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Doping sensitive optical scattering in zinc oxide nanostructured films for solar cells

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ABSTRACT

The nanostructured ZnO thin films are used in solar cells as heterojunction window layer as well as to enhance the junction area. Nanostructures also offer advantage of light scattering property to transmit more light into the absorber layer of solar cells. The optical and light scattering property of the nanostructured ZnO thin films doped with Al and Cu have been studied. The homogeneously doped ZnO nanostructured films were synthesized by a flux sublimation technique at $\sim 300^\circ\text{C}$ temperature. The structural studies show hexagonal nanocrystal growth in Al doped ZnO film and nanowire structure in Cu doped ZnO film. These doped ZnO films consistently showed two direct band gaps. The low energy band gap of Al and Cu-doped ZnO films originates from the macroscopic structural feature in the film, and the higher energy band gap due to the quantum confinement of nanostructure clusters in the film. Increased transmission in the lower wavelength region is caused by the forward light scattering by the nanostructure. Simulation of the optical absorption spectra of the Al and Cu-doped ZnO films using the modified Mie scattering theory shows consistent match with the experimental absorption spectra. The results show that increased forward scattering of light could be harvested by increasing the nanoparticle density which will enhance the photocurrent generation from the thin film solar cells by using doped ZnO nanostructured film as a window layer or as a transparent conducting electrode. Copyright © 2013 VBRI press.

Keywords: Nanostructures; Al and Cu-doped ZnO; mie theory; light scattering; solar cells.



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Alok Rastogi is a Professor in the Electrical and Computer Engineering Department and Associate Director, Center for Autonomous Solar Power (CASAP) at the State University of New York at Binghamton, USA. He has held leadership positions over past 20 years in photovoltaic energy conversion devices with specific contributions to the development of CdTe and CIGS thin film solar cell technologies. His current research is on the nano semiconductors, hybrid solar cells and

ultracapacitors for energy conversion and storage. His other researches are on polymeric and oxide ferroelectrics for nonvolatile memories, transparent electronics and multiferroic thin films for spintronics.

Introduction

Photovoltaic solar electricity is one of the key technologies for reducing the world's reliance on fossil fuels for energy generation. Reduced costs and higher conversion efficiencies are essential for making photovoltaics economically competitive. Optical nanostructures have a major role to play in improving the efficiency of solar cells by increasing the absorption of incident light, especially for thin-film applications. Light harvesting in efficient solar cells strongly depends on the photonic absorption of nanoparticles and can be enhanced in many ways [1]. Nanostructured zinc oxide (ZnO) thin films have received considerable attention due to their distinguished performance in the electronic, optical and photonic devices. Research has been carried out to fine tune the properties of ZnO nanostructures to adopt for various optoelectronics applications. In the context of thin film solar cells, ZnO films have been used as heterojunction window layer due to high transmissivity in the visible range because of its wide (~ 3.3 eV) band gap.

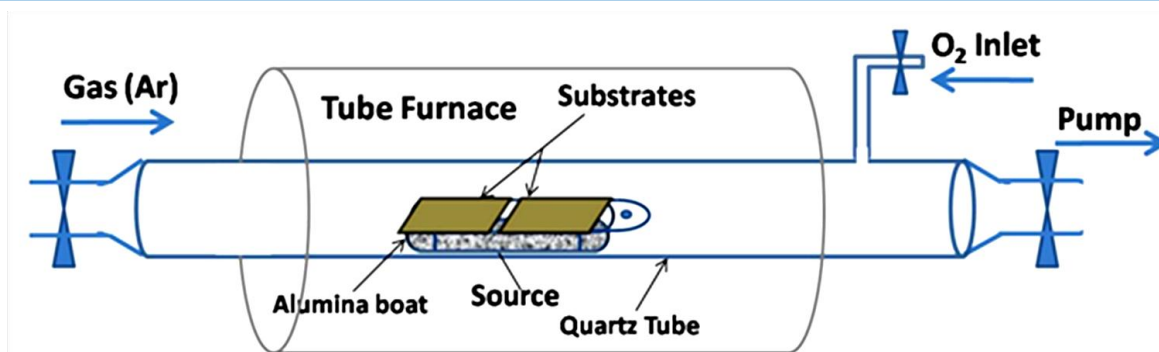


Fig. 1. Schematic diagram of the reactor assembly used for the growth of Al and Cu-doped ZnO nanostructured films by the closed space flux sublimation method.

