nanocrystallites by using Zn dust as starting material.

Findings

The band gap of 24.9 to 22.0 nm sized ZnO nanocrystallites which were produced via mechanical milling by using Zn dust as starting material is found to be in the range of 3.15 to 3.02 eV.

Conclusion

Energy band gap is found to be the nanocrystallite size dependent and as the size decreases the band gap also decreases.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Band Gap Engineering of ZnO Nanocrystallites Prepared via Ball-Milling

Araştırma Makalesi / Research Article

Telem ŞİMŞEK[1*], Abdullah CEYLAN[2], Gülçin Şefiye AŞKIN[1], Şadan ÖZCAN[1,2]
[1]Nanoteknoloji ve Nanotıp A.B.D., Fen Bilimleri Enstitüsü, Hacettepe Üniversitesi, 06800, Ankara, Türkiye
[2]Fizik Mühendisliği Bölümü, Hacettepe Üniversitesi, 06800, Ankara, Türkiye

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ABSTRACT

Zinc oxide (ZnO) nanostructures have become the foremost prevalent metal oxide materials for technological applications due to their tunable optical properties. However, a simple, cheap and green method is required for the mass production of these nanostructures. In the present investigation ball-milling technique was used to tune the band gap of ZnO nanocrystallites. Samples were synthesized using metallic Zn powder and distilled water via wet-milling followed by dry-milling. The crystallite size of the ZnO samples were determined in the range of 24.9 – 22.0 nm depending on the dry milling time. UV-vis absorbance measurements and Kubelka-Munk theory were used to calculate the band gap of the ZnO nanocrystallites. The energy band gap of the samples was successfully tuned in the range of 3.15 - 3.02 eV depending on the nanocrystallite size. This behavior was explained by the surface states and energy traps on the band edge, created by delocalization of molecular orbitals.

Keywords: Band gap engineering, dry-milling, zinc oxide, wet-milling.

Öğütme İle Üretilen ZnO Nanokristallerin Bant Aralığı Mühendisliği

ÖZ

Çinko oksit (ZnO) nanoyapıları, ayarlanabilir optik özelliklerinden dolayı teknolojik uygulamalar için en yaygın kullanılan metal oksit malzemeler haline gelmiştir. Ancak bu nanoyapıların seri üretimi için basit, ucuz ve çevreci bir yöntem gerekmektedir. Bu araştırmada, ZnO nanokristallitlerinin bant aralığını ayarlamak için bilyeli öğütme tekniği kullanıldı. Örnekler, metalik Zn tozu ve damıtılmış su kullanılarak ıslak öğütme ve ardından kuru öğütme yoluyla sentezlendi. ZnO örneklerin kristalit boyutu kuru öğütme süresine bağlı olarak 24,9 ila 22,0 nm aralığında olarak belirlendi. UV-görünür soğurma ölçümleri ve Kubelka-Munk teorisi, ZnO nanokristalitlerinin bant aralıklarını hesaplamak için kullanıldı. Örneklerin enerji bant aralığı, nanokristalit boyutuna bağlı olarak 3,15 ila 3,02 eV aralığında başarıyla ayarlandı. Bu davranış, moleküler orbitallerin yer değiştirmesiyle oluşan bant kenarındaki yüzey durumları ve enerji tuzakları ile açıklandı.

Anahtar Kelimeler: Bant aralığı mühendisliği, kuru öğütme, çinko oksit, ıslak öğütme.

