Effect of Zinc Oxide on the Efficiency Enhancement of Al/Li₂O/PSi/Si/Al solar cell

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Abstract

In this paper, electrochemical etching of the p-type silicon wafer is used to prepare p-type porous silicon with current density of 10 mA.cm^{-2} for 10 minutes. Field Emission Scanning Electron Microscopy (FESEM) has been used to study porous silicon layer surface morphology. Zinc oxide and lithium oxide nanoparticles are prepared separately by chemical precipitation method and simple precipitation method, respectively and deposited on glass substrates by drop casting method. Moreover,, the structural properties of the films were analyzed by using XRD and SEM. The XRD results showed that the ZnO and Li_2O films are polycrystalline with hexagonal wurtzite structure and cubic structure, and preferred orientation along (101) and (003) planes, respectively. Using Scherrer's formula, the crystallite size was measured and it was found that ZnO and Li_2O thin films have a crystallite size of 22.04 and 45.6 nm respectively. Surface topography of the prepared thin films is studied by using Scanning Electron Microscopy (SEM). Later, certain proportions of both materials were mixed and deposited on porous silicon using drop casting method at thickness of $1.4 \mu\text{m}$. After that, the characteristics of the solar cell were investigated. Mixing zinc oxide nanoparticles in particular proportions with lithium oxide played a major role in increasing the solar cell's performance. The highest prepared film efficiency was obtained at mixing ratio (0.5: 0.5) for (ZnO: Li_2O) and its value was (11.09 %).

Introduction

Since the first practical solar panels were demonstrated more than forty years ago, single or multi-crystalline silicon solar cells have been the mainstay of the photovoltaic (PV) industry. About 85% of the 90 MWP of worldwide PV module shipments in 1996 were based on crystalline silicon [1]. Visible light emission measurement of porous silicon (PS) has shown that quantum size effects can influence the optical properties of silicon dramatically [2]. Recently, the exponential increase in the energy absorption coefficient in porous silicon samples has been due to the crystallite size distribution and the change in the optical transitions oscillator strength with the confinement of the crystallites [3].

Because porous silicon films can be formed by relatively simple procedures, new solar-cell structures incorporating porous silicon can conceivably be developed at low cost. An early application of porous silicon, which focused on minimizing the optical losses in single- and multi-crystalline Si solar cells, was reported fifteen years ago [4]. After the formation of the diffused p^+n junction, the anodic dissolution process for the processing of PS was carried out. By preparing a very thin ($\sim 100 \text{ nm}$) and highly porous layer, which allowed the deposited contact metal to reach the base silicon, the reflectance reduced from 37% to 8% [5].

The current-voltage characteristic of multi-crystalline solar cells indicate that the PS coating, short-circuit current, and open-circuit voltage improved, whereas the series resistance, fill factor, and shunt resistance were slightly influenced. A recent study has demonstrated that porous Si increases both the performance of conversion and the stability of non-aqueous solution Si photocathodes [6]. The increased conversion efficiency has been due to the role played by the PS layer at the Si substrate/solution interface in

decreasing charge recombination. Furthermore, by blocking the creation of an oxide layer at the interface, the porous layer stabilizes the Si photocathode from photo-oxidative corrosion. In another study, optical losses were minimized by electrochemical etching a 10 μm -thick porous layer on single-crystal Si substrates and treating this cell in an HF-based solution [7, 8]. Investigations into the use of porous silicon in silicon solar cells have shown that PS/Si solar cells exhibit an improvement in conversion efficiency (about 25-30) % compared to a cell without a PS layer. At the same time, the efficiency of PS layered silicon solar cells is greater than that of traditional ARC silicon solar cells [9]. Ag-induced chemical etching with low surface reflectance (<5)% of multicrystalline silicon solar cells containing nanoporous black silicon, results in a major efficiency improvement of (26) % [10]. The manufacture of nanoporous structures on screen-printed silicon solar cells using wet chemical etching with size-controlled silver nanoparticles shows less than (5)% reflectance and (15.7)% efficiency [11]. One of the main reasons for improving PS/Si solar cell efficiency is the low value of effective reflectance (about 1-3) % for nanoporous silicon layer that significantly reduces optical losses. A wide-band gap of nanoporous silicon (up to 1.9 eV) leads to the widening of the cell's spectral photosensitivity area to the ultraviolet portion of the solar spectrum and promotes the performance of PS-layered silicon solar cells to increase. In addition, the PS layer acts as a luminescence down converter that transforms blue solar light into red-orange light, producing additional pairs of electron-hole pairs [12]. The use of porous silicon Bragg mirrors on the back of silicon solar cells will improve performance [13]. The passivation and properties of Si-H and Si-O bonds on pore surfaces are also of high significance since they can increase the lifetime of minority carriers [14,15]. In the present work, the mix (ZnO:Li₂O) film was synthesized by the use of drop-casting method. The properties of prepared (ZnO, Li₂O) films were each studied separately. In addition, the solar cell was prepared by using different mix ratio of (ZnO:Li₂O) nanoparticle on the porous silicon. This study focuses on the effect of mixing (ZnO:Li₂O) nanoparticles when deposited on porous silicon to improve the conversion efficiency of porous silicon(p-type) solar cells.

