

# Investigation of Mechanical and Non Linear Optical Properties CdS Nanofilm

Raghad A. Al Aloosi, Hussein A. Jawad

<sup>1</sup>Asst. Lectuer, Al -Khawarzmy Engineering College/University of Baghdad/Baghdad, Iraq

<sup>2</sup>Asst. Prof., Institute of Laser for Postgraduate/University of Baghdad/Baghdad, Iraq

## Abstract

Different thicknesses (100-230 nm) of deposited nanocrystalline (cds) thin films have been prepared using CBD technique. The thinner film has been annealed in vacuum for 1 hour at different annealing temperatures in the range of (250 – 400 °C). Z-Scan technique was used to study the nonlinear optical properties. The roughness of the nanocrystalline CdS increases with the increase of CdS thin film, also the roughness increased with the grain size the present work is to manufacture CdS nano film and to investigate some of there optical and mechanical properties.

## Keywords

Z-Scan, CdS, nano film , Roughness, CPD

## I. Introduction

Nanostructure materials are traditionally defined as those with grain sizes smaller than 100 nm, grains in excess of 100 nm are typically present in the microstructure primarily as a result of the broad distribution of grain sizes that evolves during processing [1].

Nanostructure materials -NSM- are materials that exhibit unique features and properties in different fields, they exhibit wide variety of nonlinear optical properties, which have attracted attention of the nonlinear optical devices [2]. Nanomaterials have technological applications in areas like electronic, magnetic, optical and mechanical devices [3]. They have attracted considerable attention in recent years and offer interesting possibilities related to many structural applications [4]. The z-scan measurement is completed by detecting the transmittance of a nonlinear medium through a finite aperture in the far field as a function of the sample position ( $z$ ) measured with respect to the focal plane [5]. The nonlinear absorption study carried out using single beam femtosecond open aperture z-scan technique (OA) [6]. The mechanical behavior of nanostructured materials have a great interest in originates from the unique mechanical properties first observed and/or predicted for the materials [7]. The Aim of the work are Investigation of mechanical and non linear optical properties CdS nanofilm.

## Methodology

Films were deposited on glass slides by, 30 ml of 0.1M Cadmium Sulfate [ $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ], 99%, GCC(U.K), 30ml  $\text{NH}_3$  solution [ $(\text{NH}_4\text{OH})$ , 25%, GCC (U.K)] and 30 ml of 0.2 M thiourea [ $\text{CS}(\text{NH}_2)_2$ , 99% , GCC (U.K)]. The beaker was placed in a water bath at temperature ( $80 \pm 2^\circ\text{C}$ ). The solution was stirred with a magnetic stirrer type (L.I.P England). It was heated with continuous stirring to the required temperature of deposition, and the pH measured with pH meter (type Oakton(USA)). Substrates were then taken out after a suitable time 20 minte . The CdS thin film was analyzed using a typical XRD system. The X-ray diffraction pattern was obtained with a PW 1840 diffractometer equipped with a radiation source (40 kV, 20 mA) and  $\lambda = 0.154$  nm. The CdS thin film transmission was tested using UV-visible spectrophotometer. z-scan measurements were performed into two parts, closed and open aperture. Each part was employed at 1064 nm and 532 nm. The closed-aperture z-scan was used to measure the nonlinear refractive index, while the open-aperture was used to measure the nonlinear absorption coefficient A roughness instrument type (Surface Roughness tester ) TR 240 (China, 2001) was used to

measure the average roughness (Ra) for the samples at different thicknesses.

## Results and Discussion

### Effect of annealing temperature

The effect of annealing of 100 nm pure CdS thin films prepared by CBD technique on glass substrates deposited in optimum conditions where temperature is  $80^\circ\text{C}$ , pH 11.5 and a deposition time of 20 min. are shown in Figure (1) XRD patterns of annealed films for 1 hr. in the range  $250^\circ\text{C}$  to  $400^\circ\text{C}$  exhibit single diffraction peak at  $2\theta = 26.6^\circ$  which correspond to either the (002) hexagonal or the (111) cubic planes. As annealing temperature increases the intensity of diffraction peak increases and the diffraction peak becomes sharper. From XRD analysis, our films didn't show any phase transition or presence of any other peak even for annealing temperature of  $400^\circ\text{C}$ , this means that crystalline of the films was enhanced. Furthermore, a tendency of the peak shift towards lower  $2\theta$  values can be observed when the annealing temperature increases, which was in good agreement with the Ref. [7,8]

