Photovoltaic Properties of CdO/Porous Si Heterojunction Photodetector.

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Abstract

CdO/porous Si heterojunction photodetector have been fabricated by rapid thermal oxidation (RTO) of Cd on porous has been presented. The electrical and photovoltaic properties of this structure have been studied. The electrochemical etching process has been used as a technique to control the porosity of silicon wafer by controlling the time of etching in the range (600s-2400s). The results revealed that all our detector parameters are highly dependant on etching time. The minimum value of ideality factor was 1.28 for the detectors prepared with etching current density of 40mA/cm^2 for 600s. The results of quantum efficiency showed that these detectors had two depletion regions, the first one between CdO film and porous silicon layer, the second between the latter and the crystalline silicon. The

first peak of quantum efficiency curve was 77% at wavelength 550nm while the second one was 88% at 700nm. The maximum specific detectivity was $87\times10^{11}\ cm\ Hz^{1/2}\ W^{-1}$ at wavelength 550nm for the detectors fabricated with etching current density $40mA/cm^2$ and etching time 2400s. All the detectors are working on the spectrum region 400-700nm. The maximum I_{sc} and V_{oc} were 19□A, 0.28mV respectively for the detectors fabricated with etching current density $40mA/cm^2$ and etching time 1200s.

ألخلاصة:

تم تصنيع كاشف ألمفرق ألهجين نوع (CdO/Porous Si/Si/Al) بطريقة ألأكسدة ألحرارية ألسريعة (Rapid Thermal Oxidation) وذلك من خلال ترسيب أغشية CdO على ألسليكون ألمسامي نوع p- بالطريقة ألمذكورة آنفاً.تم دراسة ألخصائص ألكهربائية وألفولطائية ألضوئية للكاشف ألمحضر على قواعد سليكونية مسامية. استخدمت عملية ألتنميش ألكهروكيميائية للتحكم بمسامية الشرائح السليكونية من خلال السيطرة على زمن التنميش ضمن المدى الزمني (600s-2400s). أوضحت ألنتائج أن جميع معلمات ألكواشف ألمصنعة تعتمد بشكل كبير على مقدار زمن ألتنميش (Etching time) للقواعد ألسليكونية ضمن المدى المستخدم. أن أقل عامل مثالية كان 1.28 للكواشف ألمصنعة بكثافة تيار تنميش $40mA/cm^2$ وزمن تنميش 600s. لقد أظهرت نتائج ألكفاءة ألكمية أن الكواشف ألمصنعة تمتلك منطقتي نضوب الاولى ما بين غشاء CdO والسليكون ألمسامي والثانية ما بين طبقة السليكون المسامي والسليكون البلوري حيث أن القمة الاولى تقع عند الطول الموجي(550nm) والثانية عند الطول الموجي (700 nm) حيث مقدار الكفاءة الكمية للقمة الاولى كان (88%) ومقدارها للقمة الثانية كان (77%). أعلى قيمة للكشفية D^* كانت عند الطول الموجي (550nm) . وكان مقدارها $87\times10^{11}\ cm.\ Hz^{1/2}\ W^{-1}$ للكاشف المصنع بكثافة تيار $40mA/cm^2$ وزمن تنميش 2400s . أوضحت النتائج أن الكواشف المصنعة تعمل للمنطقة الطيفية (400-700nm).

جرى قياس كل من تيار دائرة ألقصر I_{SC} وفولتية دائرة ألفتح V_{OC} ووجد بأن أكبر قيمة لهما كانتا 19□A و0.28mV على ألتتالي للكاشف ألمصنع بكثافة تيار تنميش $40mA/cm^2$ وزمن تنميش 1200s **.**

أجريت دراسة ألخصائص ألكهربائية والفولتائية ألضوئية والتركيبية لهذا ألكاشف بدرجة حرارة ألمختبر وتبين من خلال خواص (تيار-جهد) بأن ألكاشف غيرمتماثل ألسلوك، وأوجدنا قيمة ألمقاومة ألسطحية R_S للكاشف،عامل ألخطية وتم ألحصول على كفاءة كمية بمدى (88%-66%) وبكشفية $76x10^{11}$ cm. $Hz^{1/2}$ W^{-1} عند ألطول ألموجي (550 nm).

Keywords: porous silicon, rapid thermal oxidation, photodetector, CdO

1. Introduction

It is well known that a porous silicon (PSi) layer can be formed on one side of crystalline silicon wafer (c-Si) by an electrochemical etching process, the PSi layer, which looks like a sponge with a rigid silicon Skeleton and columnar open pore. The morphology of the PSi layers depends on the c-Si conductivity type and etching conditions basically. It has been shown that the p- type PSi layer has distributed micro – and nanoporous but n-type PSi layer contains macropores and has a rough surface [1]. PSi plays an important role in photovoltaic characteristics through the improvement of light absorption [2] and exhibits a set of unique properties such as direct and wide modulated band gap, high resistivity, large surface area to volume ratio, and almost the same monocrystalline structure as bulk silicon. These valuable properties make PSi as attractive and promising material for superior optoelectronic device fabrication [3, 4]. The optical reflectance from planar monocrystalline silicon surface is around 38% but can be minimized using KOH and NaOH texturing. Chemical texturization of single crystal silicon is ineffective due to random distribution of the grain orientations [2] but this problem was overcome by PSi formation. Up to date, few papers were published on optoelectronic properties of PSi/Si/Al photodetectors made by electrochemical anodization on high resistivity Si substrate (10-190 Ω.cm) [5-9]. The published results showed higher responsivity and quantum efficiency for these structures than that for *p-n* Si photodiodes.