In addition, doped ZnO films are also used as transparent conductor in solar cells for current collector electrode. To enhance the optical properties of ZnO several approaches have been adopted [2-4]. Polycrystalline ZnO films have been doped with group II and group III metal ions such as indium (In), aluminum (Al), gallium (Ga), copper (Cu) and cadmium (Cd) etc. with the aim to modify their electrical performance like conductivity, type and carrier concentration as well as their optical properties. The Al-doped ZnO film show high visible range transmittance and a low resistivity with relatively high stability and thus being used as top or bottom transparent conducting window layers in thin film solar cells as potentially demonstrated in CIGS solar cells [5].

The application of nanostructure ZnO film in solar cells instead of the planar ZnO has not been greatly studied. Nanostructure holds considerable promise in harvesting incident solar radiation which could be channeled into the active region of solar cells to enhance the photocurrent. The other potential use of nanostructure is in enhancing the junction area which too could result in increased photocurrent densities generated from solar cells. In this work, nanostructured Al-doped ZnO (AZO) and Cu-doped ZnO (CZO) films were prepared by closed space sublimation method [6]. The structural and optical properties of these thin films were studied. In this paper we report results of our investigation on the optical absorption as well as the light scattering properties of Al and Cu-doped nanostructured ZnO films. We have used modified Mie scattering theory to simulate the optical absorption spectra and present the comparison with the experimentally observed optical spectra of these films. The theoretical analysis demonstrates the range of nanosizes, complex refractive index and density of nanoparticles which effectively increases the optical transmission enabling more light to absorb in solar cell active region which will result in increased photo conversion efficiency.

Experimental

Nanostructure film growth

The Al and Cu-doped nanostructured ZnO thin films were synthesized by a two-step method which involves closed space flux sublimation of precursors in an inert low pressure environment followed by short periodic oxidation

by exposure to air in a tubular reactor as shown schematically (Fig. 1).

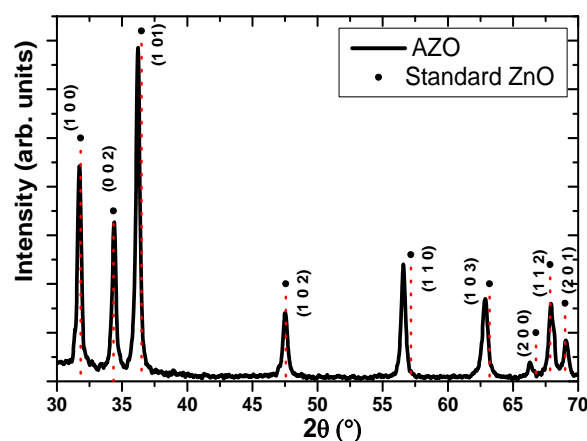


Fig. 2. XRD Pattern of a nanostructured AZO film deposited on quartz substrate. Standard diffraction peak locations from polycrystalline undoped ZnO are indicated by vertical dotted lines.