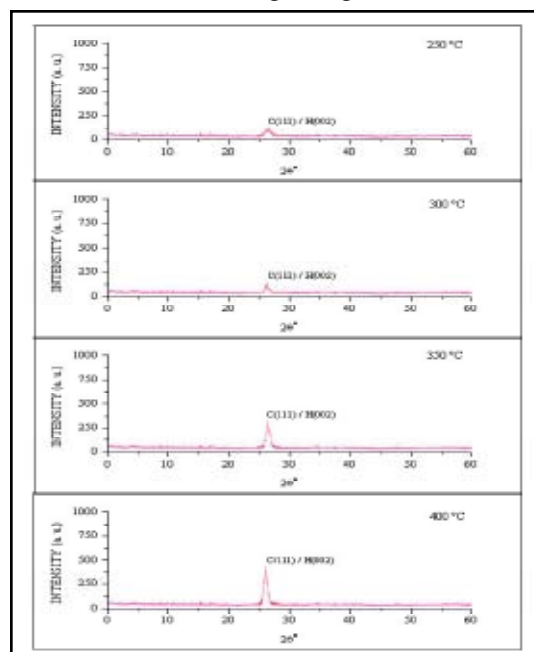


Fig. (1): XRD patterns of CBD CdS thin films annealed for 1 hr at different temperature for thin film 100 nm at temperature is  $80^\circ\text{C}$ , pH 11.5 and a deposition time of 20 minutes .

**Effect of Annealing temperature**

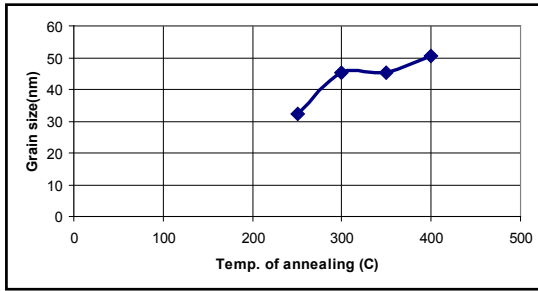


Fig. (2) Average grain size at different annealing temperatures.

In Figure (2) which illustrates the variation in average grain size at different annealing temperatures, it can be observed that as the annealing temperature increases the grains become bigger for CBD Cds thin films and that is a result of heat treatment. Further heat treatment enlarges the grain.

**Nonlinear refractive index**

In order to investigate the nonlinear refractive index, there are two cases were chosen at 1064 nm and at 532 nm ; case I in Figure. (3) shows the closed-aperture z-scan results at 1064 nm at different thickness at energy 100 mJ.

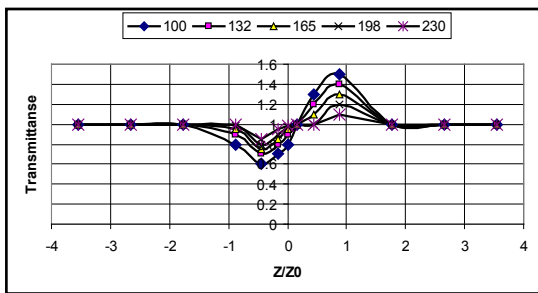


Fig. (3) : The closed-aperture z-scan results at 1064 nm at different thickness at energy 100 mJ

Case II, Fig. (4) shows the closed-aperture z-scan results at 532 nm at different thickness at energy 100 mJ

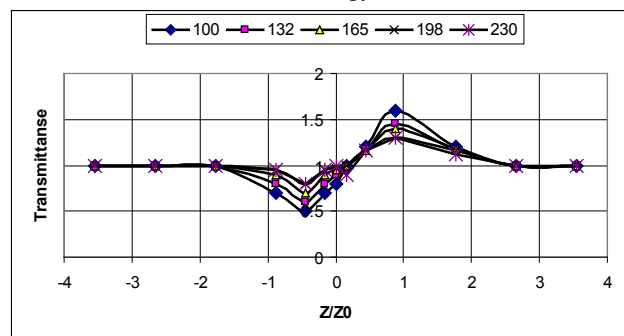


Fig. (4) The closed-aperture z-scan results at 532 nm at different thickness at energy 100 mJ

In all the closed-aperture curves, the maximum and minimum transmittance occurred at z equal to (5) mm and (-5) mm respectively.