This paper presents the results of a comprehensive experimental study of photovoltaic characteristics of CdO/porous Si photodetectors made by electrochemical anodization.

2. Theoretical background

Power calibration is done using calibrated Si power meter. R_λ Is calculated by measuring the photocurrent as function of wavelength and then divide it by power as in the following relationship [10].

$$R_\lambda = \frac{I_{ph}}{P_\lambda} \qquad (1)$$

From spectral responsivity measurements, the internal quantum efficiency η and the specific Detectivity $D*$ are calculated using the following equations [11]:

$$\eta = \frac{1.240 R_\lambda}{\lambda(nm)} \qquad (2)$$

$$D* = \frac{R_\lambda (A\Delta F)^{1/2}}{I_n} \qquad (3)$$

The minority carrier lifetime (MCLT) measurements of photodetectors are measured using photo-induced open circuit voltage V_{oc} decay (OCVD) technique. This system comprise of stroboscope type and 20MHz oscilloscope model Kenwood.

The heterojunction photodiode can be operated as a photovoltaic converter (i.e. no external voltage source is required), where the junction itself turns into a voltage source when it is exposed to the radiation. The two main parameters describe the photovoltaic properties are the open circuit voltage V_{OC} and the short circuit current

I_{sc}. It is defined as the voltage generated across the open-circuited terminals of a heterojunction photocell mathematically can be determined by setting J=0 in the equation [12]:

$$J = J_S \;[\exp\,(\frac{qV}{kT}) - 1] - J_{ph}$$

i.e. when R go to infinity, then we get:

$$\mathbf{V}_{OC} = \frac{kT}{q}\ln[\frac{J_{ph}}{J_s} + 1] \qquad (4)$$

I_{sc} is defined as the photocurrent produced in a heterojunction photocell when the two terminals are shorted together [13]. Quantum efficiency Q_E is the number of electron-hole pairs generated per incident photon [14]:

$$Q_E = \frac{(I_{ph}/q)}{(P_{in}/hv)} \qquad (5)$$

where (I_{ph}/q) is the number of the photo-generated carriers, while (P_{in}/hv) is the number of incident photons. Substituting suitable constants to get simple formula will give the quantum efficiency in term of wavelength in (nm).

If a diode and a resistance are connected together with no external voltage applied, one of them must get hotter and the other cooler. Therefore, the noise current will flow. The noise components of the two oppositely directed currents (i.e. electrons and holes) are additive. Thus the magnitude of total dark current I_d in the unbiased diode is $2I_s$. This mechanism is called as Johnson noise or thermal noise [15]. The noise component of an unbiased detector becomes:

$$I_n = (4kTG\Delta f)^{1/2} \qquad (6)$$

Where Δf is noise bandwidth and G is the dark conductance.

The dark conductance of a diode with zero bias is [16]:

$$G = \frac{q}{kT} I_S \tag{7}$$

$I_d = 2I_S$, we get:

$$I_n = (2qI_d \Delta f)^{1/2} \tag{8}$$

The most basic of all figures of merit is the Detectivity,

The normalized Detectivity D^* is defined as [11]:

$$D^* = \frac{1}{NEP} (A.\Delta f)^{1/2} \tag{9}$$

It can be is rewritten in terms of measured parameters for unbiased heterojunction photodetector as [11]:

$$D^* = R_\lambda \left(\frac{A.\Delta f}{2qI_d}\right)^{1/2} \tag{10}$$

3. Experimental Part

In this work, mirror-like p-type (boron doped) of (111) orientation mono-crystalline silicon wafers with electrical resistivity of (14-22) Ω.cm and 500 ± 50 µm thickness are used. First, the wafer scribed, cut into 1x1 cm^2 and cleaned carefully using acetone , ethanol , and deionizer water (DI) (to remove dirt and oil) followed by hot acid cleaning 5 minutes in each the following: HNO_3, HCl , and hot DI to remove the room temperature native oxide layer SiO_2. Porous silicon was performed by electrochemical etching (anodization) using an electrolyte containing 40% HF acid with several drop of ethanol to prevent bubbling for different etching time (600s, 1200s, 1800s and 2400s) with constant etching current density (40mA/cm^2). Optical Properties for CdO film prepared on glass are calculated after measuring the transmittance of the film using a Double beam spectrophotometer provided by Shimadzu-Japan Company. The results of XRD for

CdO film demonstrated that the CdO film it is a crystalline and have peaks for the planes (200), (111) at angles (38.85), (33.15) respectively. The home made (see Fig.1) electrochemical cell consists of the Si substrates set as anode and high purity Pt wire set as cathode (forward bias) located inside Teflon container filled with electrolyte solution, power supply type was used to provide electric field. After etching the samples rinsed in water and ethanol and CdO thin film was deposited on porous silicon and clean glass substrate by rapid thermal oxidation (RTO) as technique as follows; high purity cadmium film (99.99%) provided from Aldrich Co. was first deposited on Si using thermal evaporation technique under pressure down 10^{-5} torr followed by rapid thermal oxidation process using 650W halogen lamp .The oxidation is carried out in static air at temperature 550C for 3 minutes. K-type thermocouple was used to monitor the oxidation temperature. The set-up for RTO used here is the same that used by Raid *et al*. [12] as shown in Fig. (2):

