

Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures

A. Escobedo Morales, E. Sánchez Mora, and U. Pal
Instituto de Física, Benemérita Universidad Autónoma de Puebla,
Apartado Postal J-48, 72570, Puebla, Pue., México,
e-mail: aescobe@sirio.ifuap.buap.mx, esanchez@sirio.ifuap.buap.mx,
upal@sirio.ifuap.buap.mx

Recibido el 7 de julio de 2006; aceptado el 7 de diciembre de 2006

Optical properties of un-supported or powdered nanostructures are frequently determined through UV-Vis absorption spectroscopy of their dispersed solutions in liquid media. Though the peak position of the absorption band of semiconductor nanostructures could be defined well from such measurements, precise determination of their band gap energies (E_g) is difficult. However, using the Kubelka-Munk treatment on the diffuse reflectance spectra of such powdered semiconductor nanostructures, it is possible to extract their E_g unambiguously. We discussed the advantages of using Diffuse Reflectance Spectroscopy (DRS) over UV-Vis absorption spectroscopy in powdered nanostructured materials. Un-doped and In-doped ZnO nanostructures of needle-like morphology, grown by a low-temperature hydrothermal technique are used for the optical studies. Possible sources of mistake in estimating E_g from UV-Vis absorption spectra of dispersed samples are discussed.

Keywords: Diffuse reflectance spectroscopy; nanostructures; zinc oxide.

Frecuentemente las propiedades ópticas de nanoestructuras en forma de polvo o no soportadas son determinadas dispersando el material en medios líquidos y efectuando espectroscopia de absorción UV-Vis. Aunque la posición de la banda de absorción para estos semiconductores nanoestructurados puede estar bien definida, la determinación precisa del valor de la energía de la banda prohibida (E_g) es difícil. Sin embargo, usando el formalismo de Kubelka-Munk en los espectros de reflectancia difusa obtenidos de las muestras, es posible conocer E_g sin ambigüedad. Aquí se discuten las ventajas de usar la espectroscopia de reflectancia difusa (DRS) sobre la espectroscopia de absorción UV-Vis en semiconductores nanoestructurados en forma de polvo. Nanoestructuras de ZnO con morfología tipo aguja, dopadas y no-dopadas con indio crecidas por una técnica hidrotérmica a baja temperatura son usadas para los estudios ópticos. Posibles fuentes de error en la estimación de E_g usando los espectros de absorción UV-Vis de muestras dispersadas son discutidas.

Descriptores: Espectroscopia de reflectancia difusa; nanoestructuras; óxido de zinc.

PACS: 78.40.-q; 78.67.Bf; 78.67.-n

1. Introduction

The energy gap (E_g) is an important feature of semiconductors which determines their applications in optoelectronics [1-4]. The UV-Vis absorption spectroscopy is frequently used to characterize semiconductors thin films [5]. Due to low scattering in solid films, it is easy to extract the E_g values from their absorption spectra knowing their thickness. However, in colloidal samples, the scattering effect is enhanced since more superficial area is exposed to the light beam. In normal incidence mode, dispersed light is counted as absorbed light and the technique (optical absorption) does not distinguish between the two phenomena. On the other hand, it is common to obtain powdered samples instead of thin films or colloids, and frequently UV-Vis absorption spectroscopy is carried out dispersing the sample in liquid media like water, ethanol or methanol. If the particle size of the sample is not small enough, it precipitates and the absorption spectrum is even more difficult to interpret. In order to avoid these complications, it is desirable to use DRS, which enables to obtain E_g of un-supported materials [6].

The theory which makes possible to use DR spectra was proposed by Kubelka and Munk [7]. Originally they proposed a model to describe the behavior of light traveling in-

side a light-scattering specimen, which is based on the following differential equations:

$$\begin{aligned} -di &= -(S + K)idx + Sjd x \\ dj &= -(S + K)jdx + Sid x \end{aligned} \quad (1)$$

where i and j are the intensities of light traveling inside the sample towards its un-illuminated and illuminated surfaces, respectively; dx is the differential segment along the light path; S and K are the so called K-M scattering and absorption coefficients, respectively. These last two quantities have no direct physical meaning on their own, even though they appear to represent portions of light scattered and absorbed, respectively, per unit vertical length [8]. This model holds when the particle size is comparable to, or smaller than the wavelength of the incident light, and the diffuse reflection no longer allows to separate the contributions of the reflection, refraction, and diffraction (*i.e.* scattering occurs).