The transmittance started with a linear behavior at different distances from the far field of the sample position (-z) with respect to the focal plane at z=0 mm. At the near field the transmittance begins to decrease until it reaches the minimum value ( $T_{valley}$ ) at approximately z=-5 mm. Afterward, the transmittance begins to

increase until it reaches the maximum value ( $T_{peak}$ ) at approximately z=10 mm. Again, the transmittance begins to decrease toward the linear behavior at the far field of the sample position (+z). The transmittance in the transmission direction is larger than the transmittance in the reflection direction with the same input energy.

The closed-aperture z-scan measures the change in transmittance of a beam, as the sample passes through the focal plane. The change in on-axis intensity is caused by self-focus or self-defocus by the sample as it travels through the beam waist. This modify refractive index distribution then acts like a focusing lens. Hence, when the sample approaches to the focal plane, it will focus the converging beam more tightly. In the far field, this increases beam divergence and is measured as a decrease in energy through the aperture. At the focal plane, the divergence of the beam is unaffected by the sample and the detector measures no change in transmittance. As it leaves the focal plane, the sample will focus the diverging beam. In the far field, this decreases beam divergence and is measured as an increase in power through the aperture.

The external self-focusing arising from the Kerr effect in CdS, which appears in the peak and valley transmittance of each of z-scan trace.

The nonlinear refractive index is directly proportional to the thickness, i.e. the small thickness reveals a larger nonlinear refractive index. The magnitude of  $n_2$  depends on the wavelength. In addition, the nonlinear refractive index was found to exhibit distinct behavior depending on the excitation pulse length. For short pulse length, at 532 nm, the magnitude of the nonlinear refractive index is independent of the pulse energy (Kerr nonlinearity); this property is more enhanced at 532 nm with the same results (but at less effect) at 1064 nm. In addition the sensitivity of the experiment to refractive nonlinearities is entirely due to the aperture. The removal of the aperture will make the z-scan sensitive to absorptive nonlinearities alone.

In all the closed-aperture curves, the peak to valley difference  $\Delta T$  is between (1.1) to (0.15) at the highest thickness. The maximum and minimum transmittance occurred at z equal to (10) mm and (-5) mm respectively.

The closed-aperture z-scan defines variable transmittance values, which is used to determine the nonlinear phase shift  $\Delta\Phi$  and the nonlinear refractive index. these results are explained in Table (1)

Table (1) : Nonlinear refractive index and nonlinear phase shift

| Thickness (nm) | $\lambda$ (nm) | $L_{eff} \times 10^{-9}$ | $T_{Peak}$ | $T_{Valley}$ | $\Delta\Phi$ | $\Delta T$ | $n_2 \text{ cm}^2/\text{GW}$ |
|----------------|----------------|--------------------------|------------|--------------|--------------|------------|------------------------------|
| 100            | 1064           | 26.653                   | 1.50       | 0.60         | 2.21         | 0.90       | 3.787                        |
| 132            | 1064           | 34.404                   | 1.40       | 0.70         | 1.72         | 0.70       | 2.279                        |
| 165            | 1064           | 44.033                   | 1.30       | 0.75         | 1.35         | 0.55       | 1.385                        |
| 198            | 1064           | 53.502                   | 1.20       | 0.80         | 0.98         | 0.40       | 0.834                        |
| 230            | 1064           | 63.055                   | 1.10       | 0.85         | 0.36         | 0.15       | 0.260                        |
| 100            | 532            | 29.576                   | 1.60       | 0.50         | 2.70         | 1.10       | 5.217                        |
| 132            | 532            | 41.117                   | 1.45       | 0.60         | 2.09         | 0.85       | 2.898                        |
| 165            | 532            | 44.285                   | 1.40       | 0.70         | 1.72         | 0.70       | 2.218                        |
| 198            | 532            | 53.849                   | 1.30       | 0.80         | 1.23         | 0.50       | 1.303                        |
| 230            | 532            | 63.945                   | 1.30       | 0.80         | 1.23         | 0.50       | 1.097                        |

As mentioned the increase in thickness lead to a decrease in  $n_2$ . This was attributed to the higher transmission in the transmission process, which leads to the higher nonlinear effect especially at

near the focal plane, due to the difference in the transmission ratio of the beam splitter.

The behavior of  $n_2$  to the different thickness can be concluded from Figure. (5) at different wavelength.