Experimental Work

Fabrication of porous silicon

p+ silicon wafer (5 Ω/cm^2 , 500 μm), from (Bioanalyse, Turkey) with orientation of (100) was used as a substrate. It was first washed by ultrasound bath twice with acetone and methanol. HF (40%) was then diluted at a 1:10 ratio to distilled water (DI), and the surface was engraved to eliminate any remaining particles on the Si-surface. Porous silicon was prepared by electrochemical etching of Si wafer surface. Instead of a mixture of HF (45%) and absolute ethanol, cleaned Si was put on the bottom of the Teflon cells with ratio 1:1. A gold ring was used within 10 min as an electrode with a current density of 10 mA.cm^{-2} . After that, the porous silicon was soaked in distilled water before it dries by nitrogen gas [16], as seen in Figure1.

Preparation of nanoparticles

a. ZnO nanoparticles

ZnO NPs were prepared by chemical precipitation method. Zinc chloride (ZnCl_2) and sodium hydroxide (NaOH) were used as precursors and Poly (vinyl chloride) (PVC) as a stabiliser. Using a standard procedure, 13.6 g of ZnCl_2 (Central Drug House (P) India, 97.0%) solution was prepared in 100 ml of DI water and kept under constant stirring at 75 °C for complete dissolution, which shows transparency. Then, the desired amount (25 ml) of NaOH (1 M) and 0.5 g of PVC (Sigma Aldrich USA, 99.9%) was used during a typical transaction. At the end of the reaction, the solution was allowed to settle, and the supernatant layer was poured off and washed with double distilled water and ethyl alcohol. The washing procedure was done several times in order to remove the residual impurities present in the sample. The final white products were dried at 500°C in a hot air oven for 1 hour to obtain nanosized ZnO powder particles.

b. Li_2O nanoparticles

Li_2O NPs were prepared using simple precipitation method. An amount of 0.6 g of lithium powder (MART India, 99.9%) was dissolved in 100 ml of DI water and kept under constant stirring at 80 °C for complete dissolution. Lithium intensively reacts with water, producing high flammable lithium hydroxide and hydrogen. The highly alkaline solution is colorless [17], as shown in the reaction:

Further heating decomposes lithium hydroxide (LiOH) to obtain white colour (Li_2O), according to the reaction [18]:

Device Fabrication

Zinc oxide and lithium oxide ($\text{ZnO}:\text{Li}_2\text{O}$) were mixed and deposited in predetermined proportions on porous silicon (p-type) by the drop casting method which was heated at temperatures ranging from 50-80 °C and thickness (1.4) μm . The mask was used as an electrode for the deposition of an aluminum (Al) wire (99.9%) mounted on the prepared films and the aluminum electrode was deposited as an electrode by thermal evaporation at a pressure of 10^{-3} pa and a thickness of 250 μm , with an area of 0.1 cm^2 on the ($\text{ZnO}:\text{Li}_2\text{O}$) / PSi / Si sheet. The procedure produced a heterojunction for solar cells Al/($\text{ZnO}:\text{Li}_2\text{O}$)/PSi/Si/Al, as shown in Figure 2.