The precursor flux basically comprised of fine (100 mesh) zinc powder with BiI_3 both thoroughly grounded and mixed in the 3:1 weight ratio. For doping with Al, aluminum 2, 4-pentanedionate and for Cu doping, CuI was added in the weight ratio of 1:1 with Zn to the precursor. The sublimation-deposition assembly comprised of an alumina boat filled with powdered precursor flux and a substrate carrier placed atop the boat separated ~5 mm from the flux. Substrates were polished quartz plates and micro glass slides. Argon gas is supplied from the left end through a flow control valve, and air is supplied from the right end of the quartz tube. A mechanical high vacuum pump is connected to the right end of the reactor tube through a metering valve. Such an assembly serves to contain the source vapor which is critical for the formation of nanostructures. Loaded at the center of quartz tube reactor, the source assembly was heated to ~300°C to initiate the flux sublimation at a reduced 0.3-0.5 Torr pressure under Ar gas flow rate of ~100 sccm controlled through a calibrated mass flow controller. The film deposition involves in step-1, flux sublimation and deposition on substrate for 3-5 min and in step-2, a short (30s) exposure to the air at atmospheric pressure via the

outlet end of the quartz tube. Both step sequences were repeated several times to build-up the doped nanostructure ZnO film thickness.

Analysis technique

The Al and Cu- doped nanostructured ZnO films were characterized for crystallographic structure by recording X-ray diffraction (XRD) patterns on a PANalytical's X'Pert PRO Materials Research Diffractometer with Cu K α radiation using a Ni filter. Nanostructure morphology of the films was studied by scanning electron microscopy (SEM) using the field-emission Supra 55 VP (Zeiss). Optical transmission measurements were carried out using Beckman DU 7400 spectrophotometer in the 280-800 nm range.

Results and discussion

Crystalline structure

The crystalline structure of AZO thin film was evaluated by the XRD measurements. **Fig. 2** shows the XRD pattern of AZO thin film in the 30°-70°, 2 θ range with all diffraction peaks well indexed to the standard diffraction pattern of hexagonal phase ZnO consistent with the reported values (JCPDS file No. 36-1451).

The absence of secondary phase viz. Al or Al₂O₃ excludes the existence of Al-based clusters or their oxide phases in the AZO film within the detection limit. The films exhibit a dominant peak at 2 θ = 36.25° corresponding to the (101) plane of ZnO. In addition, the strong intensity and narrow width of other diffraction peaks corresponding to (100), (002) and (110) planes, confirm that the resulting products have high crystallinity of ZnO film [7-8]. The average crystallite size (*D*) for the AZO film was calculated from line broadening of the first three major XRD peaks using the Scherrer's formula [9].

$$D = \frac{K * \lambda}{\beta * \cos(\theta)} \quad (1)$$

where, λ is the wavelength of the X-ray radiation i.e. 1.54 Å, *K* is the shape factor, which is a constant taken as 0.9, θ is the Bragg's angle in degree, β is the full-width at half-maximum (FWHM) in radians of the (100), (002) and (101) planes. The crystallite size of the AZO film calculated by Eq. 1 yielded 247.4 Å, 265.2 Å and 266.5 Å for the first three peaks, respectively. So, the average grain size of the AZO film was estimated to be ~259.7 Å. Similar to the AZO films grown by the flux sublimation method CZO nanostructured films also showed neither the presence of dopant metal nor the dopant oxide peaks [10]. These observations clearly indicate homogeneous doping in the ZnO nanostructured films.

Nanostructure morphology

Determination of the nanostructure morphology of the Al and Cu-doped ZnO nanostructured thin films deposited on quartz substrate by the closed space sublimation technique was carried out using SEM. **Fig. 3 (a)** shows a FESEM micrograph of an AZO film, which depicts that the

