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Evaluation of energy band gap of porous silicon using Newton-Raphson method

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Abstract

Silicon thin films have been prepared on sapphire substrate using pulsed laser deposition (PLD) technique. The films were deposited in vacuum from a silicon target at a base pressure of 10^{-4} mbar within energy range from 400 to 800 mJ. A Q-switched Nd:YAG laser of wavelength 1064 nm and 5 ns duration, 10 Hz) keeping the number of pulses fixed to 10 pulses has been used. The influences of the laser energy on the structural, morphological and optical properties of the Si thin films were investigated. Structural investigation was carried out using x-ray diffraction. Result shows, that film grown have a amorphous structure; the deposition parameters strongly affect the film surface topography film.

Keywords: Nanoparticles, Optical properties laser ablation, Laser deposition.
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1. Introduction

Silicon nanostructures have attracted much attention for their possible applications in optoelectronics [1]. Nanocrystalline silicon (nc-Si) consists of an aggregate of crystallites with sizes of the order of a few nanometers embedded in an amorphous matrix. Thin film solar cells with nc-Si layers incorporated showed high stability and conversion efficiencies. Thin film transistors (TFTs) with nc-Si as the active layer exhibited higher performance, higher electron mobility and increased threshold voltage stability [2,3]. Another advantage is the low cost of fabrication, since thin films of nc-Si can be deposited directly over large-area substrates. Silicon thin films can be grown by various deposition techniques, including sputtering, hot-wire chemical vapor deposition (HW-CVD), and molecular beam epitaxy (MBE) methods [5-7]. Among them, the pulsed laser deposition (PLD) method is found to be an excellent choice [8,9]. PLD is a convenient technique for depositing high quality nanostructured thin films of several technological relevant materials; it offers the advantage of tuned ion kinetic energy and ion flux density parameters of the deposition species, simply by changing the laser parameters. The use of toxic gases can be avoided, reducing safety issues during deposition [10-12]. In this paper we report on the structural, morphological

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and optical properties of nanocrystalline silicon thin films prepared by pulsed laser deposition method at a laser energy between 400 and 800 °C.

2. Experimental Work

Crystalline Silicon substrates, n-type Si (phosphorus doped) with resistivity of (1.5-4 Ω-m) and (111) orientation. The silicon wafer has (111) orientation with dimensions of (1x1) cm^2 to select various interaction areas with an Nd:YAG pulsed laser were used for laser ablation (LA) technique. Q-Switched Nd:YAG laser system (Huafei Co.) of a 1.06 µm wavelength, (1000 mJ) maximum power output and (9 ns) pulse duration has been used. The substrate used for deposition of silicon nanoparticales is borosilicate (BK-7) glass slides.

The deposition process was carried out under 5×10^{-5} torr at room temperature. The pulsed laser was focused on a rotating target to minimize a pit formation using lenses mounted inside the vacuum chamber. The target mount was fixed at optimum angle of 45° with the incident laser pulse to reduce the interaction between the laser beam and evaporating materials and to ensure that the maximum of the ejected materials reach's the substrate. Silicon nanoparticales films were deposited on glass substrate under various preparation parameters such as number of pulses and laser energy.

The phases present in the as-deposited films were analyzed by x-ray diffraction in conventional *θ–2θ* configuration.

The optical transmission and absorption of silicon nanostructured film deposited on glass substrate was examined by *CECILE CE-7200* spectrophotometer within the wavelength range (150-1100) nm. The glass substrate was used as a reference sample in the direction of the reference beam to prevent the effect of the reference sample during the measuring process. The estimated data from the transmission spectrum was used to determine the optical band gap graphically of samples prepared under different preparation conditions using the following equation [13, 14]:

$$\alpha \equiv \frac{1}{d} \ln \frac{1}{T} \tag{1}$$

where d and T are the thickness and transmission to the nanostructure films.

3. Result and Discussion

The silicon films thickness deposited by pulse laser ablation (PLD) has been measured optically. Fig. 1 illustrates the effect of the incident laser energies and the number of laser pulses on the film thickness prepared by PLD. A deposited film thickness as a function of laser energy (300-600 mJ) with constant number of pulses (10) pulses. Increasing laser energy leads to increase in the amount of absorbed energy from the silicon atoms and subsequently increase the number of ejected particles from the target have higher kinetic energy leading to increasing the number of particles reaching the substrate causing increase in the film thickness. This could be attributed to decrease in the laser power density due to removal of the ejected target material and change in the target surface. Schottky contacts were made on (100) polished surface of non-intentionally doped n and p-type GaAs ($N_D, N_A \cong 2\cdot10^{16}\,cm^{-3}$). The ohmicity of back contacts was checked before each experiment.