In the limiting case of an infinitely thick sample, thickness and sample holder have no influence on the value of reflectance (R). In this case, the Kubelka-Munk equation at any wavelength becomes:

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \equiv F(R_\infty); \quad (2)$$

$F(R_\infty)$ is the so-called remission or Kubelka-Munk function, where $R_\infty = R_{\text{sample}}/R_{\text{standard}}$ [9].

In the parabolic band structure, the band gap E_g , and absorption coefficient α of a direct band gap semiconductor are related through the well known equation [10]:

$$\alpha h\nu = C_1 (h\nu - E_g)^{1/2}, \quad (3)$$

where α is the linear absorption coefficient of the material, $h\nu$ is the photon energy and C_1 is a proportionality constant. When the material scatters in perfectly diffuse manner (or when it is illuminated at 60° incidence), the K-M absorption coefficient K becomes equal to 2α ($K=2\alpha$). In this case, considering the K-M scattering coefficient S as constant with

respect to wavelength, and using the remission function in Eq. (3) we obtain the expression:

$$[F(R_\infty) h\nu]^2 = C_2 (h\nu - E_g). \quad (4)$$

Therefore, obtaining $F(R_\infty)$ from Eq. (2) and plotting the $[F(R_\infty) h\nu]^2$ against $h\nu$, the band gap E_g of a powder sample can be extracted easily.

2. Experimental

Powder zinc oxide samples with different indium (doping) contents were prepared by a low-temperature hydrothermal synthesis and subsequent thermal annealing at 300°C in argon atmosphere for two hours [11]. All the samples were characterized by UV-Vis absorption spectroscopy (Shimadzu, UV-3101PC double beam spectrophotometer), diffuse reflectance spectroscopy (DRS) (Varian Cary 100 UV-Vis Spectrophotometer with DRA-CA-30I Diffuse Reflectance Accessory), powder X-ray diffraction (XRD) (Phillips X'Pert diffractometer with Cu K α radiation), and scanning electron microscopy (SEM) (Jeol JSM 5300). All the optical measurements were carried out at room temperature. For UV-Vis absorption measurements, the powder samples were dispersed in deionized water with a fixed concentration (5mg/4ml).

3. Results and discussion

The XRD patterns of the samples are shown in Fig. 1. The diffraction peaks revealed the wurtzite structure of ZnO. Apart from zinc oxide, it is possible to recognize a second phase (indium hydroxide, $\text{In}(\text{OH})_3$) in the as-grown sample doped with 2% In, which is dissociated through the annealing process (Fig. 1b). As can be seen from the XRD patterns of as-grown and annealed samples, the crystallinity of the nanostructures decreased on indium doping. The nanostructures present a needle-like morphology with 450 nm in diameter and $5 \mu\text{m}$ average length (Fig. 2). From the SEM images we can see that the surfaces of the ZnO nanostructures after thermal annealing are not as smooth as un-annealed ones.

The UV-Vis absorption spectra of as-grown and annealed samples are shown in Fig. 3. All the spectra revealed a characteristic absorption peak of ZnO. However, the peak is not well resolved for all the samples. In as-grown sample, the absorption peak is blue-shifted on 0.5% In doping. As the nominal concentration of In increased further, the absorption peak shifted towards higher wavelengths. The peaks in the absorption spectra do not correspond to the true optical band gap of ZnO, which is about 3.37 eV (at room temperature).

