Journal of Alloys and Compounds 515 (2012) 96–100

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# Bandgap variation in size controlled nanostructured Li–Ni co-doped CdO thin films

R.K. Gupta[a,*], Z. Serbetçi[b], F. Yakuphanoglu[c,d,**]

[a] Engineering Research Center, North Carolina A&T State University, Greensboro, NC 27411, USA
[b] Department of Chemistry, Bingöl University, Bingöl, Turkey
[c] Department of Physics, Firat University, Elazig 23169, Turkey
[d] Department of Physics and Astronomy, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

ARTICLE INFO

*Article history:*
Received 20 August 2011
Received in revised form
16 November 2011
Accepted 22 November 2011
Available online 30 November 2011

*Keywords:*
CdO
Lithium
Nickel
Bandgap
Quantum confinement

ABSTRACT

Li and Li–Ni doped CdO thin films were fabricated using sol–gel spin coating technique. Surface property and particle size of the pure CdO and doped CdO films were investigated using atomic force microscopy. The particle size of the films is of nanometer size and it changes with the doping concentrations. The optical study revealed that the bandgap of the films decreases with Li doping level. On the other hand for Li–Ni co-doped films, the bandgap first decreases with increase in Li–Ni concentrations and then increases with further increase in Li–Ni doping concentrations. The observed results are explained on the basis of quantum size effect. The obtained results indicate that the nanostructure and optical bandgap of the CdO film can be controlled by Li and Ni–Li co-dopants.

## 1. Introduction

Bandgap engineered nanostructured semiconductors have attracted considerable research interest because of their wide applications in semiconductor and optoelectronic devices [1–3]. Among different oxide semiconductors, cadmium oxide (CdO) is considered as a promising material for photovoltaic applications due to its high electrical conductivity and optical transmittance in the visible region of solar spectrum [4]. CdO is an *n*-type semiconductor with bandgap of ~2.5 eV [5]. Due to its low optical bandgap, CdO is not widely used in optoelectronics and photovoltaics, although CdO thin films show low resistivity due to defects of oxygen vacancies and cadmium interstitials [6].

It is reported that the optical properties and thus the optical bandgap of CdO can be modify by doping such as aluminum [7]. It was observed that the bandgap of the CdO film decreases with increase in aluminum doping level. On the other hand, Deokate et al. [8] have reported that fluorine doping increases the bandgap of CdO films. The tin doping produces a blue shift in the optical bandgap and a decrease in the electrical conductivity of CdO film [9]. The change in the optical bandgap in nanostructured materials can be explained on the basis of quantum size effect [10]. The quantum size effect is observed in cadmium sulfide (CdS) films, where the bandgap of the films is decreased with increase in particle size. Multilayer matrices of alumina capped zinc oxide nanoparticles with mean radii in the range of 1.8–3.6 nm were grown using pulsed laser deposition method to obtain size-dependent bandgap up to about 4.5 eV [11]. Our recent studies have evidenced that the bandgap of the CdO could be tuned by copper (Cu) doping [12]. It was observed that the bandgap of the CdO film is decreased by Cu doping and among the Cu doped CdO films, the bandgap was observed to increase with increase in copper doping level.

In this work, for the first time we report the synthesis and optical properties of Li and Li–Ni doped CdO films using sol–gel spin coating method. Motivated by our previous results on Cu doped CdO [12], in this work we study the effect of co-doping (Li–Ni) on the structural and optical properties of CdO films. We have compared the properties of Ni doped and Li–Ni co-doped CdO films. The detailed structural and optical properties of the films are presented in the following sections.

## 2. Experimental details

Sol–gel spin coating method was used to deposit Li doped CdO and Li–Ni co-doped CdO thin films. The required high purity (99.99%) chemicals were purchased from Alfa Aesar and used without further purification. Cadmium acetate dihydrate

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* Corresponding author. Tel.: +1 336 256 1152x2315; fax: +1 336 256 1153.
** Corresponding author at: Department of Physics, Firat University, Elazig 23169, Turkey.
*E-mail addresses:* ramguptamsu@gmail.com (R.K. Gupta), fyhanoglu@firat.edu.tr (F. Yakuphanoglu).