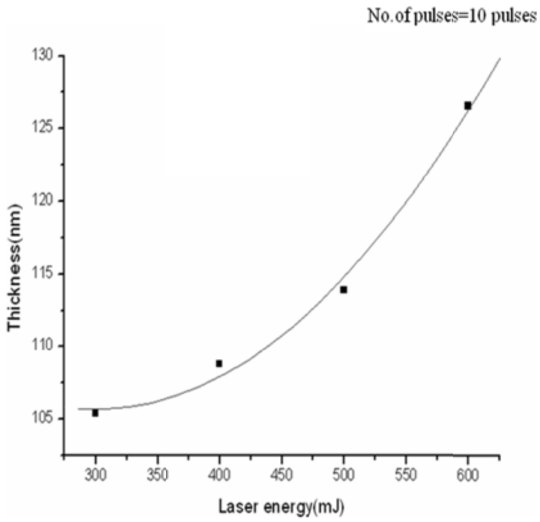

Fig. 1: Thickness of samples prepared by LA versus laser energies.

To study the crystallinity of silicon nanostructure films, samples were analyzed by XRD as shows in Fig. 2 of Si films deposited by PLD under different laser energies and with constant number of pulses. It is observed that the large broad background related to the nanoparticles sizes indicates the degree of crystallinity of deposited films is amorphous silicon, and this figure does not show any peaks and we conclude that individual Si nanoparticles are amorphous. It was found that the broad peak was positioned at the scattering angle (25.5°) when the laser energy of (300 mJ) was used and the estimated nanoparticles size was (4.1 nm).This peak shifts towards a smaller scattering angle (21.5°) and becomes broader for higher laser energy (800 mJ), where the nanoparticle size was found to be (3.12 nm). This may be due to the formation of a smaller particles size at higher energy. Further, Fig. 2 shows that the peak intensities increases with increase the laser energy .which may be due to amount of small silicon particles in the deposited film for high laser energy.

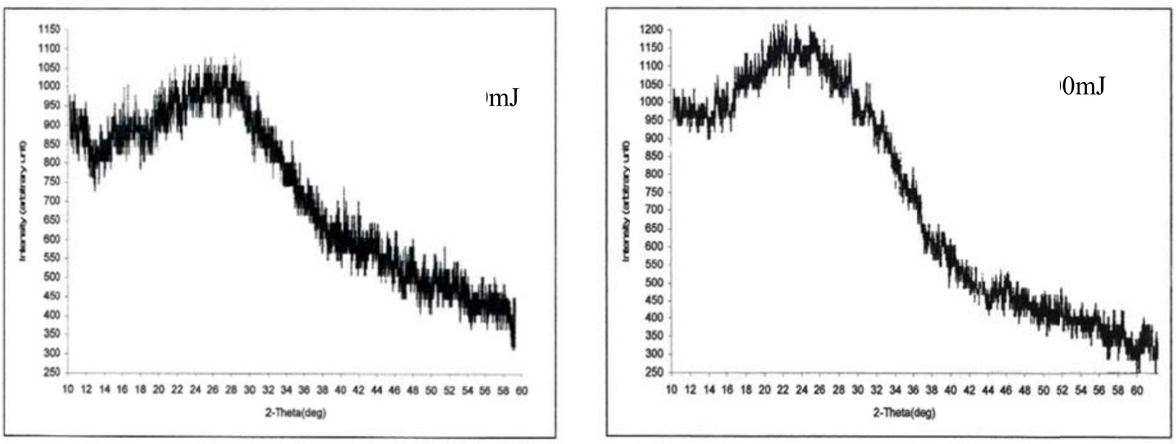

Fig. 2: X-Ray diffraction of Si nanoparticles films prepared by PLD at laser energy. 300 mJ & 800 mJ.

The optical transmission of prepared films depends on the surface morphology of these films and the degree of crystalline structure. Fig. 3 illustrate the effect of preparation parameters on the transmission spectra. The transmission of the deposited film was examined in the ultraviolet and near infrared (UV-NIR) spectral region. It was found that all films prepared by this technique have high transmission at longer wavelengths.

Fig. 3 shows the optical transmission of the silicon nanostructures films prepared under different laser energy (300-600 mJ) with constant number of pulse (10) pulses. It is the exponentially depend of transmission versus wavelength. Also, it is obvious from this figure that the transmission curves decreases with increasing laser energy of the incident pulsed laser for certain wavelength. When the laser energy increases, high amount of energy will absorbed from the atoms of target and this leads to increase the amount of ejected particles from the surface substrates these particles have high energy and lead to increases the particles deposited on substrate.