It is interesting to note that in as-grown samples, the absorbance increases as the photon energy increases, and subsequently at energies higher than the absorption band edge it decreases. The latter behavior is very different from the common absorption characteristic of thin films [12]. This behavior is due to the scattering phenomenon in colloidal samples. Experimentally obtained absorption spectra of the samples

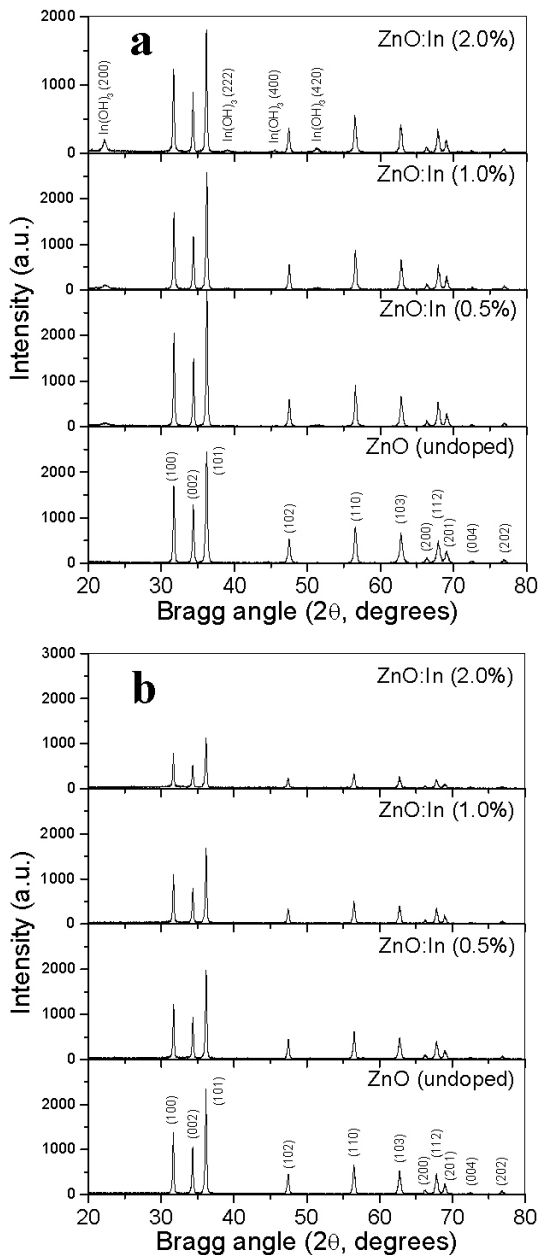


FIGURE 1. Powder X-ray diffraction patterns of nanostructured ZnO before (a), and after (b) thermal treatment.

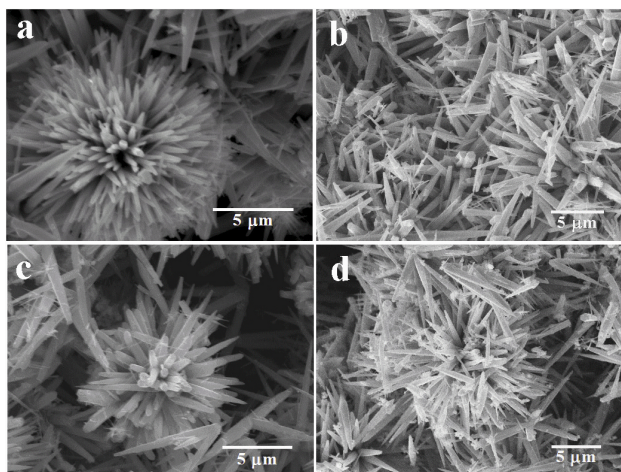


FIGURE 2. Typical SEM micrographs of un-doped and In-doped (0.5%) ZnO nanostructures before (a and c) and after annealing (b and d).

