Electronic Supplementary Information, ESI

For CrystEngComm

Full Paper:

X-Ray Studies: CO_2 pulsed laser annealing effects on crystallography, microstructure and crystal defects of vacuum deposited nanocrystalline ZnSe thin films

X-Ray Studies: CO_2 pulsed laser annealing effects on crystallography, microstructure and crystal defects of vacuum deposited nanocrystalline ZnSe thin films

By

Ahmed Saeed Hassanien[a,b,*,1], Alaa A. Akl[c,d]

a) Mathematics and Eng. Physics Dept., Faculty of Engineering (Shoubra), 11629, Benha University, Egypt.
b) Physics Department, Faculty of Education, Afif Governorate, Shaqra University, 11921, Saudi Arabia.
c) Physics Department, Faculty of Science, Minia University, El Minia, 111559, Egypt.
d) Physics Department, Faculty of Science and Humanities in Ad-Dawadmi, Shaqra University, 11911, KSA.

All the equations used to investigate and discuss the results obtained in this article (from equation 1 to equation 11), in addition to the graphs (from figure 3 to figure 9) which were plotted to illustrate the relationships between the different variables have been transferred to this section, according to the instructions of the Editorial Office

Electronic Supplementary Information, ESI

For CrystEngComm

Full Paper:

X-Ray Studies: CO_2 pulsed laser annealing effects on crystallography, microstructure and crystal defects of vacuum deposited nanocrystalline ZnSe thin films

First : The equations used in the article

- The lattice spacing or inter planar distance (d) can be calculated from Bragg's diffraction law, which is given as:

$$d = \frac{n\lambda}{2sin\,\theta}$$

(1)

- The lattice parameter (a) can be estimated in terms of the lattice planes or Miller indices (hkl) from the equation of the cubic structures [26]:

$$a = d(h^2 + k^2 + l^2)^{1/2} \quad \textbf{(2)}$$

- The observed integral breadth of X-ray diffraction line profile analysis (LPA-XRD) can be treated as a convolution of two parameters due to the instrumentation and the sample parameters. This convolution relation can be expressed as follows [29,30]:

$$F_{obs}(2\theta) = F_{ins}\,(2\theta)\ {}^{*}\ F_{pure}\,(2\theta) + background \quad \textbf{(3)}$$

Where (*) is a convolution operator, $F_{obs}(2\theta)$ is a function defines the observed broadening (B) and $F_{ins}(2\theta)$ is another function belongs to the instrumental or the standard sample broadening, (b), while $F_{pure}(2\theta)$ is a third function specifies the sample broadening (β). As obvious, these three operators are functions in the Bragg's diffraction angle, 2θ [17].

- The correction in the broadening profile of pure samples has been treated as a pseudo-function between the Cauchy-Lorentzian and Gaussian distribution, as follows [17]:

$$\beta = ((B - b)(B^2 - b^2)^{1/2})^{1/2} \quad \textbf{(4)}$$

- The value of the microstrain $<\varepsilon>$ can be calculated using the following formula [15,17]:

$$<\varepsilon> = \frac{\beta\cot ▯}{4} \quad \textbf{(5)}$$

- The values of crystallite size, D can be estimated by using the Scherrer formula, which is given by the following equation [25,29]:

$$D = \frac{k\lambda}{\beta\cos \theta} \quad \textbf{(6)}$$

Where D is the crystallite size perpendicular to the normal line of (hkl) plane, (k) is the shape factor that will be taken here equals to 0.94, λ is the wavelength of the used X-ray source. β is the corrected integral breadth method or full width at half maximum (FWHM) of the coherent domain along a direction normal to the peak and Θ is Bragg's diffraction angle in degrees. This equation can be successfully applied to solids, which has a crystallite size ranged between 2 and 300 nm [30-34].

- The interfacial free energy per unit area, S_a is related also to the bulk modulus of thin-film samples by the following equation [29,34]:

$$\frac{\Delta a}{a_o} = -\frac{4\,S_a}{3KD} \quad \textbf{(7)}$$

Where, D is the crystallite size, which means that it is the diameter of the crystallite that is considered to have a spherical shape. Hence, S_a can be determined by knowing the value of the estimated lattice strain, as follows [29]:

$$S_a = -\frac{3}{4}\left(\frac{\Delta a}{a_o}\right)KD \quad \textbf{(8)}$$

- The number of crystallites per unit area (N) of the polycrystalline thin films can be evaluated using the crystallite-size values, D from the relation [29,32]:

$$N = {}^{t}\!/_{D^3} \quad \textbf{(9)}$$

where (t) is the film thickness.