nanocrystals are uniformly distributed covering the entire surface area of the substrate. Consistent with the XRD, there is no preferred directional growth rather these nanocrystals are hexagonal in shape and densely packed. The smaller crystals are grown in the form of clusters and nanospheres with average size of 30nm. The large size well developed hexagonal crystals are ~ 100-200nm in size. Elemental Zn, Al, Bi and O composition of the nanocrystals by the energy dispersive X-ray analysis (EDAX) corresponds to 52, 2.5, 0.5 and 45 at%, respectively. Al concentration in the 2 at% range has been optimally shown to result in highly conducting AZO film [11]. Zn composition is close to 50 at% which is important for well-formed hexagonal nanocrystals seen in the SEM micrographs of the AZO film. FESEM micrograph of CZO film grown on quartz substrate is shown in **Fig. 3(b)**. SEM images show the nanowire like morphology of the Cu-doped ZnO film deposited over quartz substrate. These nanowires are densely packed in clusters, scattered randomly and covering the entire surface area of the substrate. Average diameter of the synthesized nanowires varies from 20-30nm with lengths varying between 3-5 μ m. Elemental Zn, Bi, Cu and O composition of the nanocrystals by the energy dispersive X-ray analysis (EDAX) corresponds to 35, 0.75, 4.5 and 59.75 at%, respectively.

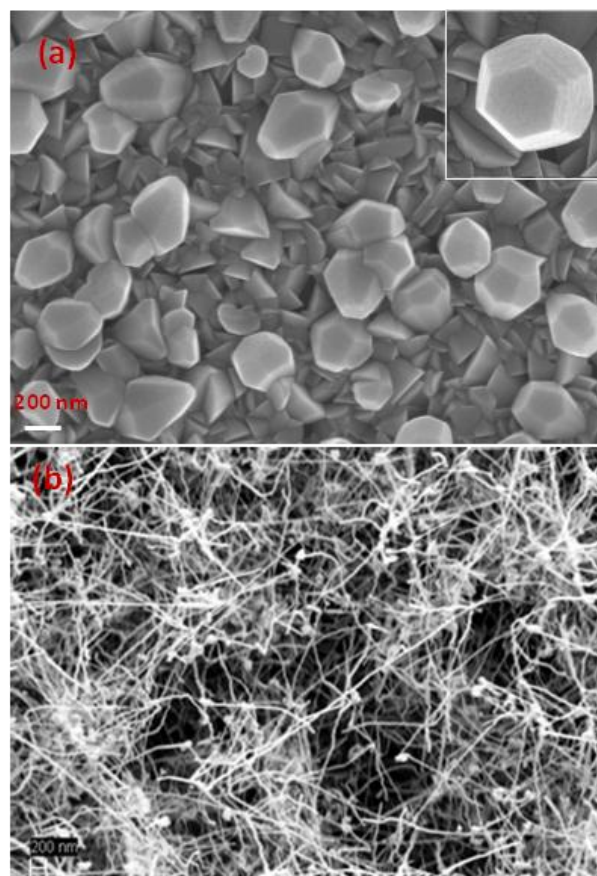


Fig. 3. SEM image of (a) densely packed AZO nanocrystals grown on quartz substrate. Inset shows the high magnification of the nanocrystals showing near spherical shape (b) CZO nanowires grown on quartz substrate.

Optical band gap

UV-Vis transmittance spectrum of a nanostructured AZO film is shown in **Fig. 4(a)** and that of a bulk AZO film in **Fig. 4(b)**. For the nanostructured AZO film, a gradual change in the transmission is seen in the wavelength range corresponding to the band gap energy. This is attributed to the nanostructure, as the loss of long range translational symmetry yields localized band gap states which can result in a graded variation in the absorbance in the energy range near the band gap. For the bulk AZO film, the transmission spectrum shows a sharp transition near the band gap energy.

