Rapid thermal oxidation of copper nanostructure thin film for solar cell fabrication

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Abstract
In the present work is the deposition of copper oxide using the pulsed laser deposition technique using Reactive Pulsed Laser as a Deposition technique (RPLD), 1.064μm, 7 nsec Q-switch Nd-YAG laser with 400 mJ/cm² laser energy’s has been used to ablated high purity copper target and deposited on the porous silicon substrates recorded and study the effect of rapid thermal annealing on the structural characteristics, morphological, electrical characteristics and properties of the solar cell. Results of AFM likelihood of improved absorption, thereby reducing the reflection compared with crystalline silicon surface. The results showed the characteristics of the solar cell and a clear improvement in the efficiency of the solar cell in the case of copper deposition or not.

Key words
PLD, Cu₂O, Surface morphology, Solar cell properties.

Introduction
The crystalline silicon is an important and dominant material over several years due to its well-known properties and established infra structure for photovoltaic manufacturing [1]. Due to wide use of solar energy, there is the need of creation of new technologies and materials hence; porous silicon is expected to be promising one. Presently, an increasing interest has been shown in antireflection coating made from porous silicon by researcher[2-7]. For solar cell, porous silicon layer acts as graded layer with varying expanded band gap offers increased absorption in visible spectrum regions [8-12]. The reduction in surface reflectance of multicrystalline silicon based solar cells still represents one of the most important ways of improving their...
It is now well established that nanoporous silicon (PS) is a promising candidate to replace traditional texturization followed by the deposition of a SiO$_2$:TiO$_2$ double-layer as a passivation and antireflection coating (ARC) for these cells [13-16]. Beside that nanostructure semiconductors are easily accessible and in the last decade a great number of semiconductors materials have been manufactured as nanoparticles. Semiconductors Nanocrystals are well suited for the development of novel opto-electronic devices, due to their flexibility and simple processability combined with their optical properties. One of these semiconductors materials is cuprous oxide, it is a p-type semiconductor material with a band gap of 2.17eV. This transition metal oxide has been investigated extensively due to the potential application in solar cells, gas sensor, electrode materials and others [17-21].

In this work, a combination between two materials above has been achieved through the fabrication of (Cu$_2$O /Ps/Si) multi-layer solar cell. Quantum efficiency filling factor and other parameter was measured and result was discussed.

**Experimental**

A commercially available p-type silicon with 1-3Ω.cm resistivity and square shaped has been used. (Cp4) solution and ultrasonic cleaner to prepared the sample. Porous silicon as a substrate containing silicon nanocrystal was obtained using electro-chemical etching process. The Si wafer was immersed by a mixture of electrolyte solution HF, 40% and ethanol, 99% concentrations. The formation of PS layer is using the AC process in the chemical solutions HF: ethanol (1:4) at current density 30mA/cm$^2$ of 20 min under external incandescent light. A Q-switched (1.06µm, 9nsec) Nd-Yag laser was employed to evaporate a 99.999 copper metal (Fluke CO.) on the surface of (Ps substrate) so, a nanostructure thin film of this material was obtained using pulsed laser deposition technique at (423K) as a substrate temperature and (10$^{-3}$) as a vacuum ambient. A (P-type) Cuprous oxide (Cu$_2$O) nanostructure thin film was obtained using Rapid thermal oxidation (RTO) technique, with the aid of halogen lamp at oxidation temperature of 720K and 90 sec as an oxidation time. The conductivity type of the film was investigated using Seebeck effect measurements. A thin Aluminum film on top and back of the device was used as Ohmic contact. Quantum efficiency, filling factor of the solar cell were measured by placing it under illumination of a 100mW/cm$^2$ tungsten filament lamp, placed 15 cm away. The fill factor (FF), is a measure of the junction quality and series resistance of a cell. It is defined as:

$$\text{FF} = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}FF}$$  \hspace{1cm} (1)

The efficiency of a solar cell is determined as the fraction of incident power which is converted to electricity and is defined as:

$$\eta = \frac{P_{max}}{P_{inc}}$$  \hspace{1cm} (2)

where $P_{max} = V_{oc} I_{sc} FF$

where $V_{oc}$ is the open-circuit voltage; where $I_{sc}$ is the short-circuit current; and where FF is the fill factor where $\eta$ is the efficiency[22].

The J-V characteristics were measured using a DC power supply and Keithley electrometer. The Photoconductive property of semiconductors can be used to determine the excess minority carriers lifetime. The experimental setup is schematically illustrated in the following Fig. 1.
Results and discussion

Structural and morphological properties

The x-ray diffraction and surface morphology of the nanostructure Cu$_2$O /PSi could be recognize in Fig. 2 (a and b) respectively.