- The dislocation density, δ can be evaluated from the Williamson and Smallman's equation which is given as [33]:

$$\delta = \frac{1}{D^2} = \left(\frac{\beta\cos \theta}{k\lambda}\right)^2$$

(10)

X-Ray Studies: CO_2 pulsed laser annealing effects on crystallography, microstructure and crystal defects of vacuum deposited nanocrystalline ZnSe thin films

- The internal stresses, S of the nanocrystalline cubic crystal structure can be estimated from the following equation [17,29]:

$$S = \frac{E}{2\gamma}\left(\frac{a - a_0}{a_o}\right) = \frac{E}{2\gamma}\left(\frac{\Delta a}{a_o}\right) \quad \textbf{(11)}$$

Second: The supporting graphical representations

X-Ray Studies: CO_2 pulsed laser annealing effects on crystallography, microstructure and crystal defects of vacuum deposited nanocrystalline ZnSe thin films

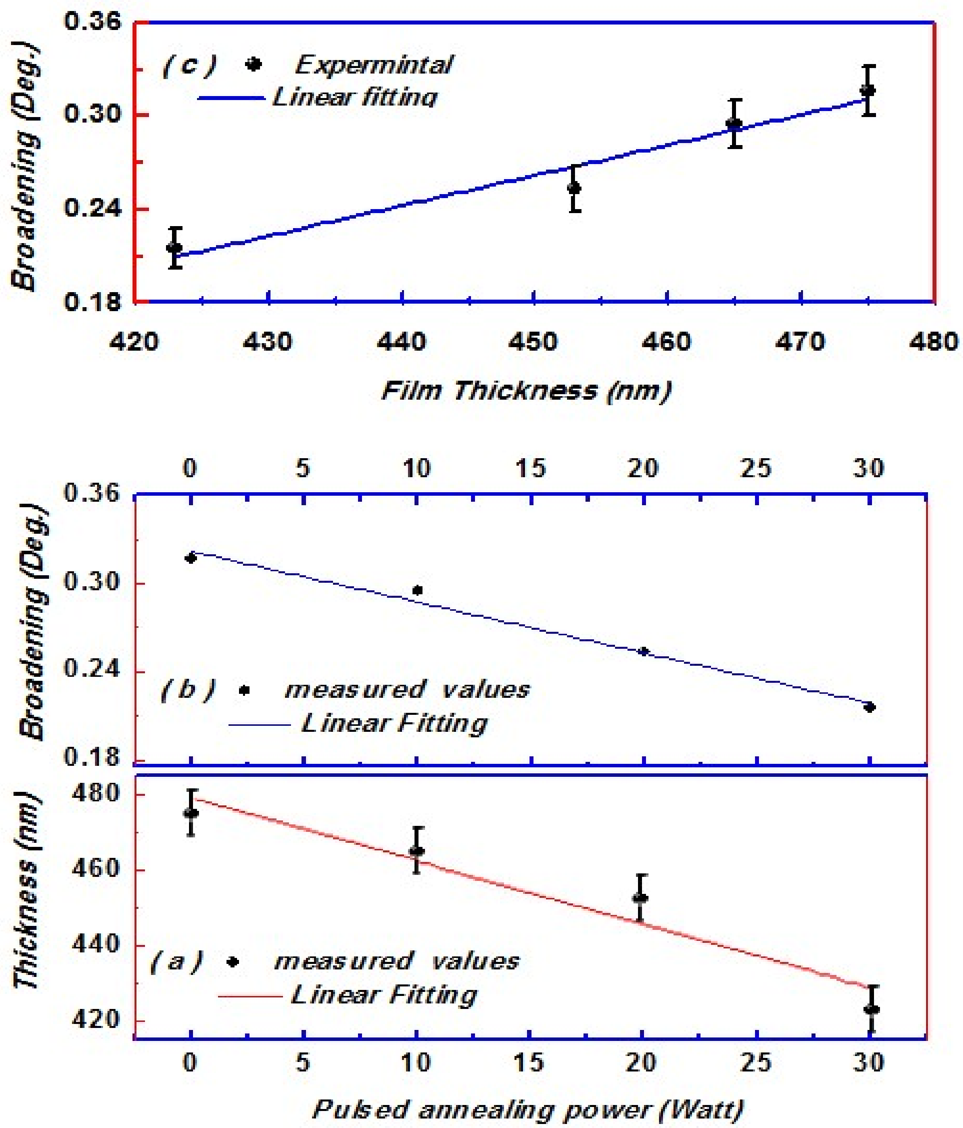

