Improve the Performance of Porous Silicon for solar application by the embedding of Lithium Oxide nanoparticle

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Abstract. The present research concerns the manufacture of porous silicon (PSi) by means of electrochemical etching method at (10 mA.cm⁻²) current density and approximately 10 minute etching time. The porous silicone layer was investigated by XRD, AFM and FTIR, and then Li₂O nanoparticles (NPs) were prepared by a simple chemical method. And freshly embedding three drops of (Li₂O) solution using the drop casting technique on the 40⁰C porous silicon (n-Psi) method to produce the heterojunction Al / Li₂O / PSi / Al. The results of current-voltage (I-V) test showed that the solar cell’s maximum power conversion efficiency (PCE) was 2.49% and thus the fill factor was 66.12%. A diffusion of Li₂O NPs on PSi solar cell characteristics assures an improvement on their properties.

Keywords: Porous silicon, Li₂O NPs, Electrochemical etching, XRD, solar cell.

1. Introduction: Since the 1950s, Uhlir and Turner have recognized the formation of porous silicon in an anodizing setting as pioneering work at Bell Labs[1, 2]. But it took more than 30 years to invent an electrochemical drilling process by Lyman and Bean to produce arrays of large pores arranged in silicone[3]. Other groups followed, and this new subject was developed in materials science as an significant field. The silicone pattern thus covers several times in size the “growth” of the pores in the silicon. Structures with pores below a small nanometer are considered nanometers, according to the IUPAC nomenclature for porous materials[4]. Its formation must be mechanically described by quantum[5]. Medium structures range between 2 and 50 nanometres. The bigger follicle is termed the big follicle. The pore morphology obtained depends on the properties of silicon (stimulants, resistance, orientation), electrolyte composition (organic, organic and concentration), and external parameters such as temperature, voltage, and lighting. Besides several review articles that can be found in the literature (for example [6-8]). Large structures etched into an aqueous solution of hydrofluoric acid (HF) allow us to specifically design sample parameters among the different methods of making porous silicone. This method developed an understandable and applicable instrument for the manufacture of devices and molds. One important feature is the possibility of producing arranged pore arrays of
specific diameters and lengths. The diameters of Pore can be varied between several hundred nanometers and the several micrometres. Curiously, a few hundred micrometers deep may be digged to the pores. So you can get the dimensions of 500:1 and more without loss Pore structure and form. The basic mechanisms for creating large pores in silicone will then be discussed more in detail below, this objective of this work is to prepare a PSI, thus it is included by Li$_2$O NP to improve the porous silicone porous cell’s efficiency.

2. Experimental work

2.1. Fabricate of porous silicon

Electrochemical etching was used to produce porous silicon(n-PSi) that used a silicon wafer substratum with an electrolyte Teflon cell that contains about 43 percent(HF) acid and 99.9 percent pure ethanol with volume 1:1, as seen in Figure 1. The sample made from monocrystalline silicone was treated with a 10 Ω.cm resistance and direction (100) direction. The chemical treatment for n-Psi was to generate a guard using current 10 mA.cm$^{-2}$ at 10 minutes, and then the wafer’s back side was deposited at 10$^{-5}$ Torr vacuum around (200μm) thick aluminum back contact.

![Fig. 1: Electrochemical etching set-up scheme diagrams.](image)

2.2. Prepare of Li$_2$O nanoparticles by simple chemical method

Li$_2$O NPs has been produced by a method of chemical precipitation. A standard procedure dissolved 0.6 grams of Lithium Powder (MART India) in 100 ml volumetric flask. The solution was applied with a stirring into a round-bottom glass bottle. The mixture was white in colour. Lithium oxide (Li$_2$O) depositing on the glass substrate using a drop-casting process, seen Figure (2). The solution of (Li$_2$O) was deposited at 40 ° c on pre - heated transparent conductive porous silicon(n-type) by the same method, time sintering time is 1 minute. The thin film thickness was calculated by weight method for the lithium oxide, and the thin film thickness would be about (250 nm).