1.INTRODUCTION

In recent years, ZnO nanocrystals have been produced most commonly by thermal decomposition [[19],[20]], pulsed laser deposition [[21],[22]], vapor liquid–solid processes [[23]] and sonochemical method [[24]-[26]]. Although these approaches are convenient to obtain high purity ZnO nanoparticles, they either needs high temperature processing or expensive experimental equipment. Xu *et al*. and Yadav *et al*. successfully synthesized ZnO nanoparticles by using mechanochemical technique to overcome these problems [[27]-[28]]. Even tough mechanochemical process provides low-cost fabrication and simple operation, usage of chemical precursors is not a green route. Alternatively,

Glushenkov *et al*. milled Zn powder by filling the vial with oxygen up to 210 kPa above atmospheric pressure [[29]]. Although pure ZnO nanopowder has been reported in this work, the difficulty of fabrication, scalability, and uniformity are very challenging in terms of mass production. Another common approach to produce ZnO nanopowders is using mechanical milling by starting from ZnO dust [[30]-[35]]. But dynamic heating during milling is shown to cause grain growth leading size limitation that make impossible to produce nanoparticles with desired physical properties [[36]]. Wet-milling of metal dust in the presence of H_2O has shown to be an effective activation route to produce metal oxide nanocrystals. Recently, Balaland *et al*. synthesized ZnO nanorods using wet-milling and investigated the effects of experimental parameters on the metal to metal oxide conversion [[37]]. However, the effect of nanocrystallite size on the optical properties and band gap of ZnO has not been reported yet.

Here we report the band gap engineering of ZnO nanocrystallites via wet-milling of micron-sized Zn dust with H_2O, followed by dry-milling to control over the crystallite size. This technique is sustainable, facile and

*Sorumlu Yazar (Corresponding Author)
e-posta : telem@hacettepe.edu.tr

low-cost room temperature processing method that doesn't require any heat treatment step, enabling large scale production. Here we controlled the milling parameters to optimize the crystallite size and optical properties of the samples. Structural and optical analyses revealed that milling is an effective method for tuning the band gap of ZnO nanocrystallites.

2. EXPERIMENTAL

In the synthesis of ZnO nanocrystallites metallic Zn powder (Sigma- Aldrich, %99,9~45µm) was used as starting material in the presence of distilled water. In order to obtain 5 g ZnO, Zn (4.07g) and 2 mL of distilled water was loaded to 500 mL stainless steel vial. Stainless steel balls with 10 mm diameters were used in the experiments with 1:20 powder to ball ratio. Mechanical wet milling was performed for 24 h of durations at 250, 300, 350 and 400 rpm speeds. Retsch PM 100 CM model planetary mill was used in the experiments. In order to investigate particle size dependence of the optical properties, a second sample set was fabricated by dry milling the as-fabricated sample at 400 rpm speed for 1, 3 and 6 hours of durations.

Structural measurements of the samples were performed by using a Rigaku D-max B horizontal diffractometer with Cu Kα radiation and FEI Tecnai G2 Spirit Biotwin transmission electron microscope (TEM). TEM grids were prepared by dispersing milled powders in isopropyl alcohol using an ultrasonic probe. Then controlled amount of this solution was dropped to 400 mesh carbon coated copper grids. UV-vis absorption measurements were performed by utilizing Hitachi U-3900 model spectrophotometer.

3. RESULTS AND DISCUSSION

During the wet-milling process, the reaction of the Zn powder with distilled water follows the reaction below:

$$Zn+2H_2O \rightarrow Zn(OH)_2+H_2 \quad (1)$$

This reaction shows that the surface passivation hinders the oxidation of Zn with H_2O, preventing ZnO production. However, the energy transferred to Zn during mechanical milling produces clean surfaces with high reactivity, which enables oxidation of surface Zn atoms [[38]]. Thus, as the nanocrystallite size decreases the oxidation of Zn nanocrystallites could be controlled. XRD patterns of the as-synthesized samples which were refined by using Materials Analysis Using Diffraction (MAUD) software are depicted in Figure 1 [[39]]. As summarized in Table 1, results showed that the sample milled at 250 rpm contains ZnO, $Zn(OH)_2$ and Zn crystalline phases. As milling speed increases, the weight ratio of the Zn and $Zn(OH)_2$ phases decrease and the sample milled at 400 rpm contains almost single phase ZnO with very little remanant Zn phase (Table 1). This behavior originates from the fact that milling initiates ZnO seeding and increased milling speed enables more fraction of ZnO growth on the Zn surface. This result is in good agreement with the previous reports on the growth mechanism of thin ZnO layer on the Zn surface induced by mechanical milling [[37]]. In addition, as the milling speed increases the width of the (101) reflection increases as a result of crystallite size reduction. Crystallite sizes calculated by using Scherer Formula are summarized in Table 1. Results show that as milling speed increases from 250 to 400 rpm, crystallite size decreases from 30.4 to 25.0 nm.