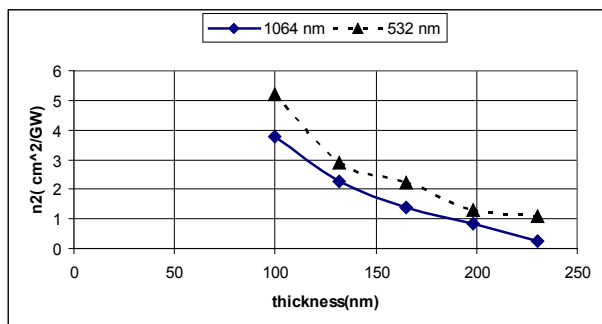


Fig. (5) : Variation of nonlinear refractive index with different thickness at 1064 nm and 532nm

The magnitude of  $n_2$  decrease as the coated film thickness of CdS. The same behavior can be observed at 532 nm, as shown in figure (5).

This variation may arise from such contributions as self-focusing of a sample. The nature of the nonlinear response can be inferred from its dependence on thickness,. Since, the CdS film exhibit a third order (Kerr) nonlinearity over the intensity range measured. The values of  $n_2$  for as a function of thickness, implies a dependence of the nonlinear refractive index on the input thickness.

### Nonlinear absorption coefficient

In order to investigate the nonlinear absorption coefficient, two wavelengths were considered 1064 nm and 532 nm .Figure (6) and (7) shows the respectively open-aperture Z-scan at 1064 nm and 532 nm at different thicknesses.

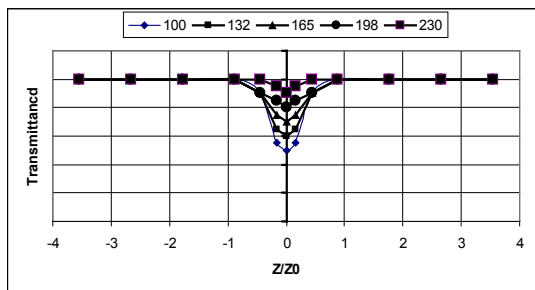


Fig. (6) : The open-aperture z-scan at 1064 nm different thickness

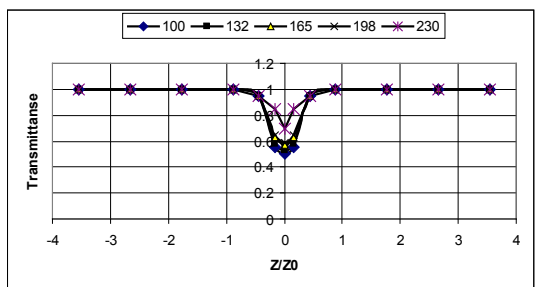


Fig. (7) : The open-aperture z-scan at 532 nm different thickness

The behavior of transmittance started linearly at a distance from the far field of the sample position (-z). At the near field the transmittance curve begins to decrease until it reaches the

minimum value ( $T_{min}$ ) at the focal point, where  $Z=0$  .Afterward, the transmittance begins to increase toward the linear behavior at the far field of the sample position (+z). In the open-aperture z-scan. The transmittance is sensitive to the nonlinear absorption as a function of different thicknesses. The change in intensity is caused by two-photon absorption in the sample as it travels through the beam waist. In the focal plane where the thickness is greatest, the largest nonlinear absorption is observed. At the far field of the Gaussian beam, where  $|z| \gg z_0$ , the beam intensity is too weak to elicit nonlinear effects. The higher order of the two-photon absorption present in the measurement depends on the wavelength of light and the different thickness of the sample. A symmetric valley is contributed to the positive nonlinear absorption coefficient  $\beta$ , indicating the two-photon absorption. The nonlinear absorption coefficient is inversely proportional to different thickness, again, the magnitude of  $\beta$  depends on the wavelength, but this dependence is not very strong at low intensity. While, at 1064 nm, the magnitude of  $\beta$  is independent of the intensity (two-photon absorption), this property is more enhanced at 532 nm. The open-aperture Z-scan defines variable transmittance values, which used to determine absorption coefficient. This is explained in Table (2).