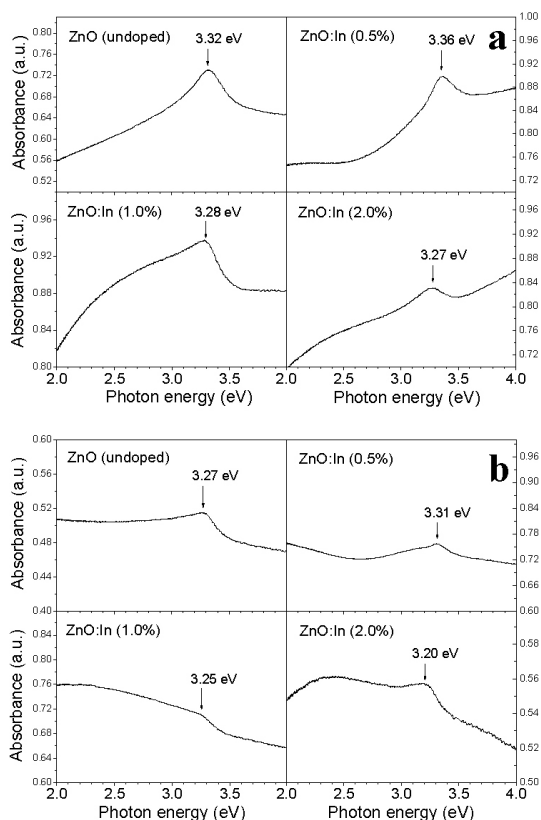


FIGURE 3. UV-Vis absorption spectra of as-grown (a), and annealed samples (b).

have two components: dispersed light due to scattering counted as absorbed light by the spectrophotometer, and optical absorption due to electronic transitions in the samples. On the other hand, in the spectra of annealed samples (Fig. 3b), the absorption at lower photon energy side (with respect to the absorption peak) is as high as the absorption peak. Electronic transitions in semiconductor materials are hardly responsible for such features. Instead, it is the result of scatter-

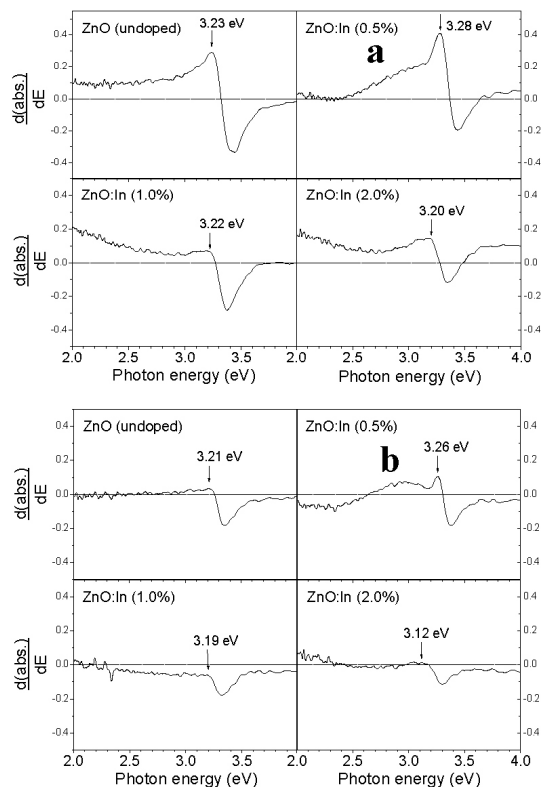


FIGURE 4. First derivative absorption spectra of as-grown (a), and annealed samples (b).

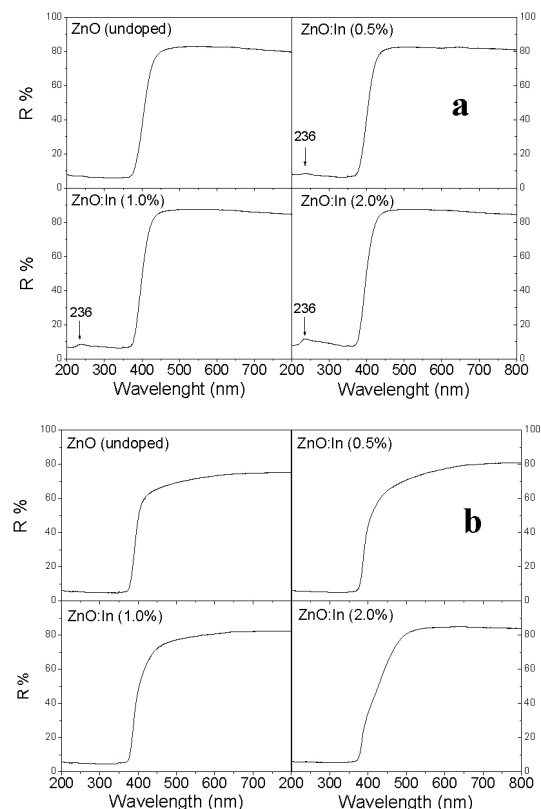


FIGURE 5. Diffuse reflectance spectra of as-grown (a), and annealed samples (b).