2.3. Fabricate of Al/Li$_2$O/PSi/n-Si/Al Heterojunction
Drop-casting deposited Li$_2$O's precursor solution was impregnated with hot substrate porous silicon (n-type) at 40 °c as Three drops to produce an Al / Li$_2$O / PSi / Si / Al heterojunction for solar cells, a hot substrate was left to cold at room temperature. And place foil Al with area 0.1 cm$^2$ as electrodes on the layer Li$_2$O / PSi / n-Si, as can be seen in Figure 2.

Fig. 2: The basic structure of typical Al/Li$_2$O/PSi/n-Si/Al heterojunction

3.The Results

3.1. XRD measurement

The X-ray diffraction patterns for the synthesized's crystalline nature (n-PSi and Li$_2$O) are illustrated through Figure(3). By comparison with JCPDS No. 74-6256, it can be noted from this figure that the XRD patterns match the Li$_2$O powders value. All diffraction peaks of prepared thin film exhibit Rhombohedral structure, and the Li2O thin film structure has a secondary phase. This peak is assigned by (♦) in figure(1a). This diffraction peak attributed to Li$_2$O$_2$ phase by comparison with JCPDS No. 73-1640. The phase (♦) has been hexagonal structure. The average crystallite size for the film is calculated by Scherrer's formula by using the Eq.(1)[9].Where (D) is the crystallite size, (λ) is the wavelength (1.5406Å) of X-ray, (θ) is the diffraction angle, and (β) is the full width at half maximum (FWHM). The crystallite size of (n-PSi and Li$_2$O) indicates that the size of the prepared samples would be within the nanoscale as seen in Table(1). The micro strain value(η) and also the dislocation density(δ) have been determined from Eq(2,3):

$$D = \frac{0.9\lambda}{\beta \cos(\theta)}$$

(1)

$$\eta = \frac{\beta \cos \theta}{4}$$

(2)

$$\delta = \frac{1}{D}$$

(3)
### Table 1: Summary of X-ray characterization

| Sample  | 2Θ (deg) | D(nm) | δ * 10^{-14} (lin.m^{-2}) | η * 10^{-4} (lin.m^{-4}) |
|---------|----------|-------|---------------------------|---------------------------|
| n-PSi   | 44.2371  | 28.81 | 12.04                     | 0.1203                    |
| Li₂O    | 30.3195  | 45.6  | 4.809                     | 7.600                     |
|         | 33.5130  | 35.2  | 8.07                      | 9.820                     |
|         | 36.8438  | 52.06 | 3.689                     | 6.657                     |
| Li₂O₂   | 21.2907  | 36.84 | 7.366                     | 9.407                     |
|         | 31.8811  | 51.92 | 3.709                     | 6.675                     |
|         | 34.7814  | 45.76 | 4.774                     | 7.574                     |
|         | 43.4709  | 51.56 | 3.761                     | 6.538                     |
|         | 63.0207  | 66.87 | 2.235                     | 5.182                     |

### 3.2. Atomic force microscopy (AFM)

AFM is a device used for studying the shape and texture of various surfaces. This approach allows the monitoring of diversity and the assessment of the sample’s exact morphological properties, suggesting better facilities than most other microscopic methods. In 3D surface scanning of AFM, a image analysis allows selection; tends to give the mean root square roughness, the average particle height and periodicity intensity spectra throughout the order of particles[10,11]. The properties, including the roughness, porosity, medium size and particle size distribution, that influence the optical, electrical, mechanical, and magnetic properties of the sample surface can be evaluated using appropriate software. Figure(4: a) shows the (3D) AFM images and also the distribution of Li₂O film granular cumulation. That film was made with a highly dispersed disk, and also the grains are homogeneous and aligned parallel. Figure(4: b) clearly shows the (3-D) AFM images and thus the distribution chart of a n-PSi. AFM image shows also that pores were distributed uniformly within in the scanning area(500x500 nm) with individual column pores extendingwards. The average grain size for pore was calculated by AFM analysis using specialized software that was observed to be approximately 65.25

![XRD patterns of (a) n-PSi, (b) Li₂O nanoparticle.](image)
nm based on processing conditions (current density of 10 mA/cm² and 10 minute etching time). That atomic force microscope images provided information on surface roughness morphology, root mean square (RMS) and thin film roughness density as seen in Table (2). The surface roughness can all be calculated from the root mean square (RMS), which is known as that of the standard deviation of surface height from average height. Surface roughness is measured by calculating the standard deviation for so many curves or curve averages of surface irregularities.

