Fabrication and characterization of (Cu$_2$O/Ps/p-Si) nanostructure heterojunction device for photovoltaic application

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ABSTRACT

This work presents the fabrication and characteristics of (p-n-p) (Cu$_2$O/Ps/p-Si) heterojunction device prepared by rapid thermal oxidation technique without any post deposition annealing condition. A (100 nm) thick Cu$_2$O nanocrystal thin film was grown on nanocrystallines Silicon (Ps) by rapid photo thermal oxidation of pulsed laser deposited Cu film using a halogen lamp (100W) at (720K) for 90s in static air. Surface morphology were investigated and compared with other published results. Dark and illuminated I-V, C-V, spectral responsivity and time constant of (Cu$_2$O/ Ps/ Si) and (Ps/Si) heterojunction were investigated and discussed.

Keywords: Heterojunction device, Cu$_2$O, Porous silicon and RTO

1. Introduction

Cuprous oxide is an important p- type semiconductor material with a band gap of (2.137eV). This transition metal oxide has been investigated extensively due to the potential
application in solar cells, gas sensor, electrode materials and others (Joannopoulos et al., 1997; Caruso et al., 1998; Matijevic, 1994; Norris et al., 2001).

A variety of techniques have been employed for preparation of nanostructure Cuprous oxide thin film include CVD, MBE, Reactive Sputtering (Liu et al., 2005; Zhou et al., 1998; Maruyama, 1998; Figueiredo et al., 2008; Kita et al., 1994; Kita et al., 2007; Drobny et al., 1979; Ismail et al., 2005) electrode position (Gou et al., 2007), γ–irradiation (Norris et al., 2001), oxidation of Cu (Chen et al., 2007), solution-phase synthesis (Choon et al., 2006), have been employed to fabricate Cu$_2$O with various shapes. Cu$_2$O/Si heterojunction is one of the important device has been studied by many workers (Zhang et al., 2006; Xu et al., 2006), in the other hand, using porous silicon including Si nanocrystal as a substrate has not yet extensively studied. Where the heterojunction Ps/p-Si is considered as anisotype heterojunction since Ps behave like n-type semiconductor (Panek, 2004; Rasheed et al., 2009).

In this work (Cu$_2$O/Ps/p-Si) multilayer heterojunction device has been prepared and characterization of the main electrical and photo voltaic properties has been carried out.

2. Experimental Work

A commercially available p-type silicon with (1-3) cm resistivity [111] orientation and square shaped has been used. (Cp$_4$) solution and ultrasonic cleaner to prepared the sample. Porous silicon as a substrate containing silicon nanocrystal was obtained using electrochemical etching process describe in detailed on other work (Rasheed et al., 2009).

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$^{-3}$ mbar) 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 (90sec) 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.

The white light response of the photodiode was tested by placing it under illumination of a (100W) tungsten filament lamp, placed 15 cm away. The I-V characteristics were measured using a DC power supply and Keithley electrometer. The spectral responsivity of the photodiode was measured for the spectral range (450-900nm) using a calibrated monochromator. C-V measurements at a frequency of 25 kHz were made using an (hp) LCZ meter. All measurements were carried out at room temperature.

3. Result and discussion

The surface morphology of the porous layer and the nanostructure Cu$_2$O oxide film could be recognize in figure (1-a,b) respectively.
The AFM Image revealed the formation of porous surface; it is obvious from this figure that the pores are formed on the silicon surface. Porous silicon (Ps) appear as a fine network of very small voids (often called pores) surrounded by thin walls (often called nanocrystallites). 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 (Ismail, 2009).

Figure (1-b) give the (Cu$_2$O/Ps/p-Si) multilayer structure it could be recognize the increase in the nanometer size due to the additional nanostructure oxide film resulting from the pulsed laser deposition of the copper thin metal. Also we could recognize the uniform distribution of the porous surface resulting from additional nanostructure oxide thin film, which itself play an important role in enhanced the photovoltaic properties of the prepared device.

The results of the current-voltage (I-V) measurements in forward and reverses in the dark for AL/ Cu$_2$O/Ps/Si and AL/Ps/Si devices prepared at optimum conditions are shown in figure 2. These characteristics are very important to describe the device performance and all device parameters depending on it. In the following curves, the I-V characteristics were given for two devices under reverse bias (part (a)).