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doi:10.1016/j.jallcom.2011.11.098

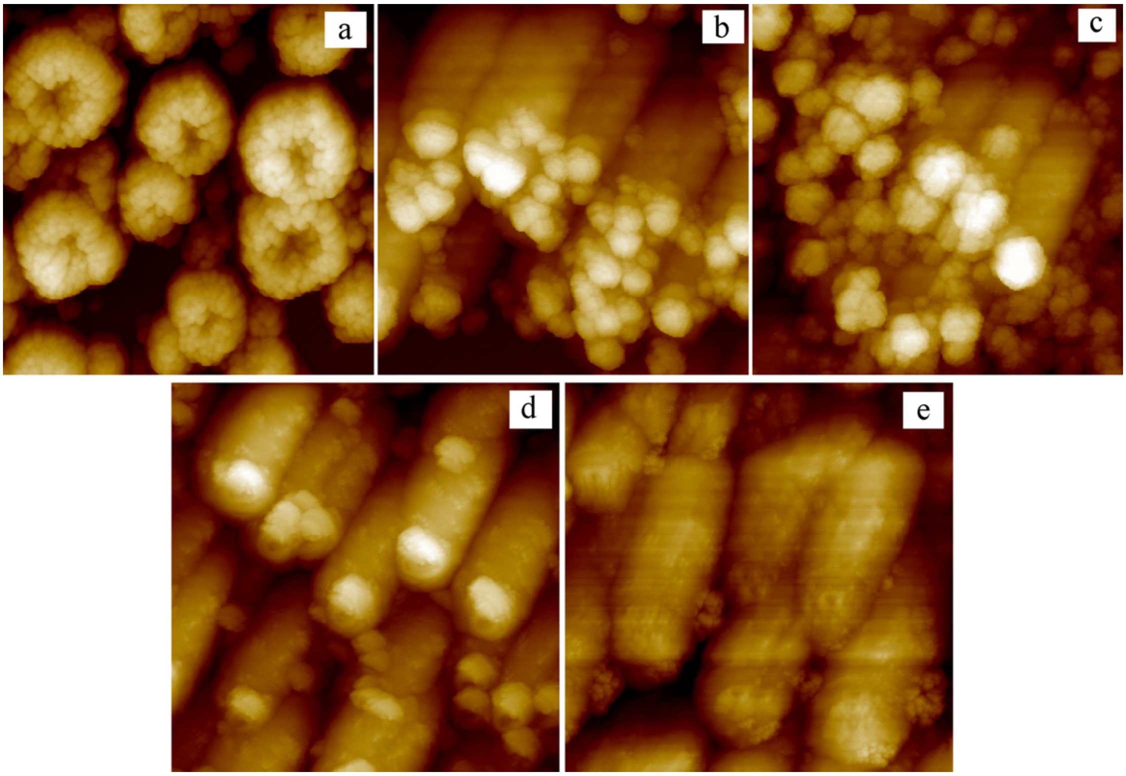

**Fig. 1.** AFM microphotographs of (a) pure CdO, (b) 0.5% Li doped CdO, (c) 1% Li doped CdO, (d) 2% Li doped CdO, and (e) 5% Li doped CdO films.