Fig. (3): *Representation of the film thickness (nm) and broadening (in Degrees) as functions of Co_2 pulsed annealing power as illustrated in Figs. (3a and 3b); and in Fig. (3c) the relation between the film thickness and the broadening.*

X-Ray Studies: CO_2 pulsed laser annealing effects on crystallography, microstructure and crystal defects of vacuum deposited nanocrystalline ZnSe thin films

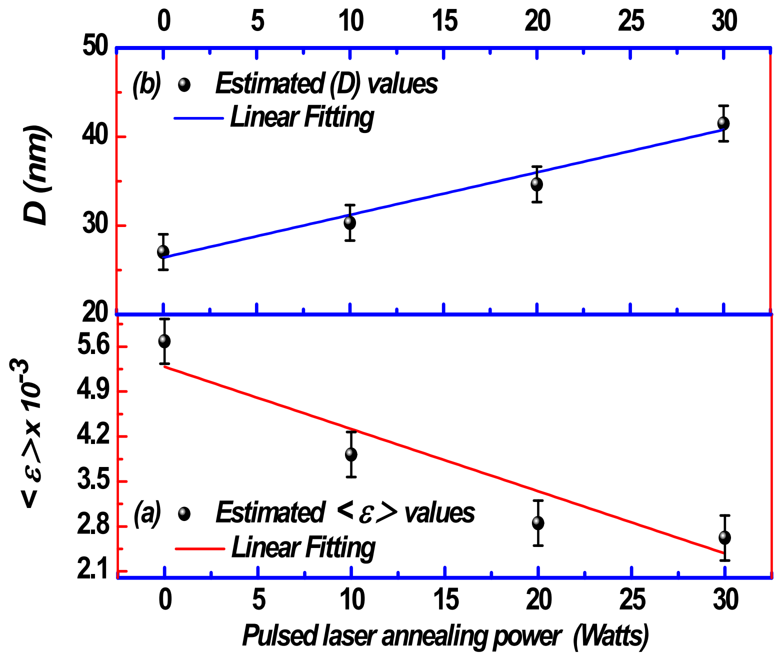

Fig. (4): *Dependence of the average microstrain <ε> and the average crystallite size, D (nm) upon the CO_2 pulsed laser annealing power of the nanocrystalline ZnSe thin films.*

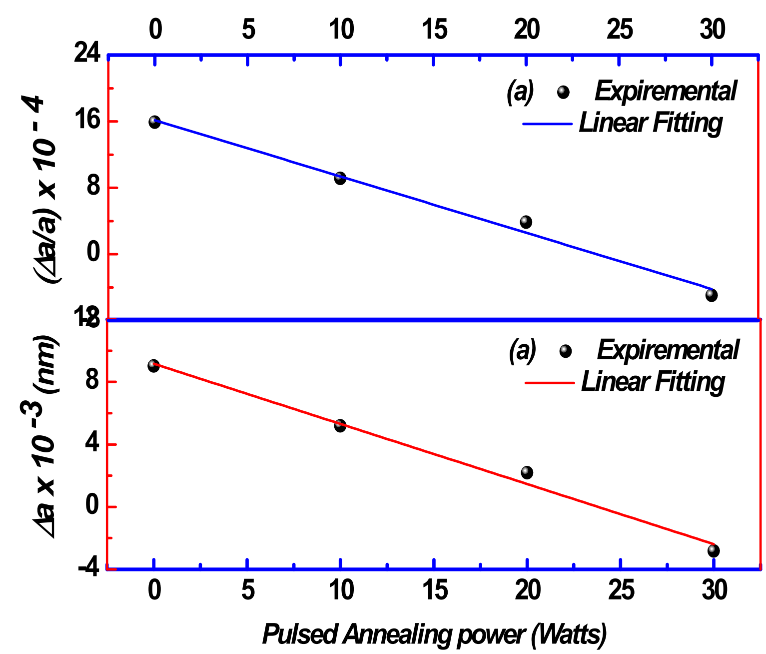

Fig. (5): *Linear variation of the change in the lattice parameter (Δa) the lattice microstrain (Δa/a) with the applied pulsed laser annealing power on the nanocrystalline ZnSe thin films.*