Results And Discussion

Structural analysis: Patterns of X-ray diffraction for the crystalline nature of the synthesized ZnO and Li_2O in Figure 3 are shown. Figure 3(a) presents the XRD patterns of (ZnO) thin films. From Figure 3(a), it should be noted that the patterns have peaks around diffraction $2\theta \sim 31.723, 34.378, 36.199, 47.493, 56.539, 62.798, 67.897$ and 68.991 , referred to (100), (002), (101), (102), (110), (103), (112) and (201) favorite directions respectively, which agree with the JCPDS card no. 00-036-1451, and also with other

reports [19]. The favorite direction is presented in Table (I). The diffraction peaks of the prepared thin film show hexagonal wurtzite structure. Accordingly, the XRD results revealed that the film obtained in this study consisted of a pure (ZnO) phase without any secondary phases. Figure 3(b) display the XRD patterns of Li₂O thin films prepared from pure Lithium. From the figure, it can be noted that the patterns exhibit diffraction peaks around 2θ~ 30.319, 33.513, 36.023 and 63.020 referring to (101), (003), (012) and (202) favorite directions respectively. The diffraction peaks of prepared thin film exhibit cubic structure, which is in agreement with the JCPDS card no. 01-074-6256. Other peaks are due to the phase formation of non-oxidized lithium and lithium oxide represented by Li, Li₂O₂, and LiO₂ which are assigned in the figure by the symbols (*,• and ♦) respectively. These results are in agreement with previous reports [19-21].

As is well known, Li's reactivity with oxygen is extremely high and in theory different Li-O compounds can arise based on the oxidative status and complexes of dioxygen together with Li-ions. [21]. The lattice parameters for ZnO were found to be equal to a = b = 0.3253 nm, and c = 0.5217 nm. Both values are consistent with the theoretical values (a = 0.3249 nm and c = 0.5206 nm) and with other studies, respectively. [22, 23]. On the other hand, the lattice parameters for Li₂O were found to be a=b=c= 4.627 nm, which is in agreement with theoretical value a=4.610 nm and other reports [24]. For the ZnO and Li₂O films, the crystallite size is determined using the Scherrer formula using the relationship. [25]:

$$D=\frac{K\lambda}{\beta\cos\theta}\hspace{1cm}\text{-----}\hspace{1cm}\textbf{(1)}$$

where, (K) is constant, (λ) is the wavelength of x-ray, which is equal to 0.15406 nm, (β) is the full-width at half-maximum, and (θ) is Bragg angle [26].

Table I: Structural parameters of (ZnO, Li₂O) thin films.

	Zinc oxide (ZnO)		Lithium oxide (Li ₂ O)	
2θ (deg)	36.199		33.513	
hkl	(101)		(003)	
d (Å)	2.479		2.671	
(FWHM) (rad)	0.0066		0.0031	
(D) (nm)	22.04		45.6	
Lattice Constants (nm)	a=b	0.3253	a=b=c	4.627
	c	0.5217		

Scanning Electron Microscopy (SEM)

Figure 4 represents SEM images with two magnifications of (ZnO, Li₂O) NPs prepared by chemical precipitation method and simple precipitation method, respectively, and deposited on glass substrate by the drop casting method. From the figure, it is observed that ZnO and Li₂O NPs have different morphologies, where Figure 4(a) shows semi-spherical shapes of zinc oxide whose dimensions do not exceed 253 nm while Figure 4(b) consists of sheets of lithium oxide whose dimensions do not exceed 1 µm.

Field Emission Scanning Electron Microscopy (FESEM)

Figure 5 represents FESEM images of p-type porous silicon. The image reveals that electrochemical etching has been effective in preparing the porous surface of the silicon wafer. Also, it can be observed that the pores distribution is irregular. The pores indicate that silicon's surface area is increased [27]. The figure shows that the pores are formed in the sphere shapes and their dimensions do not exceed 70 nanometers.

ZnO:Li₂O/p-type PSi Heterojunction Solar Cell Properties

Figure 6 shows the current-voltage for Al/Li₂O/PSi/Si/Al and Al/(ZnO: Li₂O)/PSi /Si/Al for various ratios of mixtures: (0.25:0.75), (0.5:0.5), and (0.75:0.25), in the dark and under light conditions, producing photocurrent under a 10 mWm⁻² tungsten lamp illumination, and the effective area of the cell (0.785 cm²). It has been shown that the reverse current value for the ZnO:Li₂O/ p-type PSi heterojunction under illumination at a given voltage is higher than that in the dark. This means that the light produced by the carrier-contributing photocurrent is the result of electron-hole output and light absorption. Such behavior yields useful information about the pairs of the electron-hole that are effectively produced by incident photons in the junction.