The x-ray diffraction pattern insures the formation of cuprous oxide thin film which appears at two main peaks at (111) and (002). The AFM Image revealed the formation of porous surface; a combination between porous silicon surface and Cu$_2$O nanostructure. In this case some light rays will be reflected from one side inside the key hall surface merely to strike another, resulting in an improved probability of absorption, and therefore reduced reflection comparing to the crystalline silicon surface.

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**Fig. 1:** Experimental setup for carrier life time measurement.

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**Fig. 2:** a-X-ray diffraction b-Surface morphology of Cu$_2$O/Ps.
The relationship between $I_{sc}$ and $V_{oc}$ as a function of load resistance could be recognize in Fig. 3 (a and b). The efficiency of the device has been measured in two cases the for Cu$_2$O/Ps/Si and Ps/Si for comparison. It value found to be 6.42 and 4.028 respectively, the improved in value of Quantum efficiency (QE) in the first case is due to the absorption phenomena in the surface oxide layer and at the first junction that formed between Cu$_2$O nanostructure thin film and Porous silicon, besides that, the interfacial porous silicon die oxide (P-SiO$_2$) layer between porous silicon (PS) itself and metal oxide Cu$_2$O play a significant role in enhanced the properties, science it has been found that the porous silicon could be oxidized at high temperatures forming an porous oxide layer. Heating of porous silicon to high temperature in a strongly oxidation ambient leads to vary rapid oxidation of the structure. Rapid Thermal Oxidation of porous silicon makes it suitable as dielectric layer for any electronic device. Most of its applications involve the formation of stable SiO$_2$ layers obtain by a simple technological process like thermal oxidation of porous Si at high temperature is conveniently carried out by the use of rapid thermal oxidation (RTO); involving transient heat of oxygen ambient so that careful control of the potential rapid surface reaction can be maintained.

The estimated value of the filling factor found to be 0.396 and 0.58 for two device respectively, the higher value in the second case related to higher short circuit current and open circuit voltage.

**Optical properties**

**UV-VIS**

Fig. 4 (a and b) shows the optical transmittance and absorption spectra for the deposit copper oxide thin films. The curve testify that the film surface is smooth with wavelength longer than 300 nm and that’s give an indication why we used this device in solar cell applications. As seen from the figure, the copper oxide films are suitable for optical analysis from which the absorption coefficient and energy band gap may be determined. Fig. 4-c explain linear relationship is obtained by plotting $\alpha^2$ against $hv$, based on Eq. (3) below.

$$\alpha h\nu = A(h\nu - E_g)^n$$  \hspace{1cm} (3)

where $\alpha$ is absorption coefficient, $A$ is constant (independent from $\nu$) and $n$ the exponent that depends upon the quantum selection rules for the particular material. The photon energy ($h\nu$) for y-axis can be calculated using Eq. (4).

$$E = h\nu = hc/\lambda$$  \hspace{1cm} (4)
where \( h \) is Planck’s constant \((6.626 \times 10^{-34})\), \( c \) is speed of light \((3 \times 10^8)\) and \( \lambda \) is the wavelength. A straight line shown in Fig.4-b is obtained when \( \alpha^2 \) is plotted against photon energy \((h\nu)\), which indicates that the absorption edge is due to a direct allowed transition \((n = 1\) for direct allowed transition). The intercept of the straight line on \( h\nu \) axis corresponds to the optical band gap \((E_g)\). The \( \text{Cu}_2\text{O} \) films showed a higher energy gap of 2.62 eV, this value of energy band gap give same indication for solar cell application.

Fig. 5 gives the open voltage decay pulse of the \( \text{Cu}_2\text{O}/\text{PS}/\text{Si} \) and we could recognize the long carries life time of about 115 \( \mu \text{sec} \) which give rise in the enhancement of other device photocurrent and quantum efficiency. The internal quantum efficiency may also be written in terms of the recombination lifetimes as \( \tau \) is inversely proportional to \( r \).

Define the radiative and nonradiative recombination lifetimes \( \tau_r \) and \( \tau_{nr} \).

\[
\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \quad (5)
\]

The internal quantum efficiency is then given by \( \eta = \tau / \tau_r = \tau_{nr} / (\tau_r + \tau_{nr}) \) \( (6) \).

**Conclusions**

\( \text{Cu}_2\text{O} \) Nano structure thin film was successfully deposit using reactive
pulsed laser deposition (PLD) method on porous silicon substrates. AFM showed resulting showed an improved probability of absorption, and therefore reduced reflection comparing to the crystalline silicon surface. Optical properties shows good transmission for range higher than 300 nm and energy band gap 2.62 eV. The efficiency of the device showed different in two cases for Cu$_2$O/Ps/Si and Ps/Si as a 6.42 and 4.028 respectively and the value of the filling factor found to be 0.396 and 0.58 for two device respectively, the minority carrier life time for Cu$_2$O/Ps/Si give the open voltage decay pulse and long carries life time of about 115 µsec which give rise in the enhancement of other device photocurrent and quantum efficiency.

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