![Figure 1 Surface morphology of (a) Ps and (b) Cu$_2$O/Ps](image)

![Figure 2 Current–voltage characteristics (a) forwarded bais, (b) reverse bais](image)
It is clear that the curve contains two regions: the first is the generate region where the reverse current is slightly increased with the applied voltage and this tends to generation of electron-hole pairs at low bias. In the second region, a significant increase in the reverse bias can be recognized. In this case, the current resulted from the diffusion of minority carriers through the junction. From the obtained result it is clearly that the current produce by Cu$_2$O/Ps/Si less than that obtained from the Ps/Si which is related to the large junction resistant which reduces the leakage current. The results in the figure (2, b) give the I-V characteristic behavior of the Al/ Cu$_2$O/Ps/Si and Al/Ps/Si device in the forward bias. Two regions are recognized; the first one represents recombination current the first current established when the concentration of the generated carrier be larger than the intrinsic carrier concentration ($n_i$), i.e. ($n$-$p$>$n_i^2$),which lead to recombination process for mass low applicable . The second region at high voltage represented the diffusion or bending region which depending on series resistance and in Cu$_2$O/Ps/Si case represented the tunneling region. From the comparison between the results obtained for both devices prepared at optimum condition, we recognized the values of the current improved for second case due to presence Ps layer which increase the depletion region width.

The ideality factor n of both devices was estimated (Drobsny and Pulfrey, 1979) and found to be (1.3 and 1.1) respectively. These values refer to good rectification properties for both prepared devices. The higher rectifying properties for Ps/Si related to the less lattice mismatch between Ps and Si compared to that between Cu$_2$O and Ps. For the second case beside the presence of some defect in the additional oxide layer thickness like pinhole and other which play an important role in the ideality factor of the device. Figure (3) (a,b) gives the C-V and 1/C$^2$-V measurements for both device respectively. Results show that the device capacitance is inversely proportional to the bias voltage. The reduction in the device capacitance with increasing bias voltage resulted from the expansion of depletion layer with the applied voltage.

![Figure 3. Capacitance –voltage characteristics (a) Ps/Si, (b) Cu$_2$O/Ps/Si.](image-url)
The depletion layer capacitance refers to the increment in charge per unit area to the incremental charge of the applied voltage. This properly gives an indication of the behavior of the charge transition from the donor to the acceptor region, which was found to be "abrupt" which is confirmed by the relation between $1/C^2$ and reverse bias being a straight line. The improved in value $V_{bi}$ for (Al/Cu$_2$O/Ps/Si) diode due to interfacial porous silicon oxide (Psio$_2$) layer and porous silicon (Ps) itself between metal oxide Cu$_2$O and Si substrate and this produced increase in oxide thickness, science it has been found that the porous silicon could be oxidized at high temperatures forming an porous oxide layer which play an important role in the enhancement of the device properties. 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 (Cullis et al., 1997). Figure (4, a and b) exhibits the photo electric behavior of the two devices under illumination condition. It is understood that photo electric effect result from light-induced electron-hole generation at the device and particularly at the depilation region of the P-type silicon.

![Figure 4. Photo current density of the two devices under illumination condition.](image)

Under external reverse bias, depilation region of the device extends and as a result, more incident photons will contribute to the electron-hole pairs generation that takes place in the depletion region. The internal electric field in the depletion region causes the electron-hole pairs to separate from each other and this bias becomes larger with the applied external bias. From the following figure, we can see the increase in the photo-current with increasing incident light intensity, where the large intensity refers to a great number of incident photons and hence large number of separated electron-hole pairs. From this result, we can recognize the enhancement in values of the photo current in (Al/Cu$_2$O/Ps/Si) diode comparing with (Al/Ps/Si) at the same incident light intensity. This is due to the presence of (Psio2/Ps) thin layer (anti-reflection) between the nanostructure Cu$_2$O and Si which acts as anti reflection coating that enhancement the device absorption ability and as a result increase the probability
of electron-hole pair's separation in the active region. Beside the increment in the depletion layer width which mean a large internal area for carrier separation, also the nanostructure Cu$_2$O surface layer improve the light capturing property of the device, That lead to higher photocurrent. Figure (5 a and b) show the relation between short-circuits current (I$_{SC}$) and open-circuit voltage (V$_{OC}$) with the incident photon power of the halogen lamp for both devices.