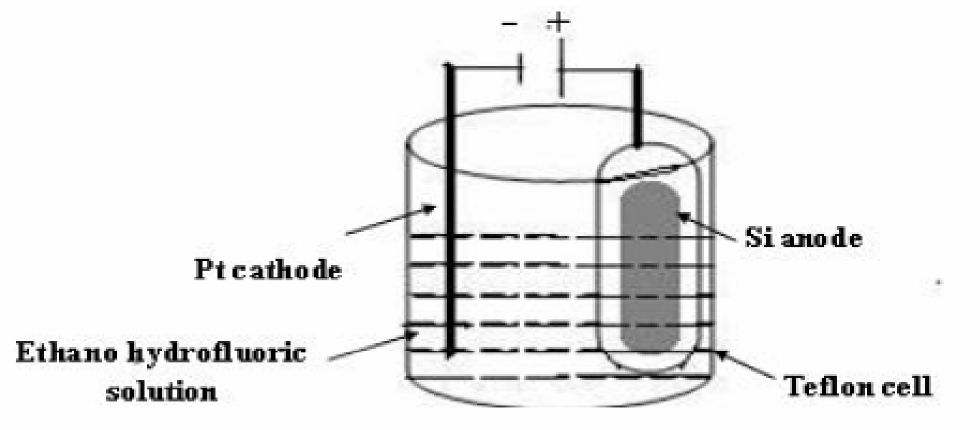


Figure1: Schematic diagram of electrochemical anodization system [12].

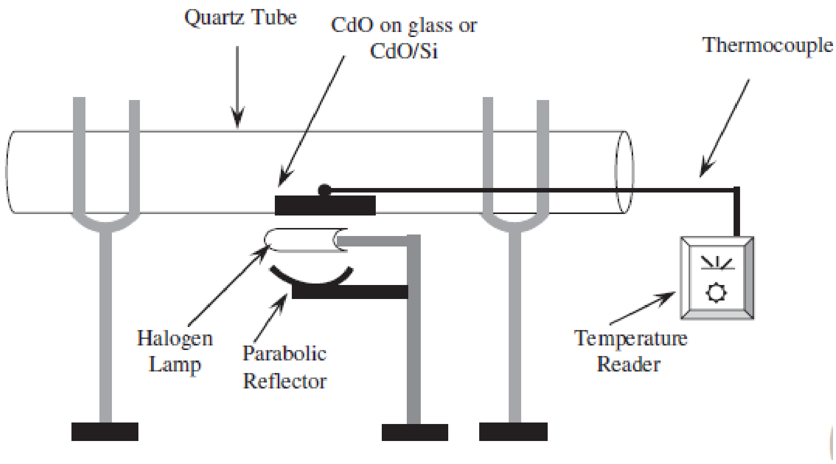


Figure2: Rapid Thermal Oxidations system.

In order to measure the photovoltaic properties of CdO thin film and CdO/Si, heterojunction, ohmic contacts are performed by evaporating of an aluminum film with purity of 99.99%. For CdO film deposited on glass substrate the ohmic contact is made through standard mask. The contacts are made on CdO/Si heterojunction by evaporating thin film (semitransparent) and thick of Al on front side of CdO film and back side of silicon wafer, respectively. Spiral tungsten is used as tool of evaporation. The evaporation process is carried out at a pressure of 10^{-5}Torr. The cross-sectional view of CdO/PSi heterojunction photodetector was presented in Fig.3.

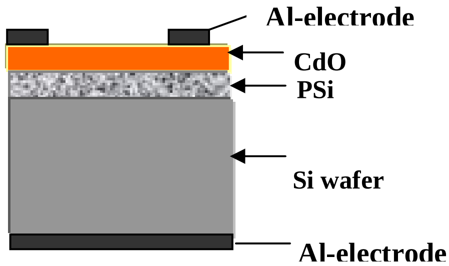


Figure3: The cross-sectional view of CdO/PS/Si/Al Sandwich heterojunction photodetector.

The photovoltaic measurements include; short circuit current I_{sc}, open circuit voltage V_{oc}, while detector parameters in this work implies Quantum Efficiency *QE*, specific Detectivity D^* and Noise Equivalent Power *NEP*. I-V measurements under dark and illumination conditions of the CdO/porous Si photodetector were carried out using an analog power supply model Farnell instrument (30V, 2A) and a mulitimeter. The photodetectors were located in black box to satisfy the darkness condition. I-V measurements of photodetectors at reverse bias under illumination are carried out using 100W halogen lamp. The optical power of the lamp was varied through varies the input electrical voltage with the aid of a variac. The light power measurement is performed using calibrated Si power meter model (Spectra-Physics (401C) Power meter). *QE* Quantum, NEP, D^* measurements were done using a monochromatic model Jobin Yvon Division Instruments in the spectral range of (400-900) nm.

4. Results and Discussions

In a previous paper [13] we have reported our results about the structural and electrical properties of CdO/PSi heterojunction prepared by RTO technique and in this paper we study the following items:

4.1 Optical properties of CdO thin film

Fig.(4) shows the optical transmittance (T) of CdO thin film, it has high average transmittance (78%) in visible and near IR regions (window effect). The transmittance of the film is low for wavelengths shorter than 600 nm due to the onset of band-to-band absorption. The absorption coefficient (α) is calculated by

$$\alpha = 2.303A/d \qquad (11)$$

Where d is film thickness and the absorbance is given by $A = \log(1/T)$.