X-Ray Studies: CO_2 pulsed laser annealing effects on crystallography, microstructure and crystal defects of vacuum deposited nanocrystalline ZnSe thin films

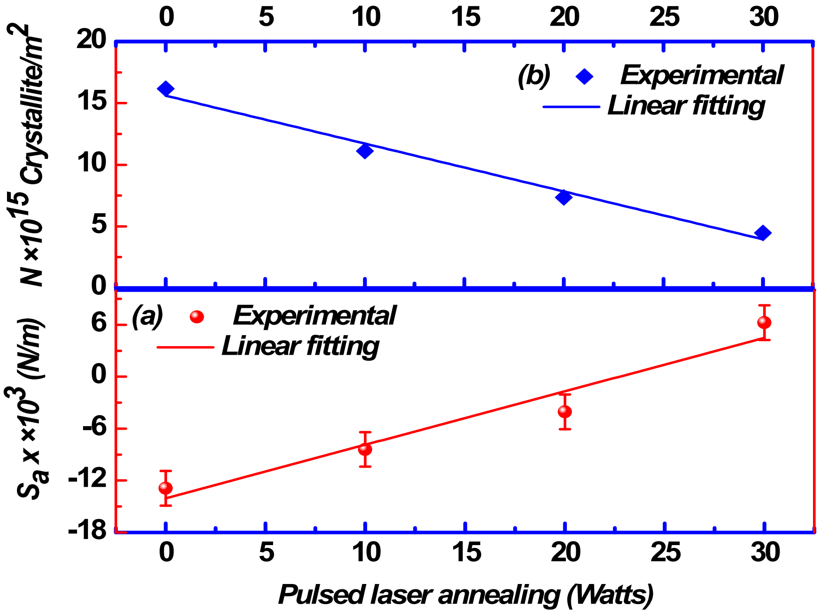

Fig. (6): *Representation of the change in the interfacial free energy per unit area (S_a) and the average number of crystallite per unit volume (N) with the pulsed laser annealing power.*

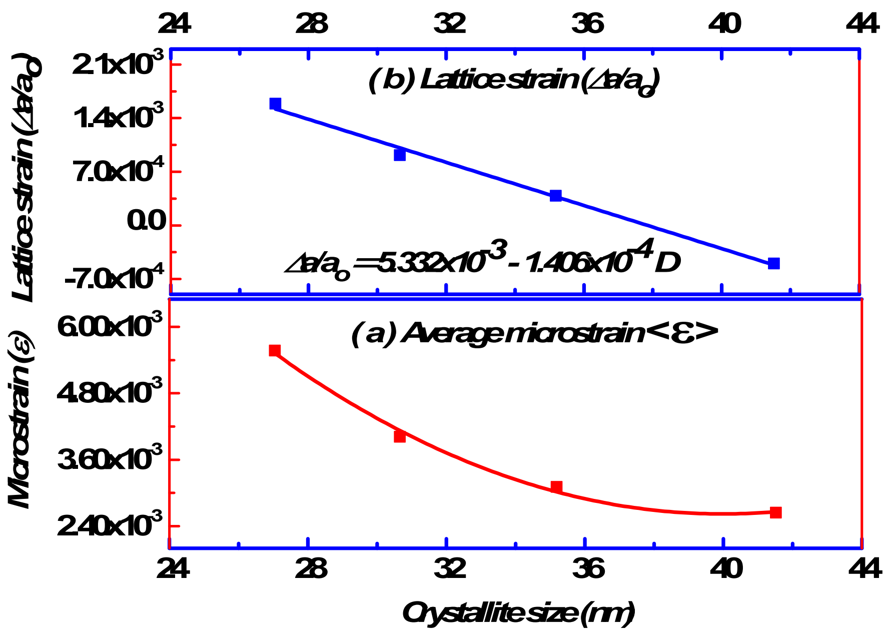

Fig. (7): *The dependence of (a) the average microstrain and (b) the lattice strain upon the crystallite size, D of ZnSe nanocrystalline thin films.*