![Figure 5](image_url)

**Figure 5.** Relation between (a) short-circuits current (I$_{SC}$), (b) open-circuit voltage (V$_{OC}$) with the incident photon power density.

From the obtained result we can recognize the linear relation between I$_{SC}$ and V$_{OC}$ with the incident photo power to reach a maximum value beyond which both values for the two devices tend to saturated and become constant. This occurs due to the total separation of the photogenerated electron-hole pairs. A large difference in the obtained result value can be obviously found comparing it. The higher result obtained for (Al/Cu$_2$O/Ps/Si) device related to the increasing of the depletion layer width by adding the Psio$_2$ oxide layer which result in larger area for electron-holl pairs separation and hence larger photo-current, Since V$_{OC}$ is depending on the photo current (Dhungel et al., 2008). Here in this case a could represented the prepared device as a double junction structure (Cu$_2$O/Ps/Si) and (Ps/Si), the porous silicon oxide (Psio$_2$) is formed at the porous layer surface during the oxidation process of the Cu metal on the Ps surface. In general For both cases the linear behavior of V$_{OC}$ versus incident power refers to good linearity of the prepared device to work as a detector or solar cell. The spectral responsivity represents the ratio between the output generated current to the incident power and it is very important because it specifies the performance range of (Al/Cu$_2$O/Ps/Si) device if used as a detector. Figure (6) gives the responsivity as a function of wavelength for both devices prepared at optimum conditions, these measurements were achieved in the wavelength range from (200-900nm). From this figure, the range of the spectral responsivity could be obtained to find extended from UV to NIR region. In the case of Cu$_2$O/Ps/Si heterojunction We could recognize two main peak of the Responsivity, the first one at(539nm) is related to the Ps layer with energy gap of (2.3eV) which formed the second junction with the Si substrate while the second peak is (590nm) which is related to the (2.1eV) band gab of the cuprous oxide surface layer which itself formed a heterojunction with lower Ps layer, The fast decrease in the responsivity in the near IR wavelength is due to recombination process in the surface and that
in bulk of the material at longer wavelength. At wavelength near the cut off region of silicon the substrate become transparency for all incident wavelengths.

![Graph of responsivity as a function of wavelength for both devices.](image)

Figure 6. Responsivity as a function of wavelength for both devices.

The improvement in the value of responsivity related to the increase in the photo current for the reason discussed above. Also the presence of thin oxide layer reduces the surface recombination process and hence increases the sensitivity to the high energy wavelength that absorbed at the surface. Figure (7 a,b) represents the obtain rise time pulse of the both devices at wavelength (840nm). The idea of the rise time depending on the developing of internal voltage with the depletion region which used to separate the electron-hole pairs resulting from the absorption of the light energy on the device surface. This mechanism take a specific time depended on the device characteristic. And since this time constant is greatly affected by, carrier diffusion time, carrier drifts time from depletion region and finally depletion region capacitance, we can understand the enhancement achieved in the case of (Al/Cu₂O/Ps/Si) device. The values found to be (78.8μsec) and (48.1μsec) for Ps/Si, Cu₂O/Ps/Si receptivity. This result gives a clear information about the enhancement achieved in the first case, hence we can recognize the large reduction appear with the rise time.
This reflected on the value of the response time achieved which found to be (56.28, 34.35 μsec) for both device receptivity. The small response time in the second case could be related to the long diffusion of the minority carrier appeared in the large oxide thickness case which related directly to the diffusion time of these carrier which reduce the response of the manufactured device.

4. Conclusion

According to the obtained electrical properties a good enhancement in the device performance could be achieve and it could recognize clearly that device has three main peak of the Responsivity, at (539nm), (590nm), and (790nm), with a peak response value of (0.32A/W) which is greater than that of (Ps/Si) Device that found to be (0.21A/W), also the rise time of Cu₂O/Ps/Si found to be shorter. The encouraged optoelectronic properties of this heterojunction suggest that it candidate to be visible- enhanced photo detectors. The method of fabricating Cu₂O layer by rapid thermal oxidation is relatively simple, cheep, and it is hoped it can be improved either by doping or annealing. The photodiode exhibited good rectifying characteristics and the turn-on voltage was around I-V. The C-V measurements showed an abrupt type junction and a diffusion potential of I-V.

References