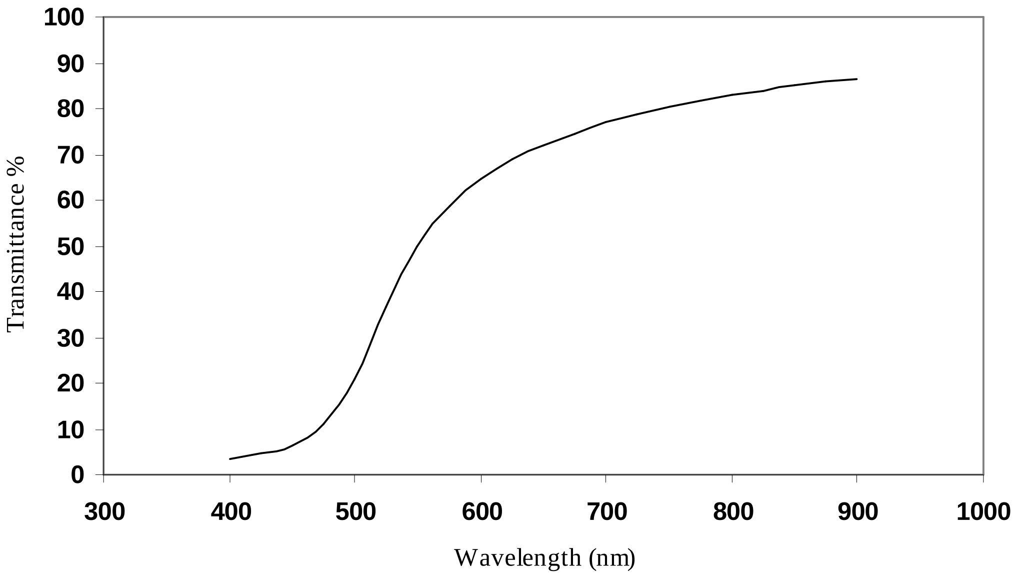


Figure4: Transmittance of CdO thin film prepared by RTO technique.

4.2 Sheet Resistance

Fig.(5) shows the variation of sheet resistance R_{sh} with etching time. The R_{sh} is monotonically increasing with etching time.

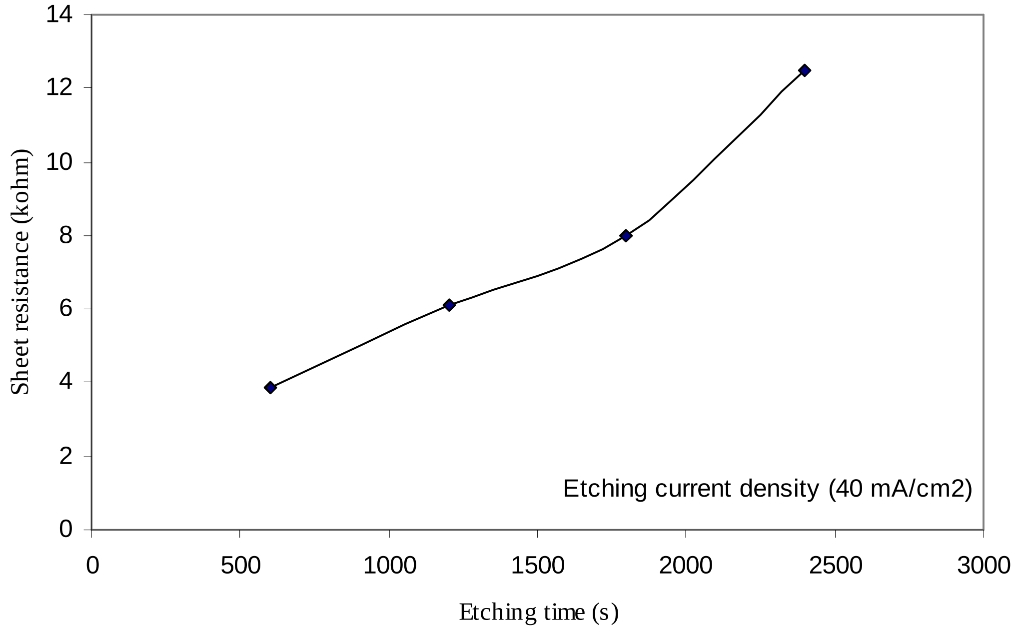


Figure5: The variation of R_{sh} as a function of etching time.

4.3 Photovoltaic Properties of CdO/porous Si heterojunction

The photovoltaic parameters (the short-circuits current I_{sc} and open-circuit voltage V_{oc}) are the most important factors in solar cells and photovoltaic detectors applications. Representing the relationship between I_{sc} and the illuminating power P on a log-log plot gives (see Fig.6) a straight line with a linearity (slope) equal to 0.27 for etching time t=2400s. The variation of V_{oc} as a function of illuminating power is presented in Fig.7 for J=40 mA/cm^2 and t=1800. It is clear that Voc is an exponential function with respect to P. Other values of V_{oc} for a constant illuminating power and variable etching time are presented in Fig.(8). It can be seen that the V_{oc} increases and has a maximum value at (t=1200s). However it decreases for a further increases of etching time.