The Table shows different values of  $\beta$ , which were determined by using equation (1-16). The value of  $\beta$  depends on the change of deposited film thickness, direction and the wavelengths used. i.e. the value of  $\beta$  is decreased as the thickness decreased. This behavior is more enhanced at 532 nm than for 1064 nm. This was attributed to the higher thickness in the transmission process. In addition, the nonlinear effect is more enhanced at 532 nm, which in turn leading to the increase in nonlinear effect at the focal point.

Table(2) Nonlinear absorption coefficients versus Intensity

| Thickness (nm) | $\lambda$ (nm) | $T_{min}$ | $\beta$ (cm <sup>-1</sup> /GW) |
|----------------|----------------|-----------|--------------------------------|
| 100            | 1064           | 0.50      | 6877                           |
| 132            | 1064           | 0.60      | 3785                           |
| 165            | 1064           | 0.70      | 1765                           |
| 198            | 1064           | 0.80      | 709                            |
| 230            | 1064           | 0.90      | 456                            |
| 100            | 532            | 0.50      | 15475                          |
| 132            | 532            | 0.53      | 7006                           |
| 165            | 532            | 0.57      | 3571                           |
| 198            | 532            | 0.59      | 1299                           |
| 230            | 532            | 0.70      | 873                            |

The same behavior can be observed at 532 nm, this can be shown in Fig. (8).

The variation of  $\beta$  is inversely proportional to the change of the deposited film of CdS thickness, the nonlinear absorption showed the intensity dependent. As the thickness increases there is a significant decreasing in the nonlinear coefficient. Since the CdS film exhibit the two-photon absorption as a function of the input intensity, this effect is greatly enhanced at high thickness for the two wavelengths.

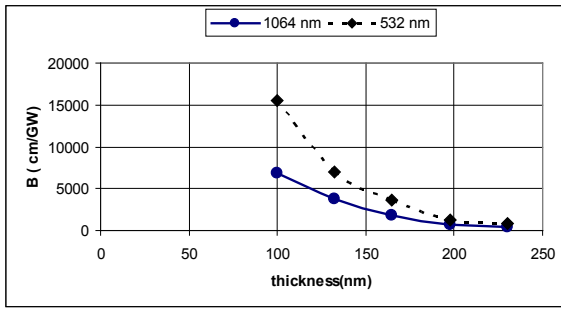


Fig. (8) : Variation of nonlinear absorption coefficient with different thickness at (1064 nm) and (532nm)  
 Effect of the incident Energy:

Figure (9) shows the change in surface roughness of CdS film with the incident energy, when energy increase the roughness of the surface will decrease, and that is attributed to the heating effect of laser beam on the surface of the CdS. Raising in temperature of surface leads to generate a surface tension associated with small melting giving the surface a non-uniform layer having a wavy shape. Using high value of power density with short period will lead to have ripples on the treated area and that will make the surface less rough.

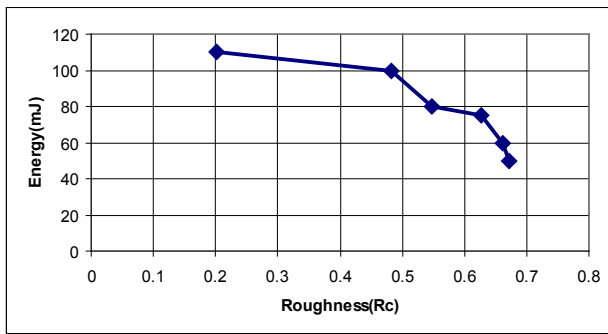


Fig. (9) : The change in surface roughness with the incident energy.

**Effect of thickness**

Figure (10) shows the relation between the roughness and the thickness. The roughness increases with the increase of thickness of the deposited film. This may related to grain size increase as the thickness of the film increase.

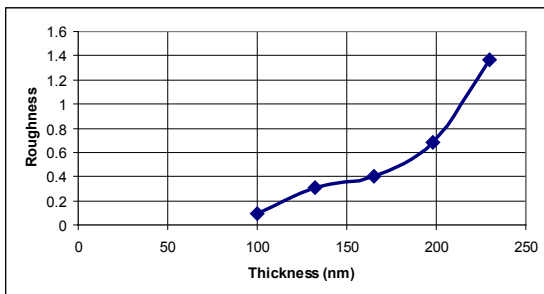


Fig. (10) : The change in surface roughness with energy  
 Effect of grain size

Figure (11) shows the effect of grain size change on roughness, the roughness increases as the grain size of the deposited thin film of CdS is increases. CdS reproduces morphology and roughness related to the sub layer underneath, which act as a seed for enhancing the CdS grain size. It has been proven that cadmium sulphide covers the layer underneath in a continuous and

homogeneous way, having a grain size dependent on substrate.