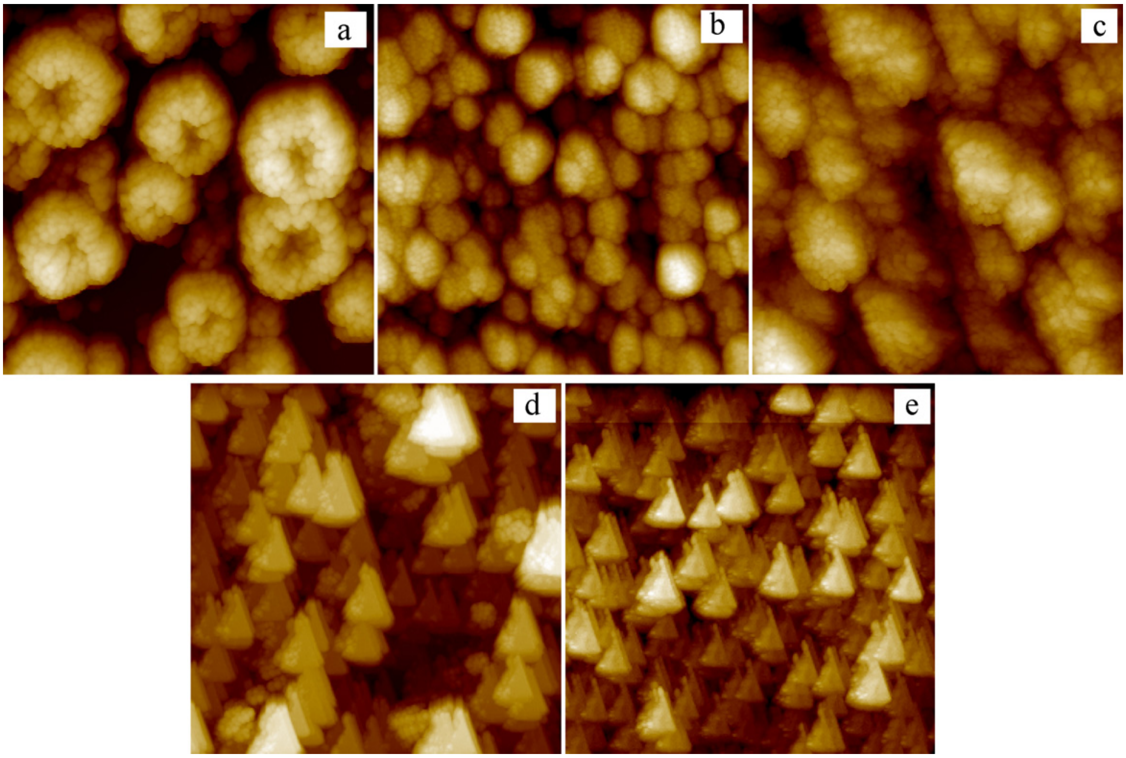

**Fig. 2.** AFM microphotographs of (a) pure CdO, (b) 0.5% Li–Ni doped CdO, (c) 1% Li–Ni doped CdO, (d) 2% Li–Ni doped CdO, and (e) 5% Li–Ni doped CdO films.

[$Cd(OOCCH_3)_2{\cdot}2H_2O$], nickel acetate tetrahydrate [$Ni(OOCCH_3)_2{\cdot}4H_2O$], lithium acetate dehydrate [$LiOOCCH_3{\cdot}2H_2O$], 2-metoxyethanol and mono ethanolamine were used for the deposition of CdO films. In typical synthesis, 0.5 M of cadmium acetate dihydrate was slowly dissolved in 2-metoxyethanol followed by the addition of mono ethanolamine. The molar ratio of mono ethanolamine to cadmium acetate dihydrate was 1.0. For doped CdO samples, the required amounts of nickel acetate tetrahydrate and lithium acetate dihydrate were mixed to the above solution. The content of Li and Ni was equally taken for co-doping of CdO sample. The prepared mixtures were stirred using a magnetic stirrer at 60 °C for about 30 min to obtain clear homogeneous solution and then sol was kept for aging for 24 h prior to film deposition. The pure and doped CdO films were deposited on microscopy glasses by sol–gel spin coating method followed by heating at 150 °C for 10 min to