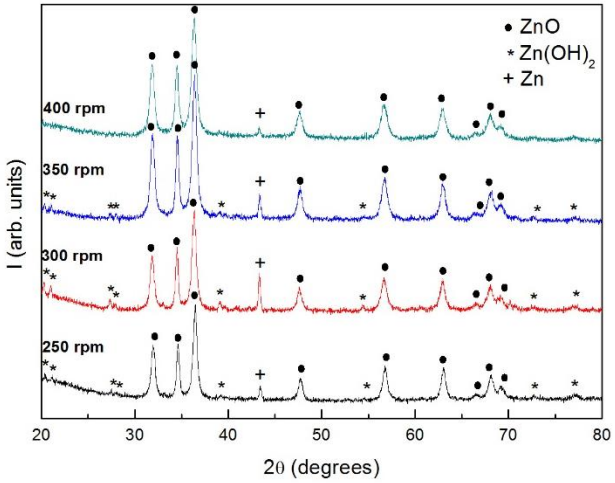

Figure 1 XRD patterns of samples wet milled for 24 h at 250 - 400 rpm

Table 1. Calculated crystallite sizes of the as-synthesized samples

Milling speed (rpm)	Crystallite size (nm)	ZnO weight (%)
250	31.9±0.8	95.1
300	27.9±0.2	94.6
350	27.3±0.3	96.9
400	24.9±0.3	98.3

To investigate the effect of crystallite size on the optical properties, the wet-milled sample at 400 rpm for 24 h was subjected to a second dry milling for 1, 3 and 6 h of durations. For the ease of readability, these samples are denoted as 24 h, 24+1h, 24+3h and 24+6h, correspondingly. XRD patterns of the samples are depicted in Figure 2. Indexed reflections belong to typical wurtzite ZnO structure (JPCDS #: 36-1451). ZnO phase is stable with increasing dry milling time and remanant Zn structure completely disappears after dry milling for 6 h, as shown in Table 2. The crystallite sizes are calculated from (101) reflection as 23.2, 22.0 and 23.6 nm for samples 24+1h, 24+3h and 24+6 h, respectively. Crystallite size decreases as the sample dry milled for 1 and 3 h of durations. Prolonged dry milling for 6 h causes sintering of the particles, which is a drawback of mechanical milling, which is usually observed after a critical particle size [[40], [41]]. In addition, there is a significant shift of (101) reflection

towards higher angles as dry milling time increases. This behavior originates from the stress induced on the samples due to the energy transferred during milling process. The variation in the lattice parameters with milling time is summarized in Table 2.

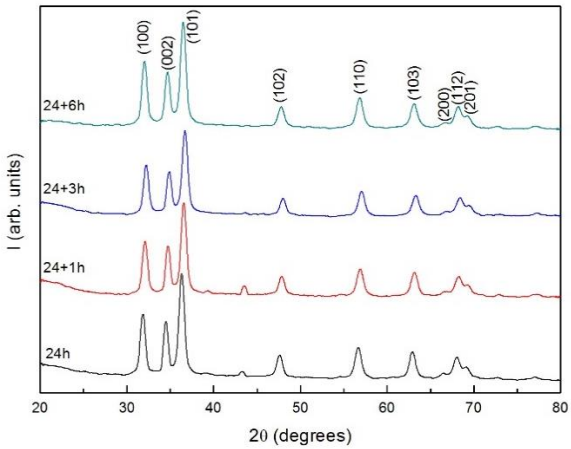

Figure 2 XRD patterns of the 24 h, 24+1h, 24+3h and 24+6 h samples

Table 2. Variations in crystallite size, ZnO weight % and lattice parameters after dry milling