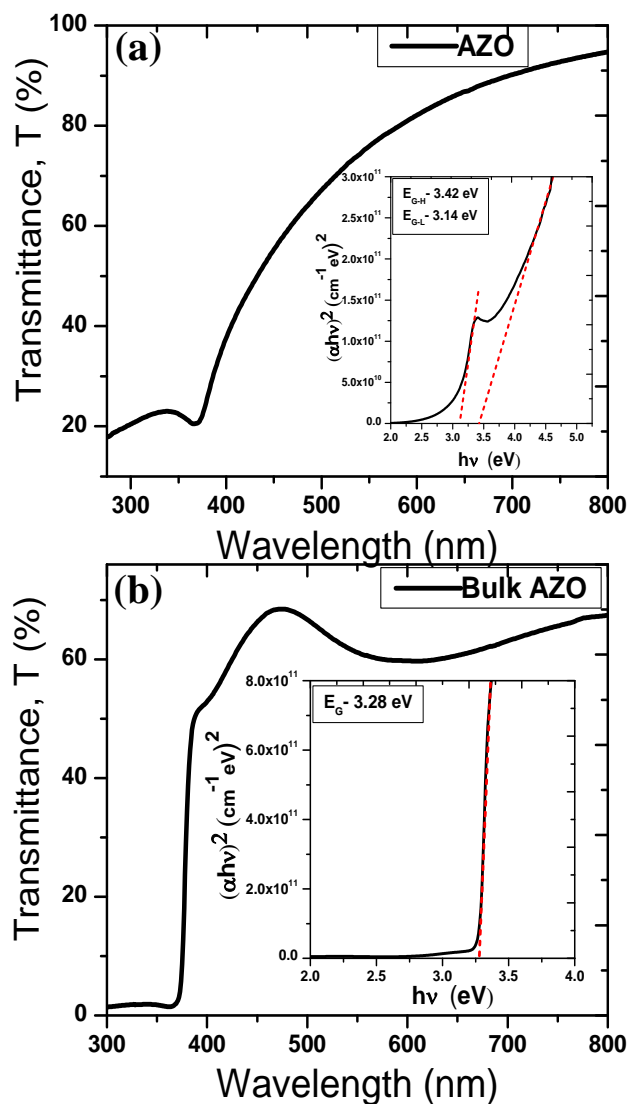


Fig. 4. (a) UV-Vis transmittance spectrum of the nanostructured AZO film. The inset shows direct band gaps at 3.14 eV from the microstructure and at 3.42 eV from the nanostructure regions of the AZO film (b) UV-Vis transmittance spectrum of a bulk AZO film. The inset shows direct band gap at 3.28 eV.

Direct optical band gap E_G for the nanostructured thin films and the bulk AZO film is determined by Tauc's relation [12],

$$(\alpha hv)^2 = A(hv - E_G) \quad (2)$$

The absorption coefficient α is determined from the measured transmittance (T) and film thickness t , using the relation $T = \exp(\alpha * t)$. The inset of **Fig. 4(a)** shows the plot of Eq. 2 for the nanostructured AZO thin film. Here, excellent straight line fits were observed in two separate energy regions, each within a narrow photon energy range. This is consistent with the interference that there may be two well defined direct energy band gaps. On the other hand, the planar AZO without nanostructure exhibits a single direct band gap at 3.28 eV as shown in the inset of **Fig. 4(b)**. Intercepts on the energy axis yields for the nanostructured AZO film one direct band gap $E_{G-L} \sim 3.14$ eV at the lower photon energy side and another at $E_{G-H} \sim 3.42$ eV at the larger photon energy side. Undoped ZnO polycrystalline films have a band gap ~ 3.3 eV. It is well known that the Al doping in ZnO tends to reduce the band gap due to increased carrier concentration closer to the degenerate levels [12-15].