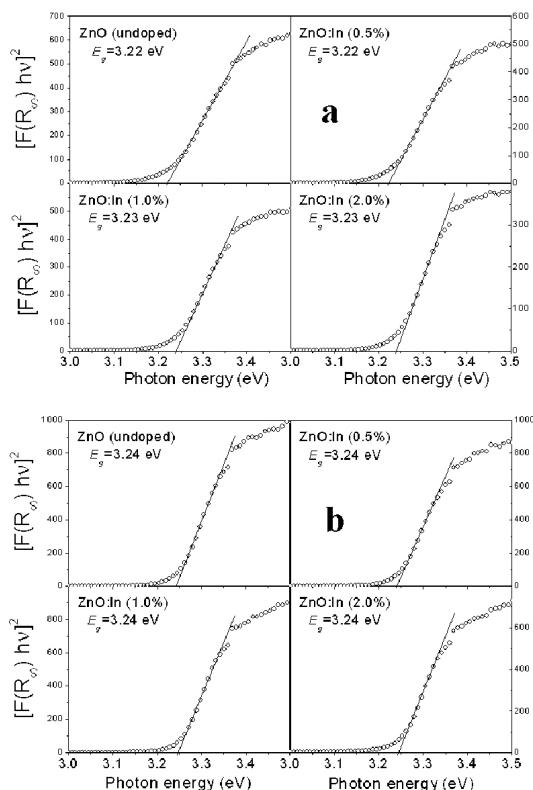


FIGURE 6. Kubelka-Munk transformed reflectance spectra of as-grown (a), and annealed samples (b).

ing from the nanostructures with rough surfaces after thermal annealing.

A common way of extracting band gap from absorption spectra is to get the first derivative of absorbance with respect to photon energy and finding the maxima in the derivative spectra at the lower energy sides [13]. The E_g is associated to the maximum in the spectrum, *i.e.* where the absorbance has a maximum increase with respect to photon energy. In Fig. 4, such derivative spectra of the samples are presented.

The first derivative method is convenient when the absorption peak dominates the spectrum (see Figs. 3a and 4a, un-doped ZnO), feature that is observed easily in colloidal

samples [14]. If the scattering effect is as high as the optical absorption process, it screens the absorption peak, making the assignment to E_g uncertain (*e.g.* see Fig. 4b, 2.0% indium doped sample).

To avoid the difficulties in obtaining E_g from UV-Vis absorption spectroscopy in dispersed samples, diffuse reflectance measurements of dry powders can be performed. Diffuse reflectance spectra of as-grown and annealed samples are shown in Fig. 5.

In as-grown samples, a considerable reduction in reflectance starts at about 460 nm and a peak centered at 236 nm appears. Intensity of this peak increases with the increase of nominal indium concentration in the samples. The origin of the peak may be the presence of indium hydroxide in the samples. The wavelength at which reduction in reflectance starts in annealed samples is not clear, suggesting the formation of band tail due to incorporation of impurity states. Absence of the peak at 236 nm in annealed samples supports the assumption of its hydroxide origin. The DR spectra of the samples after Kubelka-Munk treatment are shown in Fig. 6. The intersection between the linear fit and the photon energy axis gives the value to E_g . So, by this method the assignment of band gap can be made with certainty.