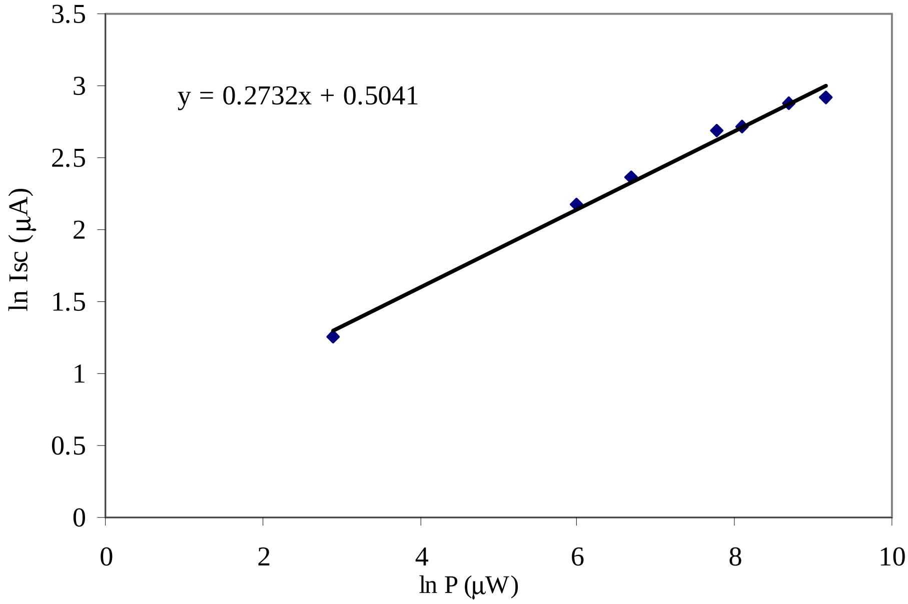


Figure6:Variation of $\ln I_{sc}$ with $\ln P$ for etching current density $J = 40\,mA/cm^2$.

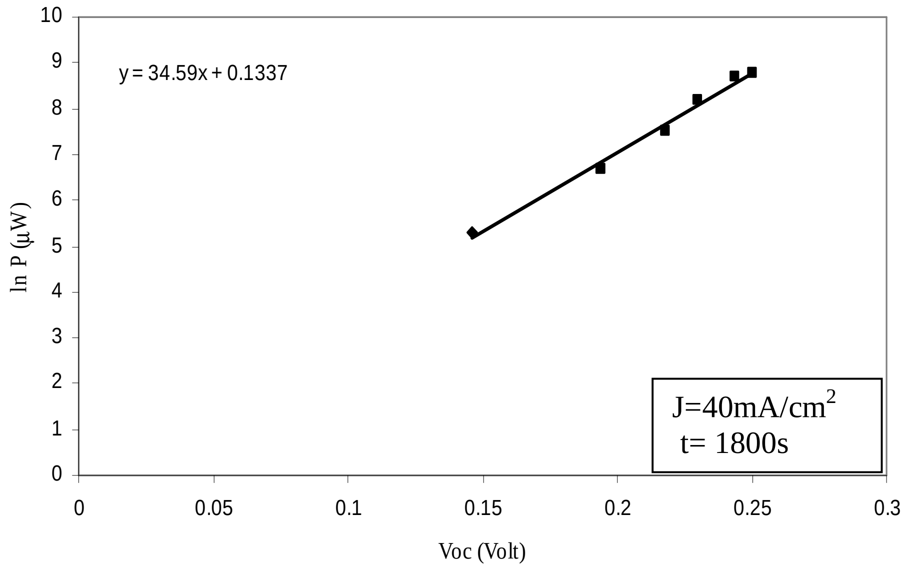


Figure7: Variation of $\ln P$ with V_{oc} for etching current density $J = 40\,mA/cm^2$.