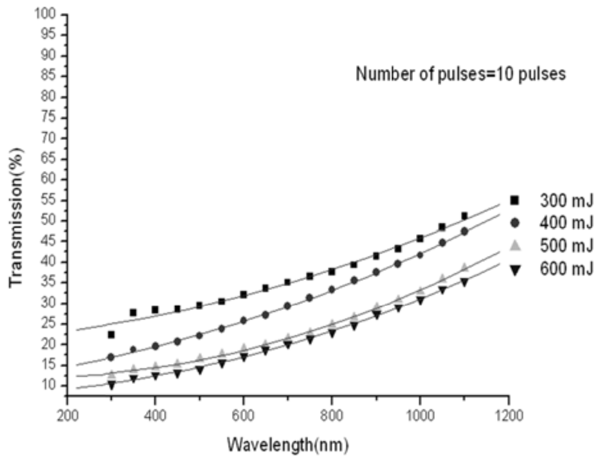

Fig. 3: The effect of preparation parameters on the transmission spectra for different laser energy.

Fig. 4 illustrates the effect each of the laser energy and number of pulses on absorption coefficient, were the samples prepared by laser ablation technique. This figure explains the relation between the photon energy with absorption coefficient of prepared samples. It is obvious that the laser energy will be increasing the absorption coefficient. The laser energy plays a significant role in the laser-target interaction. This interaction produces an ejected materials of two states; molten and vaporized material. The ratio of these states depends completely on the laser energy. Big amount of vaporized material is obtained at higher laser energy. Therefore, one could expect that higher laser energy produces small particles of higher kinetic energy which enable the particles to reach and deposited on the substrate and this will lead to increases film thickness and consequently increases the absorption coefficient.

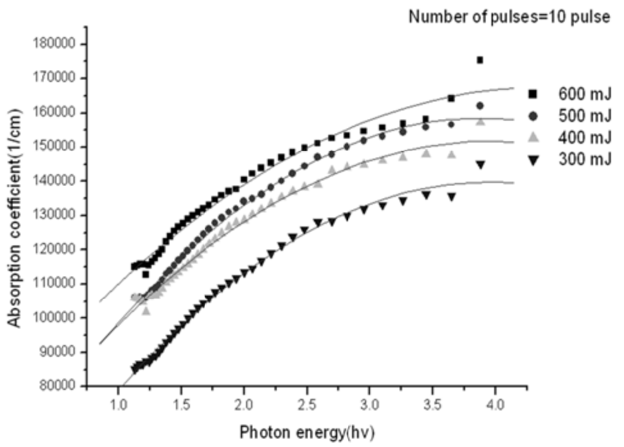

Fig. 4: Effect of preparation parameters on the absorption coefficient for different laser energy.

In order to réalise the electrical and optical specifications of the silicon nanostructures prepared films. It is very important to study and calculate the value of the energy band gap of these samples. This value depends on the arrangement and distribution of atoms in the crystal lattice and the structure of the prepared film. The energy band gap estimated in this work by two methods; Traditional method by extrapolation of the straight line of the plot $(\alpha h\upsilon)^2$ versus $(h\upsilon)$. The optical band gap (Eg) represents the value of intersection point between the straight line and photon energy axis and the second method by Newton-Raphson method [15, 16].

The analysis of using this method were summarized as follows:

<u>*Step 1*</u> Using a graphing utility to generate the behavior of experimental data pairs $(\alpha h\upsilon)^2$ *vs.* $(h\upsilon)$ (for sample prepared with laser energy=400 mJ and number of pulse=10 pulses).This behavior may be represented in terms of *xy*-plane abbreviation, i.e. $y=f(x)$. Then taking advantage of any general knowledge one have about the function to help in choosing the window.

<u>*Step 2*</u> Finding the "best fitting" or "good fitting" equation. This may be down with the aid of Matlab or Sigma-plot software package .It is found to be cubic equation yield "best" fitting to experimental data pairs $(\alpha h\upsilon)^2$ and $(h\upsilon)$:

$$y = y_0 + ax + bx^2 + cx^3 \qquad \text{Cubic equation:}$$

where,
y_0=-7.057*10^{11}, a=8.807*10^{11},
b=-3.499*10^{11} , c=0.4929*10^{11}

<u>*Step 3*</u> Finding the "roots", if needed. This may be done using 'Matlab' or 'advantage plus ^{TM} ' software .