\[
\text{Surface roughness} = \text{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (h_i - \bar{h})^2}
\]

Fig. 4: Shows (a) 3D AFM image and (b) Distribution of granular accumulation chart.
3.3. Optical properties

Figure (5) displays the optical transmittance on Li₂O thin film, that transmittance reaches its maximum value around (>70%) at UV wavelength (260 and 330) nm and increases gradually above that, that's the feature for high transmitting nanoparticles at some of these wavelengths, while increasing the transmission as wavelength increases[12]. The change in transmittance as a function of wavelength of a Li₂O nanoparticles and also the increase in UV-Vis at 330-800 nm indicate the presence of using Li₂O nanoparticles in reagent and solar cell manufacturing[13]. Figure (6) shows the optical absorption coefficient for Li₂O thin film as a function of the photon energy. It can be shown that Li₂O thin film does have an absorption coefficient value of α > 10⁵1/cm that suggests an improvement in the probability of direct transitions occurring. It has been noted that the prepared thin film has a high absorption coefficient about the visible range of ~ (1.5*10⁵)1/cm in and the near-IR spectral range that is in agreement with the other reports[14]. By using the following equation[15], the optical band gap energy (Eg) of the Li₂O can be determined by Tauc's relationship of \((\alpha h\nu)^2\) versus photon energy (eV).

\[
(\alpha h\nu) = A(h\nu - Eg)^n \quad (4)
\]

Where n is 0.5 for the direct allowed transition, α is the absorption coefficient, A is the constant sharpening of the band edge, h is the Plank’s constant and hν is the photon energy. The optical band gap energy has been calculated by plotting \((\alpha h\nu)^2\), by extrapolating the linear portion of the plot to = 0. Figure (7) shows Tauc's Li₂O thin film plot plotting the square graph \((\alpha h\nu)\) versus the photon energy (hν). The value of the Li₂O thin film band gap is found to be roughly 5.33 eV.

### Table 2: Average grain size, roughness surface and Root mean square (RMS)

| Sample | Average grain size (nm) | Roughness average (nm) | Root mean square (nm) |
|--------|------------------------|------------------------|-----------------------|
| n-PSi  | 65.25                  | 6.73                   | 7.77                  |
| Li₂O   | 83.19                  | 2.59                   | 3.03                  |
Fig. 5: UV-Visible transmission spectrum of Li$_2$O thin film.

Fig. 6: Absorption coefficient versus photon energy for Li$_2$O thin film.
Due to the vast possibilities for technological application, the characteristics of visible photoluminescence (PL) in porous silicone layers (PSLs) have given an important impulses to material studies. The PSL studies aimed at increased stability of PL over long periods. Initial work on PSLs is primarily aimed at identifying the sources of the mechanisms for radiative recombination. PL spectrum of a PSi / n-Si heterojunction formed at current density (10) mA cm$^{-2}$ and 10 minute etching time as seen in the figure (8), shows an emission peak of 671 nm for n-PSi and an emission of 500 nm for fixed excitation wavelength. PL is pronounced in the 1.847 electron Volt spectral band, and this can be due to the luminescence from the restricted silicone structures accepted with these results[16].

![Fig. 7: Tauc's plot of Li$_2$O thin film.](image)
3.4. FT-IR spectra

Figure (9:a) shows the Li$_2$O powder FT-IR spectrum which was prepared using simple chemical method. The bands that appear at (706.83) 1/cm are caused by inter-atomic vibrations correspond to (Li-O-Li). Noticed the (1625.91 and 3449.37)1/cm, possibly due to expansion and deform deformation of (O-H).The bands correspond for (O-$\delta$) showed up at (900.69)1/cm and (1044.34)1/cm for (O$_3$), respectively to absorb water on the metal surface. Kurnar and Rani reported that similar FT-IR spectra were observed in Li$_2$O, which would be a high-profile film[17]. PSi surface chemical composition can be tested with FTIR spectroscopy successfully. The FTIR spectrum for n-PSi layer was indicated by Figure (9:b) By FTIR data for n-PSi, it can be noted that the main peak was in the range about (1037.54-828.93)1/cm that was due to the presence of (Si–O–Si) wagging because the range (2099.65)1/cm was according to (Si–H)wagging mode, peak at 664.46 1/cm noticed, due to (Si–O).A small peak at (2925.44)1/cm may be attributed to angle deformation (C – H). The (1569.03)1/cm may be observed, probably due to expansion and deformation (O–H). Even so, since carbon and silicon are on the same periodic table board, there's also a possibility that the carbon atom will replace a silicon atom[18].
3.5. SEM