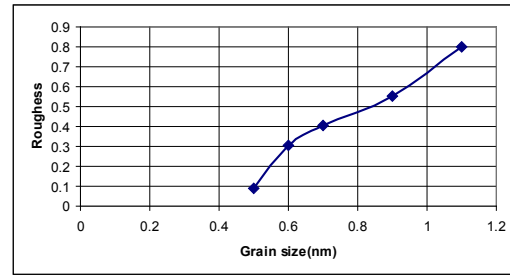


Fig. (11) : The change in surface roughness with grain size  
 Effect of annealing temperature

Figure (12) shows the effect of the annealing temperature on the roughness of the deposited film of CdS. The roughness increases as temp. increases.

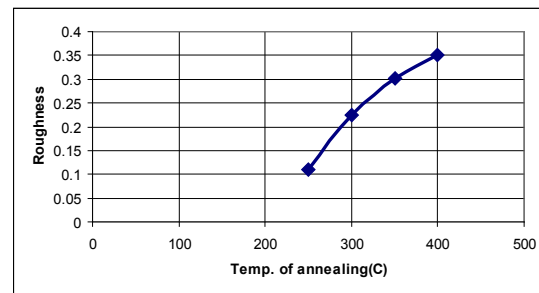


Fig. (12) : The change in surface roughness with temp. of annealing

**Conclusion**

Experimental results are summarized as follow:-  
 The optimum conditions for deposition of nanocrystalline CdS by CBD is T= 80 °C, pH=11.5, and t=20 min. The diffraction peak intensity increases with the thickness increase which in term increases the grain size and the crystal linity of the deposition of CdS films. Annealing increases the conductivity of the deposited film with the optimum annealing conditions at 300 °C for 60 min. It has been observed that the transmission of CdS thin films decreased as the film thickness increased. The absorption edge shifts towards the higher wavelength with the increase in film thickness. The nonlinear absorption coefficient is inversely proportional to the thickness. The nonlinear refractive index is directly proportional to the thickness. The nonlinear properties is more likely at the wavelength of 532 nm than at 1064 nm. The roughness of the surface decreases with incident energy increase. The roughness increase as the thickness of the deposited film increases. The grain size increases with roughness. The roughness increases with temp. of annealing increases.

**Acknowledgements**

This work has been carried out Institute of Laser for Postgraduate/ University of Baghdad/Baghdad, Iraq

**References**

[1] E. Bourgeat-Lami, "Organic-inorganic nanostructured colloids", *Journal of nanoscience and nanotechnology*, 2, 4 (2002).  
 [2] N. Venkatram, R. Kumar, D. Rao, S. Medda, S. De and G. De., *Journal of Nanoscience and Nanotechnology*, 6, 1-5 (2006).  
 [3] R. Ramanujan, *Sadhana*, 28, 81-96 (2003).

- [4] B. Han, E. Lavernia1 and F. Mohamed, *Journal of nanoscience and nanotechnology*, 9, 1-16 (2005).
- [5] Q. Yang, J. Seo, S. Creekmore, D. Temple, A. Mott, N. Min, K. Yoo, S. Kim, S. Jung, "Distortions in Z-scan spectroscopy," *Appl. Phys. Lett.*, 82, 19 (2003).
- [6]. Raied K. Jamall, Mohammed A. Hameed1, Wajehaa A. Zoba, "Study of Optical Properties (Linear and Nonlinear) and Structures for CdS Thin Film Preparation in Spray Pyrolysis Technique", *International Journal of Engineering and Innovative Technology (IJEIT) Volume 3, Issue 3, September 2013*
- [7] R Mishra, and A. Mukherjee, Oral presentation at TMS meeting, Indianapolis, Indiana, to be published in proceedings of Symp. "Mechanical Behavior of Bulk Nano-Materials." (1997).
- [8] A. Oliva, R. Castro-Rodriguez, O. Solis-Canto, V. Sosa, P. Quintana, J. L. Pena, *Applied Surface Science*, 205, 56-64 (2003).
- [9] G. Sasikala, P. Thilakan and C. Subramanian, *Solar Energy Materials & Solar Cells*, 62, 275-293 (2000).