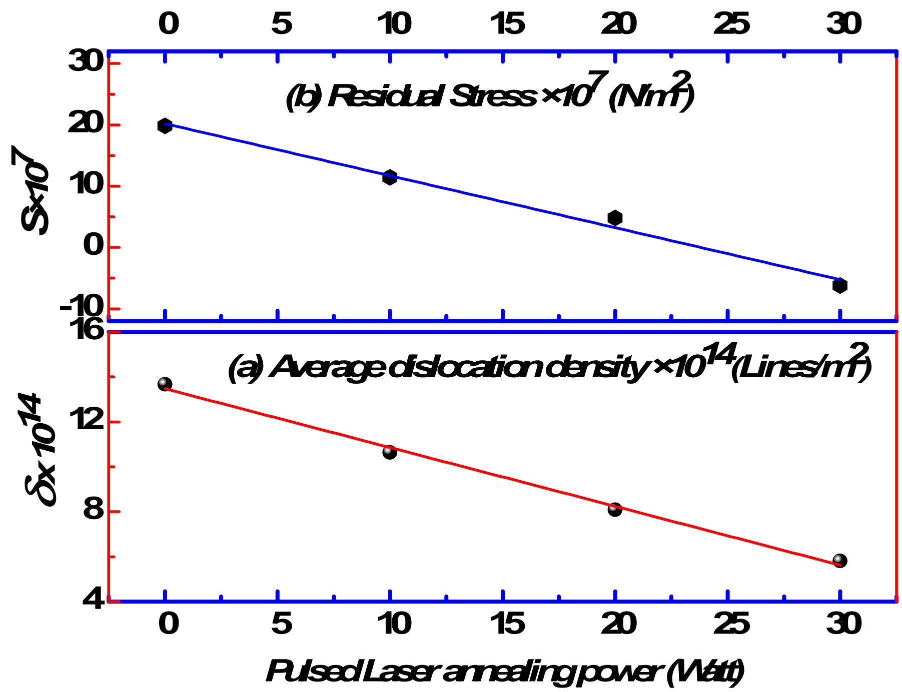

Fig. (8): *Linear dependence of: (a) the dislocation density (δ) and (b) the internal stress (S) upon the pulsed laser annealing power ($30 \geq X \geq 0$) for nanocrystalline ZnSe films.*

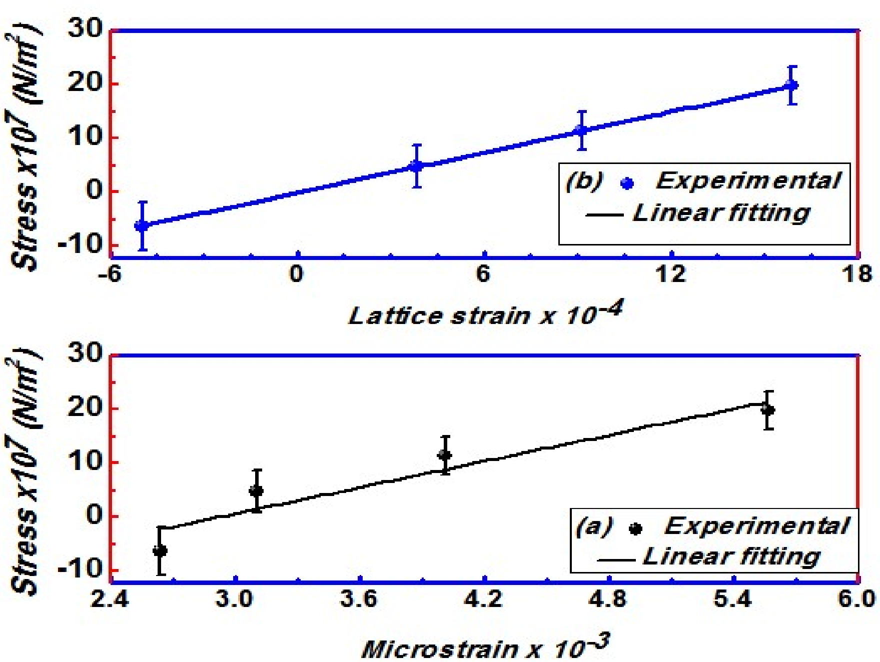

Fig. (9): *Variation of: (a) the microstrain, <ε>, and (b) lattice strain, Δa/ao with the internal stresses, S for nanocrystalline ZnSe thin films.*