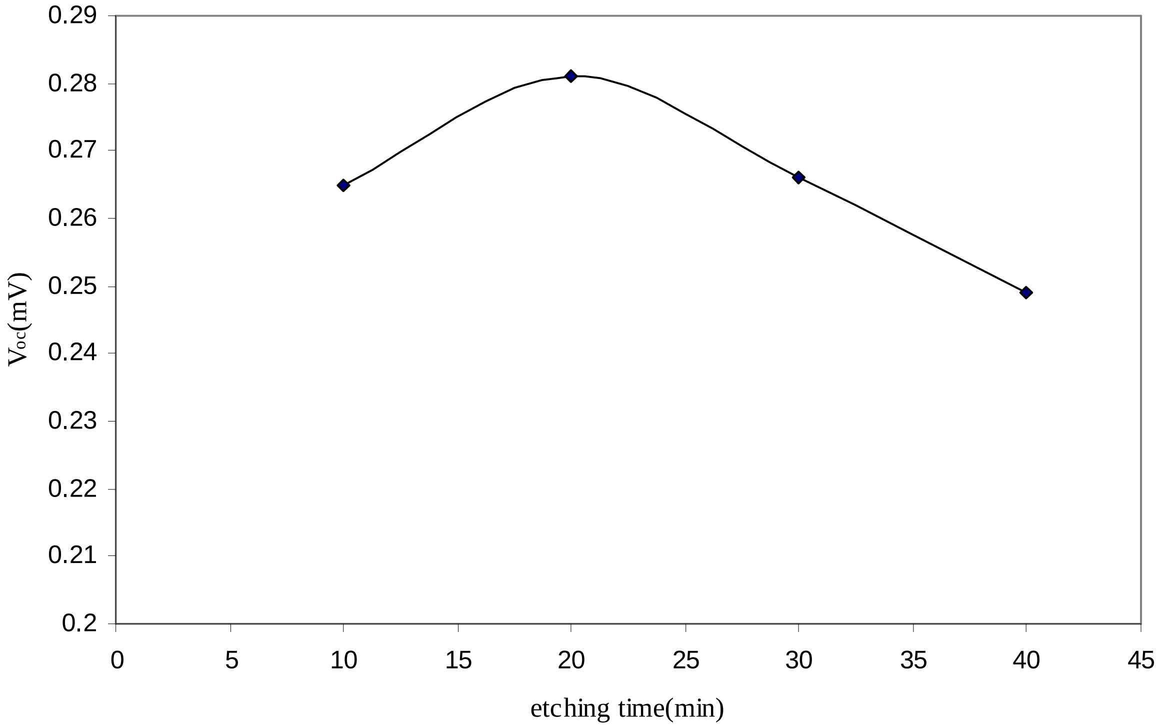


Figure8: Variation of Voc with etching time for P=0.018 mW/cm^2.

4.4 Properties of CdO/porous Si Photodiode

Fig.(9) shows the variation of the measured photocurrent CdO/PSi/Si/Al heterojunction as a function of the applied reverse bias voltage for two etching times t = 600s and t = 2400; respectively, for four different powers as indicated below. For junctions under the abrupt approximation, $\rho \approx qN_D$ for $x < W_D$, $\rho = 0$ for $x >$ W_D, the depletion width, W_D, is given by [10] $W_D = \sqrt{(2\varepsilon_s / qN_D)(V_{bi} + V_R)}$, If V_R increased, the depletion width get increased too and hence a larger number of photons can get stuck within higher electric field of the depletion region giving low recombination processes and generating a higher photocurrent.

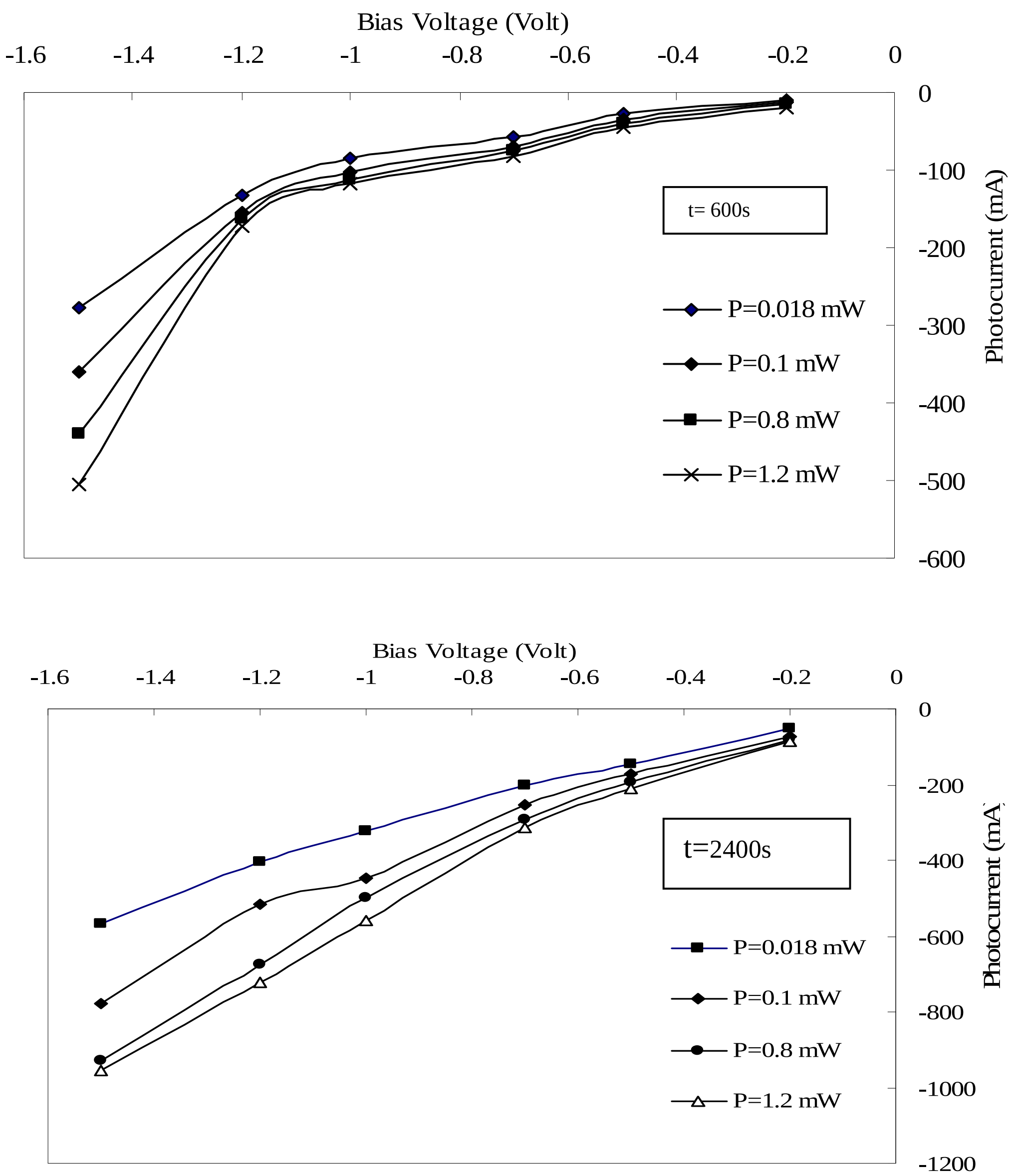


Figure9: Photovoltaic Measurement of CdO/Porous Si/Si/Al Hetreodetector

4.5 Life Time measurement

Lifetime is an important parameter in photodetector heterojunction. This parameter was measured by using Open-Circuit-Voltage-Decay technique. Figure (9) demonstrates a photograph of V_{oc}-decay curve for six. Since these samples are horizontally-diffused junction devices. Region II is generally observed in such junctions [19] as it is obvious in this Figure because, although the strobe-lamp intensity is often not sufficient to reach the high-injunction condition, it is usually enough to excite the devices to an junction level substantially higher than that which discharge of the junction capacitance limits the V_{oc} decay rate. According to this case, under these conditions the minority carrier lifetime τ can be computed from the following expression [20]:

$$\tau = \frac{kT}{q}\left|\frac{1}{dV_{OC}/dt}\right|$$

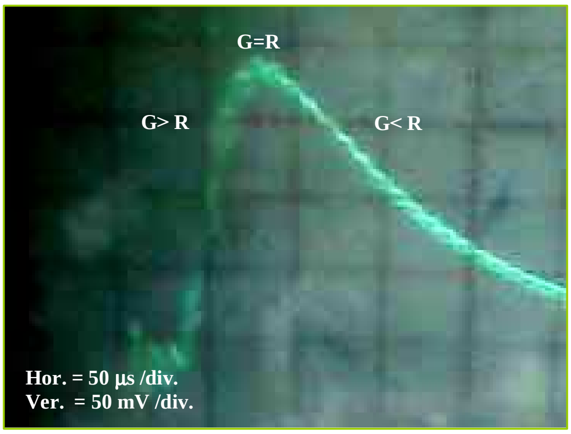


Figure10: Photo-Induced Open-Circuit Voltage Decay Photograph at ($40mA/cm^2$) Etching current density with 600s Etching time. (G: generation, R: recombination)

Increasing etching time leads to decreases lifetime as shown in Fig.(10). This can be describing to increasing of porosity percentage and in turns result in production of trapping centers crystal dislocations. The values lifetime are comparable to those for crystalline Si Solar cells. Large value of minority lifetime means high recombination losses.

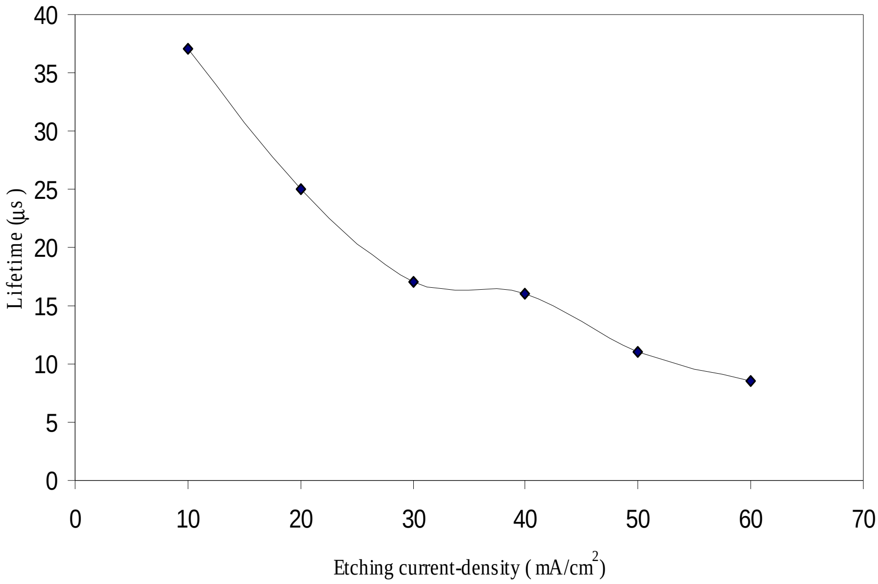


Figure11: The results of life time measured with the technique of Voc decay of minority carriers for variable etching current density.

4.6 Quantum efficiency:

The quantum efficiency is a good parameter for detector because, it is represents the ratio between numbers of electron – hole generated in the detector due to the incident light and this parameter is a function of spectral responsivity. Fig. (12) Shows the variation of quantum efficiency as a function of wavelength for porous silicon prepared at different etching time (600s, 1200s, 1800s and2400s) with constant current-density (40mA/cm^2), and is found to be (88%, 85%, 70%, and 66%) respectively. This come from the avalanche effect inside the porous silicon and later is generated by the voltage drop in porous silicon which is intrinsic and narrow as silicon wire [21].