Figure 7 shows (I-V) dark characteristics of Al/Li₂O/Si/Al and Al/ZnO: Li₂O/Si/Al solar cells in forward and reverse direction. The forward current of solar cells is very weak at voltages lower than 1.8 V. This current is referred to as a recombination current which exists only at low voltages. This is created when the conductive band is excited by each electron to form the valence band. The second high voltage region represents the diffusion or recombination region, which depends on the resistance of the series. The bias voltage will deliver electrons with sufficient energy in this field to penetrate the barrier between the two sides of the junction.

Figure (8) shows the J-V curve for Li₂O/ p-type PSi, ZnO: Li₂O/ p-type PSi heterojunction. Based on the J-V curve, the fill factor (FF) was calculated according to the formula (3) [28, 29]:

$$FF(\%) = \frac{J_{max}V_{max}}{J_{sc}V_{oc}} = \frac{P_{max}}{J_{sc}V_{oc}} \times 100\% \quad \text{----- (3)}$$

Where (V_{max}) is maximum photo voltage, (J_{max}) is the maximum photocurrent density, V_{oc} is the open-circuit photo voltage and (J_{sc}) is the short circuit photocurrent density. The efficiency of the photoelectric

conversion (η) was estimated by the following equation (4) [30]:

$$\eta(\%) = \frac{J_{max}V_{max}}{P_{in}} = \frac{P_{max}}{P_{in}} = \frac{J_{sc}V_{oc}}{P_{in}} FF \times 100\% \quad \text{----- (4)}$$

Where P_{in} is the incident power.

The measured open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF %) and efficiency (η) were calculated and depicted in Table (II). The findings suggest that the mixture of unique proportions of zinc oxide and lithium oxide improves the performance of the ZnO solar cell as well as the absorption efficiency over a greater fraction of the solar spectrum. A catalyst's photo activity is driven by its ability to create electron-hole pairs that are photo generated. It has been noted that ZnO's solar energy conversion efficiency is influenced by its optical absorption ability, which is related to its wide band energy difference. As a photo catalyst for the solar-driven photo degradation process of persistent organic pollutants, ZnO nanostructures have been shown to be a possible candidate. This is due to its low cost of production, non-toxicity and ability to absorb larger fractions of the solar spectrum[31]. It was observed that Li generates additional holes at the Zn substitution site, while it generates additional electrons at the interstitial site. It can be hypothesized that Li serves as a defect mediator in ZnO NPs [32, 33].

Li has the smallest group-I element ion radius, which is very similar to that of Zn (0.74 Å) and is a significant factor in obtaining high p-type ZnO optical efficiency. Li ions also act in significant types of Zn sites as shallow acceptors. However, it can conveniently hold an interstitial position (Li) due to the limited ionic radius of the Li-ion, which can serve as a donor. In general, the combination of ZnO with Li-ions boosts Egopt's value over that of pure ZnO films [33]. Lithium itself does not induce any visible emission of luminescence, although the relative concentration of inherent defects varies with increasing doping percentage. This will assist in tuning the emission linked to the intrinsic defect. These types of defect in ZnO NPs with the Li provide efficient use of materials in the visible light. New oxide-based catalytic materials are particularly suitable for environmentally sustainable processes and for the reduction in manufacturing costs of modern catalysis [34]. This study represents an excellent premise to obtain less expensive photo catalysts using ZnO and Li₂O to build heterogeneous structures to increase charge separation efficiency by creating photo catalysts with high efficiency and improved response capacity to visible light [35]. All results indicate that the sandwich structure of the ZnO:Li₂O/p-type PSi could be used as a solar cell. [36].

Table II: (J-V) measurements of solar cells (SC) for Li₂O/ p-type PSi hetetrojunction and different mixing of (ZnO: Li₂O)/ p-type PSi.