Milling time (h)	24	24+1	24+3	24+6
Crystallite size (nm)	24.9	23.2	22.0	23.6
ZnO weight (%)	98.3	99.0	99.2	99.7
Lattice parameter a (Å)	3.2432 $\pm 1x10^{-4}$	3.2243 $\pm 2x10^{-4}$	3.21216$\pm$ $3x10^{-4}$	3.229 2$\pm 2x$ 10^{-4}
Lattice parameter c (Å)	5.1966 $\pm 4x10^{-4}$	5.1675 $\pm 7x10^{-4}$	5.1491$\pm$9 $x10^{-4}$	5.174 5$\pm 5x$ 10^{-4}

To determine the structural properties, bright field TEM micrographs were taken, which are depicted in Figure 3. The particles have no definite shapes and particle sizes are around 20 nm, which is in accordance with the XRD analysis. Particle size decreases with increasing milling time as observed in Figure 3a, b and c. Further milling causes particle agglomerations as observed from Figure 3d.

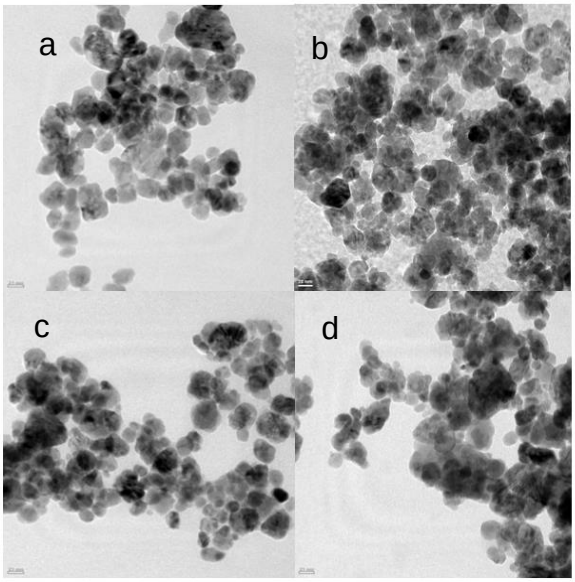

Figure 3. TEM micrographs of the (a) 24 h (b) 24+1 h, (c) 24+3h and (d) 24+6 h samples

Nanoparticles have optical properties that are sensitive to size, shape, concentration and agglomeration state. To investigate the optical properties, samples were dispersed in acetone by using an ultrasonic probe and UV-vis absorbance spectra of the samples were measured (Figure 4). The measurements show excitonic absorption feature peaked at around 386 nm. As milling time increases, there is an observed red-shift of the absorption spectra indicating a decrease in the band gap. Sample milled for 6 h doesn't follow this trend because agglomeration of the nanoparticles causes crystallite size growth as determined from structural analysis.

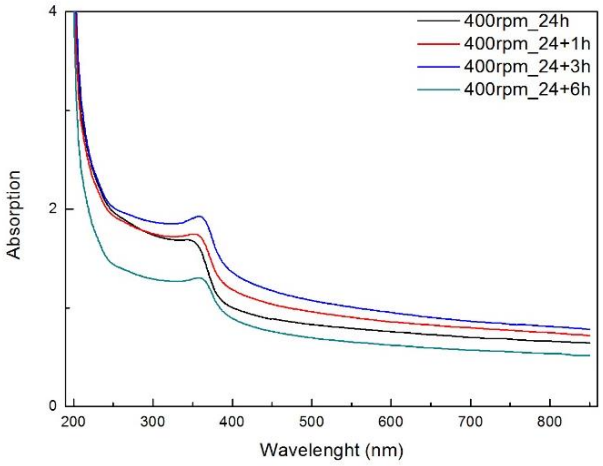

Figure 4. Absorbance spectrum of the as-synthesized and subsequently dry milled samples