As described earlier Cu doped nanostructured ZnO films were also fabricated by adding CuI in the precursor by the flux sublimation technique. The as-deposited Cu-doped ZnO (CZO) nanostructured film show similar gradual change in the transmission spectra as observed for the AZO film. The spectra were analyzed similar to that of the AZO film described above. The Cu-doped ZnO film which has nanowire like structure, the lower energy direct band gap occurs at $E_{G-L} \sim 3.17$ eV and the higher band gap at $E_{G-H} \sim 3.37$ eV (Inset of **Fig. 6**). It is apparent that the lower energy band gaps at 3.14 eV in the AZO and 3.17 eV in CZO films originate from the macrostructural or agglomerated clusters of nanoparticle regions of the film. The lower energy band gaps, which have been identified with the macrostructure regions of the films, are consistent within the published data on the nature of the dopant. Compared to the undoped ZnO which show direct band gap at ~ 3.3 eV, the Cu-doping causes band gap reduction to 3.17 eV whereas Al-doping to 3.14 eV. The higher estimate of the energy band gap E_{G-H} at 3.42 eV for AZO and 3.37 eV for CZO are consistent with the quantum confinement effect of the nanostructure. It may be mentioned that the CZO film have predominately nanowire like structure and much smaller nanosize along the diameter of the nanowire. As such CZO films show a $E_{G-H} = 3.37$ eV in the nanostructure regime.

Mie scattering: experimental vs. theoretical

Typically, for nanostructured AZO film, after the high energy absorption region, the transmittance shows a small increase. This implies that certain percentage of light is transmitted from the film. We infer this is due to the forward scattering of light from the doped ZnO nanoparticles. This high energy light could be harvested to increase the short circuit current and hence the efficiency of solar cells when nanostructured AZO is used as the window layer in solar cells. This phenomenon of light scattering of AZO nanoparticles is better understood in terms of the Mie scattering theory. In this case, the Mie theory could be applied to homogenous particles given the size of the nanocrystals in the doped ZnO film. Since the intensity of scattered light is a strong function of the

scattering angle, light scattering is essentially a geometrical effect when the particle sizes are larger than or similar to the wavelength λ of the incident light. As such, therefore the quantification by the Mie theory can produce results which produce a scattering pattern similar to an antenna lobe, with a sharper and more intense forward lobe for larger particles with least dependence on the wavelength of light. The higher energy side of the transmission spectra of the Al and Cu-doped nanostructured ZnO films has been analyzed using the modified Mie scattering theory. The Mie scattering absorption spectra is given by [16],

$$\alpha = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) [\text{Re}(a_n + b_n) - (|a_n|^2 + |b_n|^2)] \quad (3)$$

where $x = \frac{2\pi r}{\lambda}$, r is the particle radius, λ is the wavelength and m the complex refractive index of the sphere relative to the ambient. The Mie coefficients are given by a_n and b_n . Fig. 5 shows the superimposed Mie scattering absorption spectrum over the experimentally measured AZO absorption spectrum using Eq. 3. The Matlab simulation was performed by taking the complex AZO refractive index as $1.9+0.07i$ [12-13]. A better fit (curve b) was observed for the experimental absorption spectra (curve a) for a particle radius $r = 130$ nm and particle density of $1 \times 10^{14} \text{ cm}^{-3}$ in the wavelength range 330nm to 380nm. The additional resonant peak arises from the resonant surface waves on a sphere [17]. The nanoparticle size (~ 130 nm) giving the best fit to the experimental curve is consistent with the typical nanocrystal size in the AZO film obtained from the SEM study (Fig.2). The simulation studies show that the AZO nanocrystals scatter light and the forward light scattering can be explained on the basis of the Mie scattering theory.

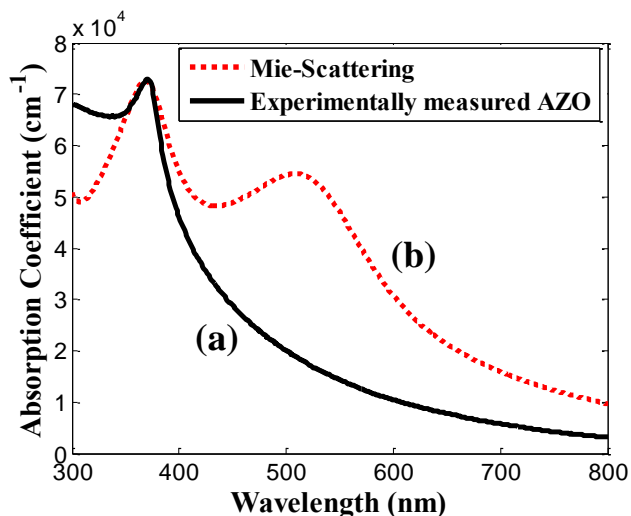


Fig. 5. (Color online) (a) Experimentally measured absorption spectrum of AZO nanoparticles. Superimposed is the (b) Mie scattering absorption spectrum calculated from Mie theory.