Mixing ratio (ZnO:Li ₂ O)	J _m (mA/cm ²) 0 ⁻²	V _m (mV)	J _{SC} (mA/cm ²) 0 ⁻²	V _{OC} (mV)	F.F%	η%
Li ₂ O	0.057	38	0.1	65.2	29.67	2.17
(0.25 : 0.75)	0.89	11.2	1.45	18.2	37.78	9.98
(0.5 : 0.5)	0.84	13.2	1.29	21.2	40.28	11.09
(0.75 : 0.25)	0.79	12.5	1.40	21.1	33.39	9.87

Comparison of the porous silicon solar cells performance

A comparison of the conversion efficiency (%) of the present study with that of the previous studies based on different studies (materials and parameters), is shown in Table (III). In this analysis, the prepared form mixing ratio Al/(ZnO:Li₂O)/PSi/p-Si/Al solar cell showed lower efficiency compared with references [38, 39], the reason is to achieve good lateral conduction of electrons and holes through the material. Also, the electrochemical environment, the physical location (depth below surface) of the pn junction, and the thickness of the porous silicon film proper were suitable for accomplishing different role of electrochemical etching conditions in the growth of (PSi) layers. In this study, higher efficiency was recorded compared to the references [37, 40] because mixing has been shown to be very effective in improving the device's working function and electrical conductivity, resulting in efficient separation and collection of electron-hole pairs in solar cells that are photo-induced.

Table III: Comparison between the efficiency of the PSi device and previous studies

Structure of PSi solar cells	η%	References
Titanium Oxide/(PSi)/n-Si	10.49	Dong Hee Shin et. al [37]
TFSA-GR/MoS ₂ /(PSi)/n-Si/TiO _x	13.18	Chan Wook Jang et. al [38]
ZnO nanoflowers/(PSi)/Si	12.95	Morteza Taheekhane et. al [39]
ZnO /CH ₃ NH ₃ PbX ₃ /CuO/(PSi)/p-Si	8.21	Kawther A. Khalaph et. al [40]
ZnO:Li ₂ O/(PSi)/p-Si	11.09	Present study

Conclusions

In this study, ZnO and Li₂O thin films were successfully prepared and deposited on glass substrates by drop casting method. XRD patterns of ZnO and Li₂O thin films show that the films are polycrystalline, with hexagonal wurtzite structure and cubic structure, respectively. The major peak characteristics are allocated to planes (101) and (003), respectively. XRD analysis of Li₂O thin films shows the presence of

other diffraction peaks which were attributed to Li, Li_2O_2 , and LiO_2 phases. FESEM research has shown that electrochemical etching has successfully prepared the porous surface of the silicon wafer (p+). ZnO and Li_2O films have been successfully deposited on porous silicon via the drop casting process.

For environmentally sustainable methods and the reduction of manufacturing costs in modern catalysis, new catalytic materials based on oxides are highly attractive. This research is a strong base for acquiring less costly photo catalysts using ZnO and Li_2O to build heterogeneous structures to increase charge separation efficiency by creating a photo catalyst with high efficiency and improving response capacity to visible light. The highest efficiency when mixing (zinc oxide and lithium oxide) reached 11.9 %, while a value of 2.17 % was attained for the pure Li_2O . Such a 448% percent increase in the conversion efficiency possibly means that by influencing the morphology, composition, or surface chemistry of the aggregates as well as the photo electrode film, the use of zinc oxide during the Li_2O aggregate synthesis could have a positive effect on the solar cell output. In addition, Si porosity enhanced the heterojunction ($\text{ZnO}:\text{Li}_2\text{O}$)/PS/Si efficiency to become very powerful materials for applications of solar cells.

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Figures

Figure 1

Electrochemical etching set-up schematic diagram.

Figure 2

The schematic structure of typical Al/ZnO:Li₂O/PSi/Si/Al heterojunction.

Figure 3

The XRD patterns of (a): ZnO NPs thin films, (b): Li₂O NPs thin films.

Figure 4

SEM Images of (a): ZnO NPs and (b): Li₂O NPs.

Figure 5

FESEM Images of p-type porous silicon.

Figure 6

I-V characteristics in the dark and under light for Li2O/ p-type PSi heterojunction and different mixing of ZnO:Li2O/ p-type PSi.

Figure 7

I-V characteristics in the dark for both reverse and forward bias of $\text{Li}_2\text{O}/$ p-type PSI heterojunction and different mixing $(\text{ZnO}:\text{Li}_2\text{O})/$ p-type PSI.

Figure 8

(J-V) curve of solar cell (SC) for Li₂O/ p-type PSi hetetrojunction and different mixing (ZnO: Li₂O)/ p-type PSi.