Figure (10) displays SEM images prepared by simple chemical method, with two magnifications of Li$_2$O NPs. It can be certain in the SEM images that these NPs have different morphologies. It has been noted that Li$_2$O NPs morphology is not uniform and is made up of several tiny irregular nanoparticles.

3.6. Li$_2$O /n-PSi Heterojunction Solar cell properties
Figure (11) shows that the particles of Li₂O are deposited on the surface of silicon by the drop casting method only (5) drops and then dry at 80°C to make the Li₂O/Si solar cell. I-V dark characteristics of Al / Li₂O / n-Si / Al Solar Cells in forward and reverse direction. Solar cell’s forward current is very small at voltages less than 2 V. This current is called recombination current and only occurs at low voltages. This is produced when each electron excited the conductive band to form valence band. The second high voltage region represented the region of diffusion or binding which depends on the serried resistance. The bias voltage can deliver electrons with sufficient energy in this region to penetrate the barrier between the two sides of the junction.

![I-V Characteristics](image)

**Fig. 11:** (I-V) in the dark characteristics for both reverse and forward bias of the Li₂O/PSi heterojunction.

Figure (12) demonstrates that the Al / Li₂O / PSi / Si / Al bright (current-voltage) characteristics producing photocurrent under a 10mWm⁻² tungsten lamp illumination. It has been shown that the reverse current value for the Li₂O / n-Si heterojunction under illumination at a given voltage is higher than that in the dark which indicates that, as a result of light absorption, the light generated carrier – contributing photocurrent as a result of electron – hole production. Such behavior yields useful information about the pairs of the electron-hole that are effectively produced by incident photons in the junction.
Fig. 12: (I–V) characteristics for forward and reverse biasing applied to Li$_2$O/PSi with illumination.

Figure (13) shows the I-V curve for Li$_2$O/n-Si heterojunction. Equations (5) and (6) [19]

$$\text{FF(\%)} = \frac{I_{\text{max}} V_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}} \times 100\% \quad (5)$$

$$\eta(\%) = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{I_{\text{sc}} V_{\text{oc}}}{P_{\text{in}}} \cdot \text{FF} \times 100\% \quad (6)$$

The measured short-circuit current, open-circuit voltage, filling factor and efficiency were calculated respectively by 1.2\(\mu\)A, 24.7 mV, 66.12 and 2.49 percent. All of the results indicate relief that the Li$_2$O/n-Si sandwich structure could be used as a solar[20].

Fig. 13: (I-V) curve of Li$_2$O/n-Si solar cell
4. Conclusions

The XRD results showed that the Li$_2$O films with preferred orientation along (003) direction are nanocrystalline. The Li$_2$O thin film synthesized was in 35.2 nm nanosized, which was prepared by chemical method. X-ray diffraction (XRD) measurements indicate that Li$_2$O particle was polycrystalline with Rhombohedra crystal structure and there was a hexagonal structure in the secondary phase of the Li$_2$O thin film. (SEM) showed that Li$_2$O was a ball-shaped particle. The optical properties showed that the Li$_2$O thin film with direct band gap was 5.33 electron Volt. By simple chemical method, the Li$_2$O / PSi / n-Si heterojunction was successfully manufactured using electrochemical silicon etching and the deposition of Li$_2$O thin films. Li$_2$O shows good transparency throughout the wavelength range (200-800) nm, and the heterojunction electrical characteristics were strongly dependent on the structure. Si porosity has improved the performance of the heterojunction Li$_2$O / PSi / n-Si to become very effective materials for solar cell applications.

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