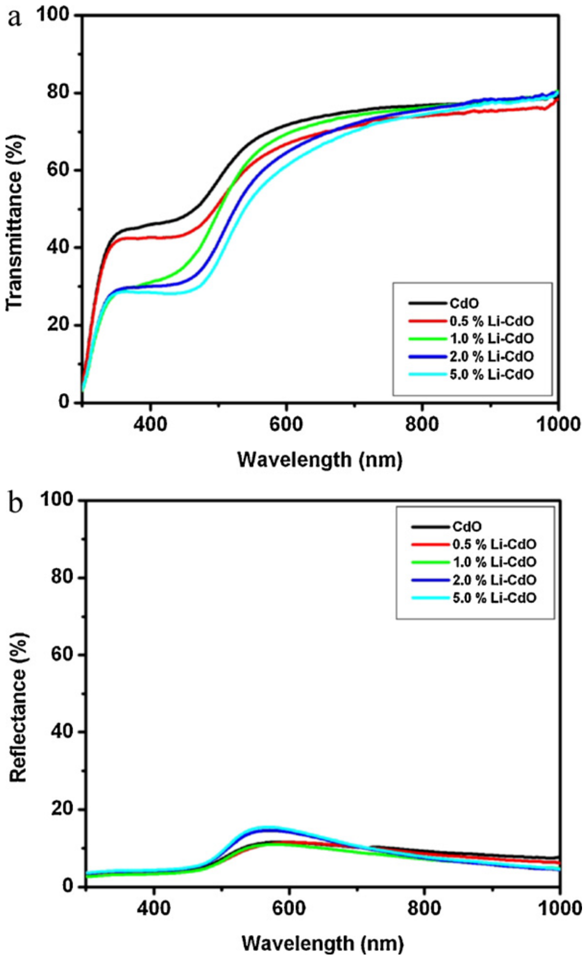

**Fig. 3.** Optical transmittance (a) and optical reflectance (b) spectra of pure CdO and Li doped CdO films.

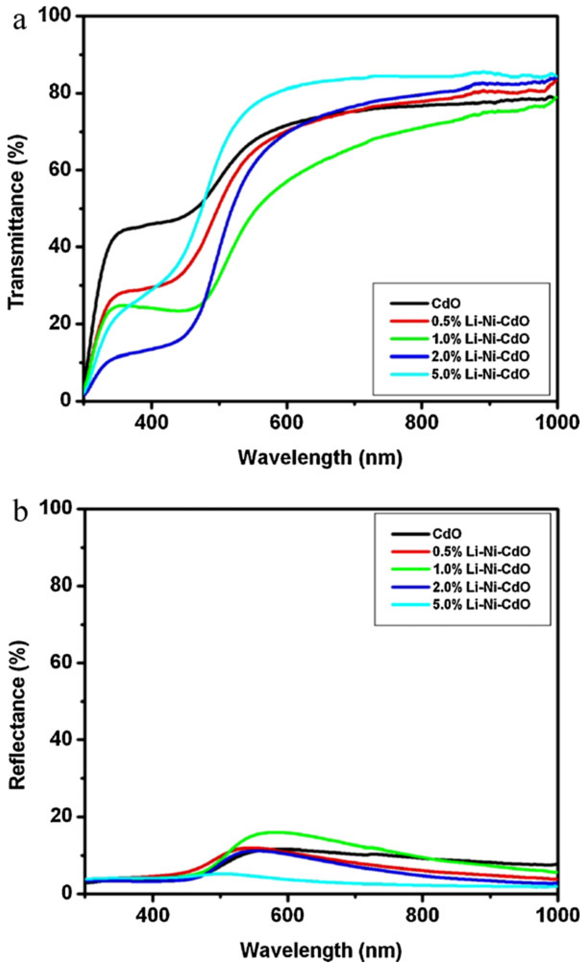

**Fig. 4.** Optical transmittance (a) and optical reflectance (b) spectra of pure CdO and Li–Ni co-doped CdO films.

evaporate the solvent and remove organic residuals. The prepared un-doped and doped CdO films were annealed at 400 °C for 1 h in a furnace. Surface morphology of the films was investigated using a PARK system XE 100E atomic force microscopy (AFM). The optical measurements the films were taken using a Shimadzu UV-VIS-NIR 3600 spectrophotometer.