To investigate the absorption curves in detail and determines the energy band gap (E_g), Kubelka-Munk function was plotted against the energy of the excitation source [[42]]. By extrapolating the linear parts of the

curves, E_g values were determined as shown in Figure 5. Results are summarized in Table 3. The energy band gap is found to be the crystallite size dependent and E_g values are found to be smaller than the bulk value of 3.37 eV. Whereas E_g of 24 h sample is 3.15 eV, it significantly decreases to 3.02 eV as dry milling time increases. Prolonged milling up to 6 h causes particle agglomeration and crystallite size growth as mentioned in Table 2. As crystallite size increases, E_g also increased to 3.05 eV, showing a pronounced increase in the band gap with increasing crystallite size. The first excitonic energy of a semiconductor cluster was predicted in 1984 by Brus [[43]] in terms of three energy terms; band gap of the bulk the semiconductor, energy induced by the quantum confinement effect and shift of energy due to columbic attraction between electron and hole pairs. Calculations showed that for ZnO particles with 6 nm size there is a 0.09 eV increase of the band gap resulting a blue shift of the absorption spectrum. In this work, crystallite sizes are much more larger than the excitonic Bohr diameter of ZnO and quantum confinement effect is not expected to be dominant to cause a blue shift. The observed trend of decrease in the band gap as particle size decreases and related red-shift is in good agreement with the previous works explaining this behavior as a result of the bulk defects that cause delocalization of molecular orbitals in the conduction band edge and create deep traps in electronic energy [[44]-[45]].

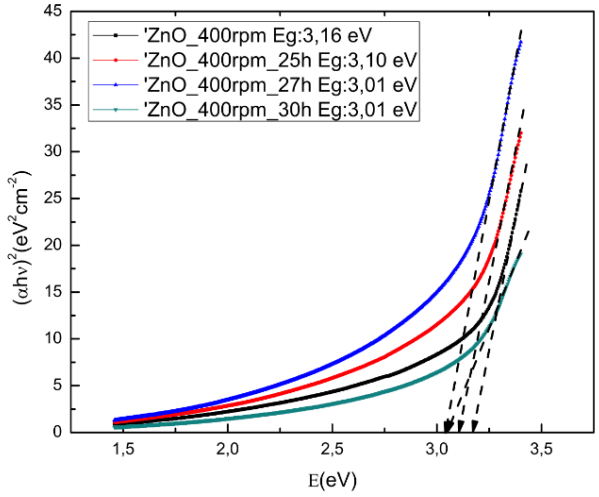

Figure 5. Kubelka-Munk function vs excitation energy for 24h, 24+1h, 24+3h and 24+6h sample

Table 3. Milling time dependence of energy band

Milling time (hour)	Crystallite size (nm)	Energy band gap (eV)
24	24.9	3.15
24+1	23.2	3.07
24+3	22.0	3.02
24+6	23.6	3.05

4. CONCLUSIONS

ZnO nanocrystallites with different sizes were fabricated by wet and subsequent dry milling. Results showed that as milling speed was increased from 250 to 400 rpm, almost single-phase wurtzite ZnO nanocrystallites were successfully produced. In order to determine the effect of crystallite size on the optical properties sample wet-milled at 400 rpm exposed to a second dry milling process. The crystallite size decreased as milling time increased up to a critical size. Further increase in milling time leads particle agglomeration and crystallite size growth. As crystallite size decreased, a red shift of the UV-vis absorbance spectra was observed. Energy band gaps were calculated from Kubelka-Munk plots showing a significant decrease in E_g as crystallite size decreases. When crystallite size decreases from 24.9 to 22.0 nm, the band gap decreases from 3.15 to 3.02 eV. This behavior was explained by delocalization of molecular orbitals that creates energy traps and surface states on the band edge.

DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Telem ŞİMŞEK: Analyse the results and wrote the manuscript.

Abdullah CEYLAN: Analyse the results.

Gülçin Şefiye AŞKIN: Performed the experiments.

Şadan ÖZCAN: Analyse the results and wrote the manuscript.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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