<u>*Step 4*</u> Calculating first and second derivatives of $y=f(x)$ for the cubic equation, this may be done 'analytically' or 'numerically'.

<u>*Step 5*</u> Finding the 'intercepts', using "Advantage plus ^{TM} "software.

Table 1: Shows the finding point of intercepts results from software.

Functions	Point of intercept	Decimal places of accuracy	Number of iterations
f(x) and f ' (x)	(2.1452,0.5996) (3.0745,1.2712)	8	4
f (x) and f ''(x)	(2.668,0.895)	4	2
f '(x) and f ''(x)	(2.564,0.585)	4	2

Newton-Raphson method:

Usually this numerical method used for solving nonlinear algebraic equations. Here, we adapted the basic idea of this method:

- When the real root x_1 is known, then one may easily compute the functional $f(x_1)$. Drawing a line tangent to the curve at point x_1 , then the tangent line intersect the x-axis at a point , say x_2 , which play a significant important in evaluating Eg values.
- Evaluating intersection point of tangent line with x-axis:

$$x_{K+1} = x_K - \frac{f(x_K)}{f'(x_K)} \tag{2}$$

Where,

x_{k+1} = approximate root after $k+1$ iterations.
x_k = approximate root after k iterations.
$f(x_k)$ = functional value at x_k.
$f'(x_k)$ = first derivative value of the functional at x_k.
k = *1,2,3,……*

As a result, intersection points gives a range of Eg values due to the cases

a. *f(x)* and *f '(x)*
[3.5375, 2.8653, 1.6453, 1.1454, ….]
b. *f(x)* and *f ''(x)*
[3.5375, 1.754, 1.6658 , 1.0258, ….]
c. *f '(x)* and *f ''(x)*
[3.965, 3.0439, 1.5632, …….]

The *average value* of Eg = 1.6248 eV, this gives an indication that this method still gives an approximated Eg value.

Using the two methods to find the optical band gap energy. Fig. 5 shows the effect of different laser energies on the optical band gap of the silicon nanostructure films, It was found that the optical band gap energy is highly affected by the incident laser energy. When low laser energy (300) mJ is employed, low number of large size silicon nanoparticales were ablated from the target and the estimated band gap energy was (1.6 eV, 1.53 eV) as shown in Fig. 5a. Increasing the incident laser energy to (400) mJ leads to increase the laser power density and this leads to increase the number of small size nanoparticles ejected from target and reaching the substrate surface, therefore the optical band gap increases. This band gap reaches (1.7 eV, 1.625 eV) as shown in Fig. 5b. By increasing the incident laser energy Fig. 5c & d, this means we will gain a high number of small size silicon nanoparticles rather than large size nanoparticles and this will leads to increases the value of optical band gap energy and reaches (1.9 eV, 1.78 eV) at higher energy. The observed shift in the band-edge can be attributed to the decreasing in the particles size according to the quantum confinement effect. According to the quantum confinement two process will happen; the first change the nature of band gap (change from indirect to quasi direct), and the second enlarge in the band gap.