## 3. Results and discussion

### 3.1. Structural properties

Atomic force microscopy was used to study the surface and grain size of the films. The AFM images of Li-doped CdO and Li–Ni co-doped CdO are shown in Figs. 1 and 2, respectively. All the images were taken in 1 μm × 1 μm area. As seen in the AFM images, the grain size of pure CdO film is 240 nm. We observed an increase in the grain size for Li-doped CdO films compare to pure CdO films. The grain size in Li-doped CdO films is over 300 nm. On the other hand, for Li–Ni co-doped CdO films, the average grain size for 0.5% Li–Ni doped CdO, 1% Li–Ni doped CdO, 2% Li–Ni doped CdO, and 5% Li–Ni doped CdO films are 125 nm, 160 nm, 115 nm, and 95 nm respectively. It is observed that the surface roughness of all the films is below 10 nm. Therefore, the grain size and the surface roughness of the co-doped films could be controlled. In the following text, we will discuss the effect of grain size on the optical properties of the doped CdO films.

### 3.2. Optical properties

The optical properties of pure and doped CdO films were studied in UV–visible region. Fig. 3 shows the optical spectra of the pure and Li-doped CdO films. It is evident from Fig. 3a that the average transmittance of CdO film is decreased by Li doping. This decrease in optical transmittance due to Li doping may be due to increased absorption by free carriers [13]. It is also observed that the absorption edge shifts to higher wavelength with increase in Li doping level. This suggests that the bandgap of CdO should decrease with increase in Li-doping level. As seen in Fig. 3b, the reflectance values of the films in the visible region of solar spectrum change with doping concentrations. The effect of Ni–Li co-doping on the optical properties of CdO films were investigated to see the effect of Ni doping on the optical properties of Li doped CdO films. Fig. 4 shows the optical spectra of Ni–Li co-doped CdO films. As seen in the transmittance spectra (Fig. 4a), the average transmittance of the films firstly decreases with increase in Li–Ni concentration and then increases with further increase in doping levels. Also it is observed that the reflectance of the films firstly increases with the doping level and then decreases with further increases in Li–Ni doping level (Fig. 4b). Such type of different behaviors in the optical properties of the Li and Li–Ni co-doped films could be due to change in the grain size of the films. To study the effect of grain size on the optical bandgap of the films, we calculated the bandgap of the pure and doped films.

The value of bandgap was calculated using the fundamental absorption, which corresponds to electron excitation from the

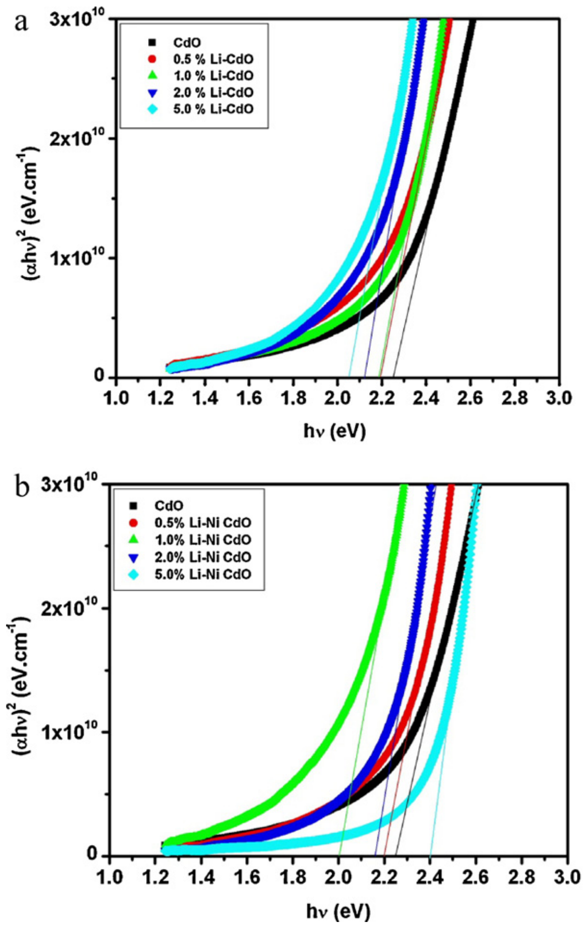

**Fig. 5.** $(\alpha h\nu)^2$ *vs.* $h\nu$ plots for (a) pure and Li doped CdO films and (b) pure and Li–Ni co-doped CdO films.