The Fig. 6 shows the similarly superimposed Mie scattering absorption spectrum over the experimentally measured CZO absorption spectrum using Eq. 3. The

Matlab simulation (curve b) shows that for a complex refractive index $1.99 + 0.01i$, particle radius $r = 110$ nm and particle density of $2.38 \times 10^{13} \text{ cm}^{-3}$, the light scattering from CZO nano particles show a better fit using the Mie theory in the wavelength range 330 to 360nm. The 360-400nm wavelength side of the fitted curve is not perfectly matching with the experimental curve due to the fact that for simulation the nanocrystals are considered to be perfect spheres, were as CZO film consisted of nanowire like structure.

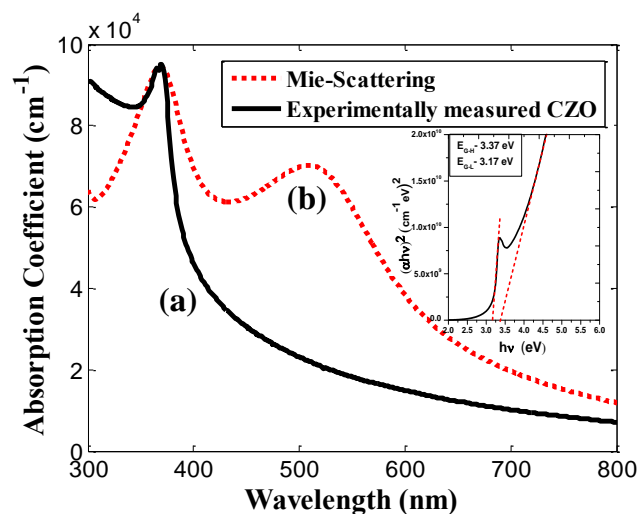


Fig. 6. (Color online) (a) Experimentally measured absorption spectrum of CZO nanoparticles. Superimposed is the (b) Mie scattering absorption spectrum calculated from Mie theory. The inset shows direct band gaps at 3.17 eV from the microstructure and at 3.37 eV from the nanostructure regions of the CZO film.

Conclusion

We have investigated the optical absorption and the light scattering property of Al-doped ZnO (AZO) and Cu-doped ZnO (CZO) nanostructured thin films. The simulation of the optical absorption spectrum of the Al and Cu-doped ZnO films using Mie scattering theory shows consistent match with the experimental absorption spectra. The results show that Mie scattering theory can be used to simulate the light scattering properties of nanostructured ZnO thin films and can be used as a tool to manage optical radiation entering the solar cell absorber layer and thus increase the conversion efficiency of solar cells.

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Reference

- Battaglia, C.; Escarre, J.; Söderström, K.; Charrière, M.; Despeisse, M.; Josef Haug, F.; Ballif, C. *Nature Photonics*. **2011**, *5*, 535. DOI: [10.1038/NPHOTON.2011.198](https://doi.org/10.1038/NPHOTON.2011.198)
- Steinhauser, J.; Feitknecht, L.; Faÿ, S.; Schlüchter, R.; Springer, J.; Shah, A.; Ballif, C. *Proc. 20th European PVSEC.1608*, **2005**.
- Čampa, A.; Krč, J.; Malmström, J.; Edoff, M.; Smole, F.; Topič, M. *Thin Solid Films*. **2007**, *515*, 5968. DOI: [10.1016/j.tsf.2006.12.093](https://doi.org/10.1016/j.tsf.2006.12.093)
- Guder, F.; Yang, Y.; Danhof, J.; Hartel, A.; Schwarz, U. T.; Zacharias, M. *Appl. Phys. Lett.* **2011**, *99*, 023105.