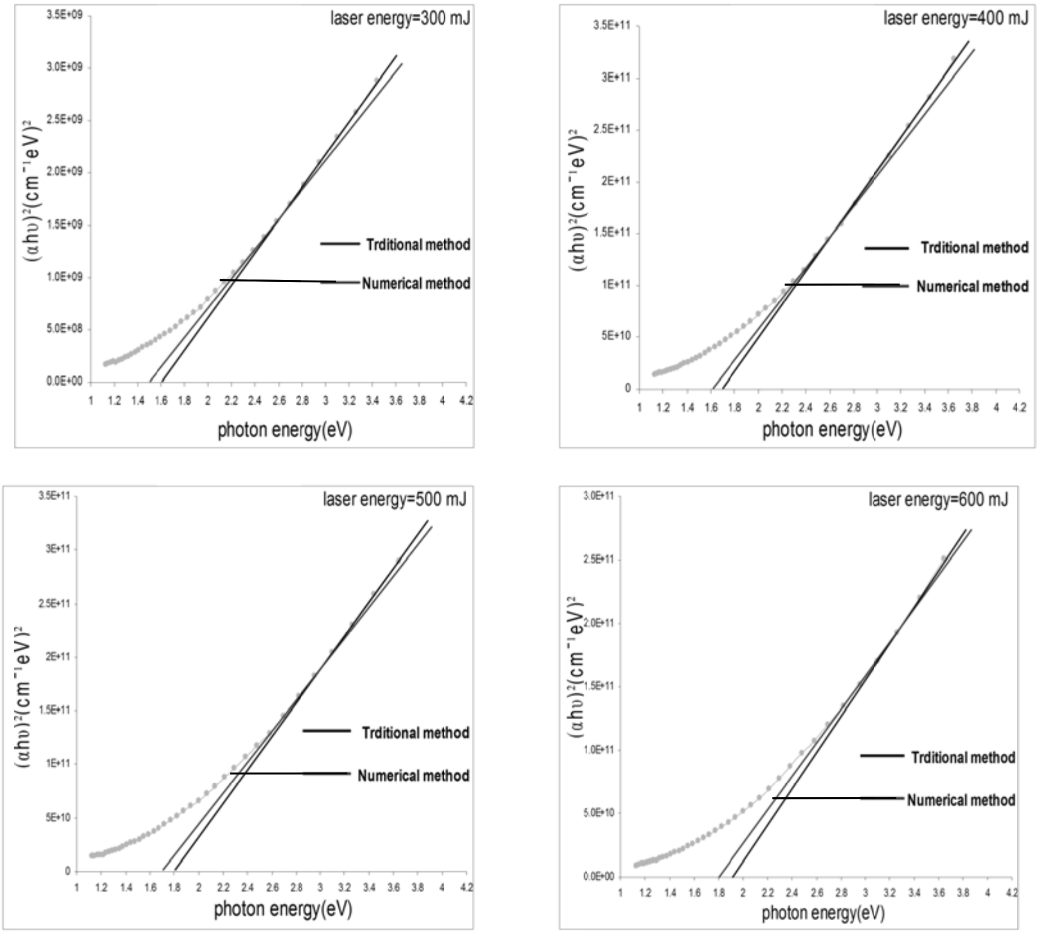

Fig. 5: Optical band gap to the samples prepared under different laser energies.

4. Conclusions

Silicon samples constituting silicon nanostructure was produced by LA technique. This technique is considered as an excellent technique to fabricate silicon nanoparticles due to the following features: good thickness, size and structural control. A surface morphology of nanosilicon films produced by laser ablation reveals that small particles are placed at the substrate edge while large particles are located at the film center. It is found that numerical analysis (Newton-Raphson method) for the optical properties give an accurate and good estimation for the band gap energy. The film transmission decreases with increasing the laser energy while the absorption increased with increasing the laser energy. It is also found that the band gap increases with increasing the laser energy duo to size reduction according to the quantum confinement effect. X-ray diffraction for the films prepared by LA show that the grain size decreases with increasing the laser energy and the film structure becomes amorphous.

References

[1] R. Ayouchi, R. Schwarz, L. Melo, R. Ramalho, E. Alves, C. Marques, L. Santos, R. Almeida, O. Conde, Applied Surface Science, **255** (2009) 5299
[2] R. Adziszewsk, S. Kac, M. Feuerbacher, Acta Physics Polonica, **117** (2010) 799
[3] C. Cohen: (Ph.D.) Thesis, Dep. Phys. Concentrator, College of William & Mary (2000)
[4] P. Willmott, J. Huber, Reviews of Modern Physics, **72** (2000) 1402
[5] S. Sinha, B. Gao, O. Zhou, Journal of Nanoscience, **6** (2004) 421
[6] T. E. Itina, M. Sentis, W. Marine, Applied Surface Science, **252** (2006) 4433
[7] W. Thomas Nichols: (Ph.D.) Thesis, Dep. Phys., University of Texas at Austin (2002)
[8] H. Chen, C. Jia, X. Zhang, W. F. Zhang, Vacuum, **85** (2010) 193
[9] T. Seto, T. Orii, M. Hirasawa, N. Aya, Thin Solid Films, **437** (2003) 230
[10] L. M. Kukreja, B. N. Singh, P. Misra, P. O. CAT, Indore, INDIA (2006)
[11] E. T. Salem: (Ph.D.) Thesis, Dep. of Applied Physics, University of Technology, (2006)
[12] M. Oszwaldowski, T. Berus, J. Rzeszutek, J.Alloys, compunds, **78** (2004) 6823
[13] R. A. Swady, Int. J. Namoelectronics and Materials, **4** (2011) 59
[14] B. Bendjemil, Int. J. Namoelectronics and Materials, **2** (2009) 173
[15] L. V. Zhigilei, A. M. Dongare Tech. Science Press CMES, **3** (2004) 539
[16] N. F. Habubi, K. A. Mishjil, H. G. Rashid, B. G. Rasheed, IJAP Lett., **1** (2008) 21