valence band to conduction band [14]. The absorption coefficient $\alpha$ and the incident photon energy $h\nu$ are related by the equation [15]

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \tag{1}$$

where $A$ is constant, $E_g$ is the bandgap and the exponent $n$ depends on the type of transition. In pure and doped CdO the allowed transition occurs which corresponds to $n = 1/2$ [16]. Thus, the bandgap of the films was calculated from the plot $(\alpha h\nu)^2$ *vs.* $h\nu$, and by extrapolation the linear portion of the curves until they intercept the photon energy axis (Fig. 5). The optical bandgap of pure CdO films is calculated to be 2.24 eV. A bandgap of 2.26 eV was reported for chemically sprayed CdO films [17]. Coutts et al. [18] have deposited the CdO thin films using chemical vapor deposition method and observed the optical bandgap of 2.4 eV.

As seen in Fig. 5a, the optical band gap of the Li doped films is decreased with increase in the Li-doping level. The bandgap values of 0.5%, 1%, 2%, and 5% Li doped CdO films are 2.20, 2.18, 2.12, and 2.05 eV respectively. The decrease in the optical bandgap of CdO after Li doping could be due to the structural modification in CdO films. The structural deformation in the CdO films could be due to the replacement of either substitutional or interstitial cadmium ions in the CdO lattice by Li ions. Such Li ions would introduce some additional energy level in the CdO bandgap close to the valence band edge, with a consequent reduction of the energy associated with the direct transition [19]. Saha et al. [7] have also observed a decrease in the bandgap after Al doping in CdO films. Dakhel [20] has reported a decrease in the optical band gap of CdO films after Li doping.

For the Ni–Li co-doped films, we observed that the optical bandgap of the films firstly is decreased with increase in co-doping level and then increase with further increase in co-doping level. The bandgap values of 0.5%, 1%, 2%, and 5% Li–Ni doped CdO films are 2.20, 2.00, 2.16, and 2.40 eV, respectively. Such type of the change in the bandgap of Li–Ni doped CdO could be due the structural modifications. Quantum confinement in semiconductor clusters provides an alternative and more fundamental explanation for the bandgap variation for nanostructured materials [21]. The possible reason for this change in optical bandgap could be due to the change in the grain size of the films. It is reported that the quantum confinement contributes to the widening of bandgap at small grain size [22]. The blue shift of bandgap ($E^*$) is related with the radius of the particle ($R$) by the equation [23]

$$E^* = E_g + \frac{\hbar\pi^2}{2R^2 m^*} - \frac{1.8e^2}{\varepsilon R} \tag{2}$$

where $e$ is the charge on electron, $E_g$ is the bandgap in the bulk, $\hbar$ is the reduced Planck's constant, $\varepsilon$ is the dielectric constant of the semiconductor, $m^*$ is the reduced mass of the electron and hole. It is clear from the above equation that the blue shift in the bandgap would occur if the radius of the particles decreases.

## 4. Conclusions

Nanostructured CdO and Li, Li–Ni doped CdO films were fabricated using sol–gel spin coating method. The grain size of the Li-doped CdO are over 300 nm, while for Li–Ni co-doped CdO films, the grain size is changed with doping level. These films are very transparent and transparency depends on doping. The bandgap of the CdO is narrowed by Li doping. For the Ni–Li co-doped CdO films, the optical bandgap of the films firstly is decreased with increase in co-doping level and then increase with further increase in co-doping level. The observed change in the optical bandgap is explained on the basis of quantum size effect.

## Acknowledgments

This work was supported by Global Research Network for Electronic Devices & Biosensors (GRNEDB) and KING Saud University.

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