- DOI:[10.1063/1.3609321](https://doi.org/10.1063/1.3609321)
5. Hur, J.S.; Song, J.B.; Kim, J.; Byun, D.; Son, C.S.; Yun, J.H.; Yoon, K.H. *J. Korean Phys. Soc.* **2008**, *53*, 437.
 6. Thankalekshmi, R.R.; Dixit, S.; Rastogi, A.C.; Samanta, K.; Katiyar, R. S. *Integrated Ferroelectrics*. **2011**, *125*, 130.
DOI:[10.1080/10584587.2011.574470](https://doi.org/10.1080/10584587.2011.574470)
 7. Chen, B.J.; Sun, X.W.; Xu, C.X. *Ceram. Int.* **2004**, *30*, 1725.
DOI:[10.1016/j.ceramint.2003.12.140](https://doi.org/10.1016/j.ceramint.2003.12.140)
 8. Mohammadi, M.; Rezaee Rokn-Abadi, M.; Arabshahi, H. *Indian J. Sci. & Tech.* **2010**, *3*, 110.
 9. Tural, B.; Sopac, Ş. B.; Özkan, N.; Demir, A.S.; Volkan, M. *J. Phys. Chem. Solids*. **2011**, *72*, 968.
DOI:[10.1016/j.jpccs.2011.05.010](https://doi.org/10.1016/j.jpccs.2011.05.010)
 10. Thankalekshmi, R.R.; Dixit, S.; Rastogi, A.C. (Unpublished)
 11. Shukla, R.K.; Srivastava, A.; Srivastava, A.; Dubey, K.C. *Journal of Crystal Growth*. **2006**, *294*, 427.
DOI:[10.1016/j.jcrysgro.2006.06.035](https://doi.org/10.1016/j.jcrysgro.2006.06.035)
 12. Caglar, M.; Ilican, S.; Caglar, Y.; Yakuphanoglu, F. *J. Mater. Sci.: Mater. Electron.* **2008**, *19*, 704.
DOI: [10.1007/s10854-007-9386-2](https://doi.org/10.1007/s10854-007-9386-2)
 13. Hsu, L.-S.; Yeh, C. S.; Kuo, C.C.; Huang, B.R.; Dhar, S. *J. of Optoelectronics and Advanced Materials*. **2005**, *7*, 3039.
 14. Yogamalar, N.; Rajeswari; Bose, A.; Chandra. *AIP Conf. Proc.* **2011**, *1349*, 363.
DOI:[10.1063/1.3605885](https://doi.org/10.1063/1.3605885)
 15. Rusu, G.G.; Râmbu, A.P.; Buta, V.E.; Dobromir, M.; Luca, D.; Rusu, M. *Materials Chemistry and Physics*. **2010**, *123*, 314.
DOI: [10.1016/j.matchemphys.2010.04.022](https://doi.org/10.1016/j.matchemphys.2010.04.022)
 16. Cetin, A.; Kibar, R.; Selvi, S.; Townsend, P.D.; Can, N. *Physica B*. **2009**, *404*, 3379.
DOI:[10.1016/j.physb.2009.05.019](https://doi.org/10.1016/j.physb.2009.05.019)
 17. Thiele, E.S.; French, R. H. *Adv. Mater.* **1998**, *10*, 1271.
DOI: [10.1002/\(SICI\)1521-095\(199810\)10:15<1271::AID-ADMA1271>3.0.CO;2-C](https://doi.org/10.1002/(SICI)1521-095(199810)10:15<1271::AID-ADMA1271>3.0.CO;2-C)

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