Table I presents the E_g values obtained from two methods: UV-Vis absorption spectroscopy and DRS. It can be noted that if erroneously the band gap energy is related directly to the absorption peaks which appear in as-collected UV-Vis spectra, it can lead to overestimate its value, with discrepancies as high as 139 meV. Although the E_g calculated from derivative spectra are close to their exact values, for the samples like ZnO:In (2.0%) the agreement is still poor, since the absorption peak is not well resolved. Errors in estimated band gap values can lead to false conclusions.

Our results obtained from nanostructured ZnO samples indicate that, though the DRS technique is not as sensitive as the UV-Vis absorption technique to a small change in optical properties of materials, it can extract the band gap values of powder semiconductors without any ambiguity.

TABLE I. E_g values for the nanostructured ZnO samples obtained from UV-Vis absorption spectroscopy and DRS.

Nominal In concentration in the sample (%)	abs. peak position (eV)	E_g (eV), from derivative abs. spectra	E_g (eV), from DRS
Un-annealed samples			
0.0	3.32(5)	3.23(7)	3.22(1)
0.5	3.36(2)	3.28(0)	3.22(3)
1.0	3.28(9)	3.22(3)	3.23(9)
2.0	3.27(2)	3.20(8)	3.23(7)
Annealed samples			
0.0	3.27(9)	3.21(2)	3.24(4)
0.5	3.31(0)	3.26(1)	3.24(2)
1.0	3.25(9)	3.19(5)	3.24(7)
2.0	3.20(4)	3.12(8)	3.24(5)

4. Conclusions

DRS is a more convenient technique to characterize unsupported nanomaterials than UV-Vis absorption spectroscopy, since it takes advantage of the enhanced scattering phenomenon in powder materials. Effects of light scattering in the absorption spectra of powder samples dispersed in liquid media can be avoided using DRS. If the absorption peak is not well resolved, even the use of derivative of absorption spectra does not guarantee the exact estimation of E_g , and can lead erroneous conclusions. Finally, the DRS tech-

nique does not require a powder sample to be dispersed in any liquid medium, so the material is not contaminated or consumed.

Acknowledgements

We are thankful to E. Aparicio Ceja and I. Gradilla Martinez, CCMC-UNAM for their helps in XRD and SEM measurements of the nanostructures. The work is partially supported by CONACyT, Mexico (Grant No. 46269) and UC-MEXUS-CONACyT (Grant No. CN-05-215).

-
1. Ü. Özgür *et al.*, *J. Appl. Phys.* **98** (2005) 041301.
 2. D.M. Bagnall *et al.*, *Appl. Phys. Lett.* **70** (1997) 2230.
 3. T. Aoki, Y. Hatanaka, and D.C. Look, *Appl. Phys. Lett.* **76** (2000) 3257.
 4. C. Boemare, T. Monteiro, M.J. Soares, J.G. Guilherme, and E. Alves, *Physica B* **308–310** (2001) 985
 5. U. Pal, D. Samanta, S. Ghorai, and A.K. Chaudhuri, *J. Appl. Phys.* **74** (1993) 6368.
 6. D.G. Barton, M. Shtein, R.D. Wilson, S.L. Soled, and E. Iglesia, *J. Phys. Chem. B* **103** (1999) 630.
 7. P. Kubelka and F. Munk, *Z. Tech. Phys.* **12** (1931) 593.
 8. L. Yang and B. Kruse, *J. Opt. Soc. Am. A* **21** (2004) 1933.
 9. J. Torrent and V. Barrón, *Encyclopedia of Surface and Colloid Science*. (Marcel Dekker, Inc.: New York, 2002).
 10. R.A. Smith, *Semiconductors*, 2nd ed. (Cambridge University Press: Cambridge, 1978).
 11. A. Escobedo, M. Herrera Zaldivar, and U. Pal, *Opt. Mater.* **29** (2006) 100.
 12. S.A. Studenikin, N. Golego, and M. Cocivera, *J. Appl. Phys.* **83** (1998) 2104.
 13. M. Becerril, H. Silva-López, and O. Zelaya-Angel, *Rev. Mex. Fís.* **50** (2004) 588.
 14. E.A. Meulenkamp, *J. Phys. Chem. B* **102** (1998) 5566.