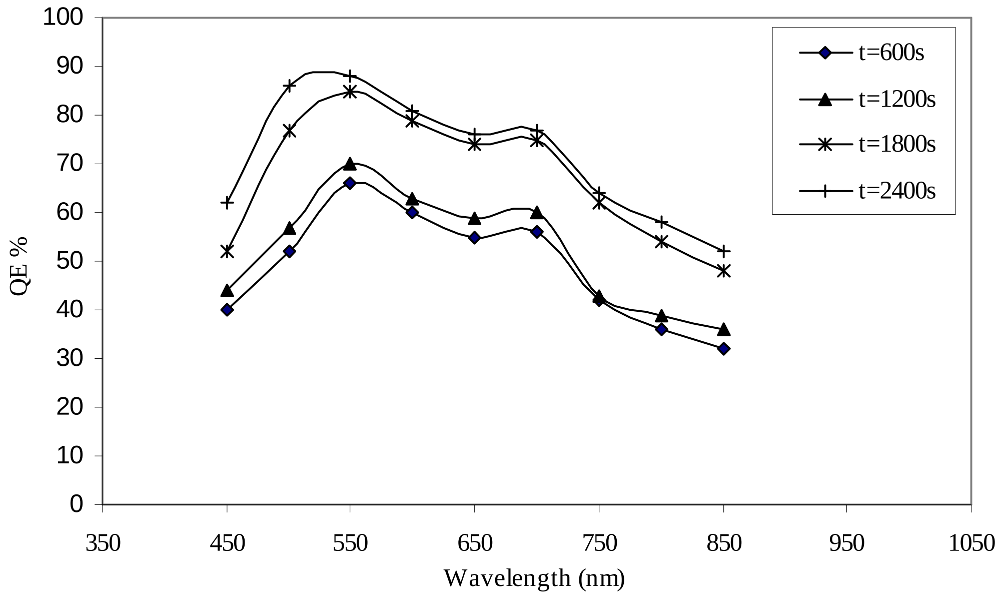
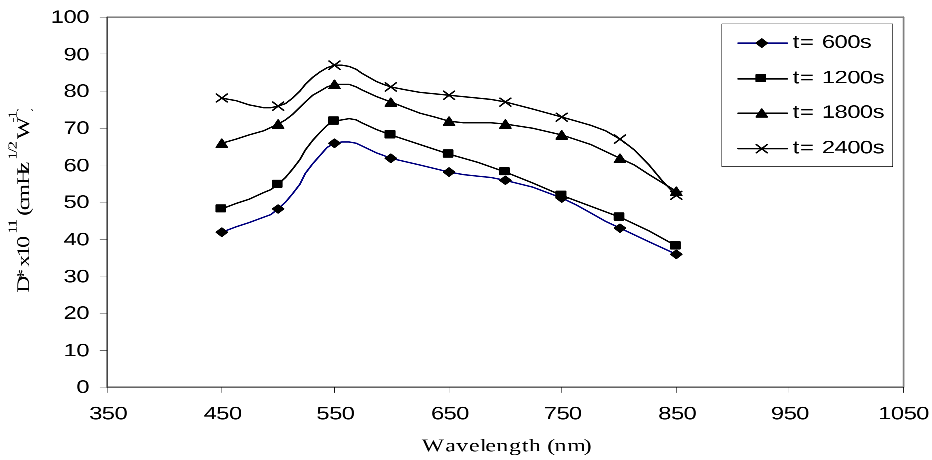


Figure 12: Quantum efficiency of CdO/Porous Silicon/Si/Al sample prepared at different etching time.

4.7 Specific Detectivity

The specific Detectivity can be calculated from the electrical current flow in detector in dark, so that represent a little power incident on detector which can be sensitive from it. We noticed from the Figure (13) increased of specific Detectivity due to decreased dark current which reduce the noise current. That figure shows a variation of specific Detectivity as a function of wavelength for (CdO/Porous Si/Si/Al) hetreodetector prepared at different etching time with constant current-density. It's found ($87*10^{11}$ cm. $Hz^{1/2}$ W^{-1}) at 550nm wavelength for (CdO/Porous Si/Si/Al) hetreodetector at $40mA/cm^2$, and its found ($82*10^{11}$ cm. $Hz^{1/2}$ W^{-1}) at 550nm wavelength for (Al/CdO/Porous Si/Si/Al) hetreodetector at $40mA/cm^2$, and its found($72*10^{11}$ cm. $Hz^{1/2}$ W^{-1}) at 550nm wavelength for(CdO/Porous Si/Si/Al) hetreodetector at $40mA/cm^2$, and its found($66*10^{11}$ cm. $Hz^{1/2}$ W^{-1}) at 550nm wavelength for(CdO/Porous Si/Si/Al) hetreodetector at $40mA/cm^2$.



Figurer13: Specific Detectivity of CdO/Porous Si/Si/Al Heterodetector Prepared by different etching time at (40mA/cm

5. Conclusions

RTO technique was used to fabricate CdO/porous Si photodetector works in the range (400-850) nm. The photodetector figures of merit were strong dependent on etching current density and etching time. Photovoltaic properties of photodetectors are investigated as function of porous silicon preparation conditions. This technique consider as promising method of simple and cheap silicon photodetector**.**

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These measurements are represented the most important measurements which describe. The performance detectors .the short-circuits current density (J_{sc}) and open-circuit voltage V_{oc} of the hetreodetector photovoltaic devices form with CdO films deposited at room temperature. The variation in V_{oc} and Current-Density at (600s) is shown in Figure () from this Figure, it can seen that V_{oc} increases and have maximum value at 30mA/cm^2, and then for a further increases current density its decreases, the variation in V_{oc} and Etching Time at (40mA/cm^2), it can seen the open-circuit voltage (V_{oc}) increases and have maximum value at (1200s etching time) and then decreases for a further increases in etching time. The variation in I-dark and current-density (at 0.6 volt) increases when increased current-density then have maximum value at 1200s etching time and then decreases for a further increasing etching time, The variation in I-dark with etching time (at 0.6 volt) increases when increased etching time continually. The variation in the current saturation (I_s) and Current-Density it can seen increases when increasing current-density, and it can seen (I_s) increasing with increasing in etching time and have a maximum value at (1200s)etching time and then decreases for a further increasing etching time.