Energy Band Diagram of FTO/porous Silicon Heterostructure

Hasan A.Hadi¹ and Raid A. Ismail²,a

¹Mustansiriyah University, Education College, Department of physics Baghdad-Iraq
²Departments of Applied Science, University of Technology, Baghdad, Iraq

a) Corresponding author: raidismail@yahoo.com

Abstract: We have proposed for the first time the energy band diagram of fluorine doped tin oxide FTO/ porous silicon PSi/ n-Si heterostructure prepared by spray pyrolysis technique and laser assist-electrochemical etching ECE. The band line-up of the heterojunction was constructed from the electrical and optical properties of FTO and porous silicon. The electrical current-voltage and capacitance-voltage measurements showed the barrier height, ideality factor and built in voltage of the heterojunction were 1.4, 0.69 V and 0.70 V, respectively. The optical energy gap and the average of the optical transmittance of FTO film were 3.6 eV and 78% respectively. The morphology of porous silicon PSi and FTO film investigated by scanning electron microscope SEM. The elemental composition of FTO film was determined using energy dispersive x-ray.

Keywords: porous silicon; photo-electrochemical etching PECE; thermal evaporation; absorption coefficient.

1. Introduction

Due to the morphology of nanoporous silicon layera and photoluminescence characteristics, porous silicon PSI considered tempting to be used in several device applications such as optoelectronics and chemical sensor.[1]. PSI deems as an engaging and appropriate material for photodetector due to its pre-eminent characteristics such as wide surface to volume ratio, it has a wide range of energy gap, and high optical absorption coefficient compared to bulk silicon [2-4]. PSI can be prepared by electrochemical etching of wafer silicon in electrolytes containing hydrofluoric acid (HF) [5]. Photo electrochemical etching PECE is one of the most extremely effective technique to form porous silicon layers. Porous structure of silicon typically contains a thickness of several microns that enables it to have a higher ratio of surface to volume compared to the bare silicon surface [6]. Porosity, thickness, pore diameter, pore morphology and distance between pores are some of the tunable properties available during fabrication [7]. The spray pyrolysis is a simple technique for growing thin films, low-cost and which can be used in large-scale production as it does not require the use of vacuum. It has been successfully used to synthesize many transparent conducting oxide films. These films are beginning to be transparent and take on some new properties such as increased transparency at certain frequencies [8]. Formation of metallic electrical contacts on the irregular and rough surface of a PSI is the prerequisite for its applications as electrically driven optoelectronic devices[9]. To get a high smart windows or transparent electrodes for photodetector and solar cell devices, a metal
conducting film is most interested by researchers because its specific properties cement many applications as a conductive layer for UV spectrum [10-12]. Transparent conducting oxides (TCO) have been used in the optoelectronic devices [13] and becoming increasingly important as critical components of a variety of thin film technologies[14] such as smart windows in heterojunction photovoltaic cells[15] and high optical transparency application[16]. The transport properties of oxidized (metal/PSi/p-Si) structures have been remarkably investigated, although relatively effective and stable electroluminescent device and photodetector structures based on oxidized PSi were fabricated [17].

Schottky barrier a potential barrier can grow from steady space charges in the semiconductor alone without the existence of a chemical layer as Schottky proposed [18]. It is fully recognized that the goodness of metal–semiconductor MS connect plays a paramount role in the work of various electronics devices. Ohmic and Schottky contacts are very important to investigate and test the electrical properties of the many semiconductor device applications [19]. At metal–semiconductor contact, a barrier higher is growing at the interface between them and it’s in charge of controlling the electrical properties such as capacitance and conduction behavior.

In this study, the energy-band schematics which clear that how to barrier height formed, and also some effects that can modify the value of this barrier [18]. It is not possible to get conduction and valence bands an aligned when they joined with different band gaps. ΔEc and ΔEv are the band offsets in conduction and the valance band which can be calculated by different methods. c-v measurement is one of the easiest electrical methods that used to located band offsets on the p or n isotype junction [20]. In the study, the junction parameters such as barrier height, ideality factor and saturation current of FTO/pours silicon have also been calculated from I–V characteristics at room temperature and the band diagram of FTO/PSi/c-Si/Al has been constructed.

2. Experimental

2.1. Porous silicon preparation

PSi layer formed by photo electrochemically etching (laser assisted PECE) n-Si wafer in (1 HF 48% : 1 99% Ethanol) electrolyte. The single-crystal Si was (100) oriented with an in the range of 7-12 Ω cm electrical resistivity.

To clean the silicon wafer, methanol and distilled water were used, ultrasonic bath and finally drying in a hot air stream. The wafer anodized at a constant etching current density of 2mA/cm² for 12 min under laser diode of 650nm wavelength and power of 53mW, the illumination carried out at room temperature. The backside electrochemical etching cell used as shown in Fig.1.a. The porous silicon layer thickness measured by weight method as reported in previous work [21]. Thickness and porosity of the PSi layers were about 132 nm and 69 % for porous silicon layer, respectively. The homemade ultimate experimental set-up electrochemical anodization process and the schematic cross section of heterostructure presented in Fig.1 a and b. Metallization on PSi also became another important area of interest, especially in Schottky diode structure. In order for ohmic contacts, a high purity of the aluminum thin film (about 117nm thickness) deposited on the c-Si substrate by thermal evaporation technique.
2.2. Fluoride tin oxide preparation:
The spray pyrolysis technique utilized to form a thin layer of fluoride tin oxide film on cleaning glass and silicon substrates. De-ionized water used to the dissolution High purity of tin chloride (SnCl4•5H2O) with a concentration of 0.1M was mixed with ammonium fluoride (NH4F) (99% purity, BHD). A few drops of hydrochloric acid added to the solution in order to prevent hydrolysis. The glass substrates used with area of 2.5 × 2.5 cm² and porous silicon with area of 1.5×1.5 cm². The temperature of the substrates were (400 ± 5 °C). The spray nozzle to the substrate distance was adjusted to be 25 cm. The duration spray was 6 s and spray period ~ 4min. The optical transmittance of ITO film was measured by uv-visible spectrophotometer in the range of 300–1000 nm. The I–V characteristics of ITO/PSi/n-Si/Al investigated using a d.c. power supply at the range of (-10 to +10) V. The current measured using a digital multimeters. The C-V characteristics measured using hp4275A-MuTi-frequency LCR meter-HEWLETT Packard at voltage ranged from -1 to 1 V at the frequency 50kHz. The photocurrent at different wavelengths investigated using a monochromatic model Jobin Yvon Division Instruments 63 in the spectral range of (400-900) nm. Power calibration performed using calibrated Si power meter. Responsivity calculated by measuring the photocurrent as function of wavelength and then divides it on power.

3. Discussion
Fig.2 showed optical photograph images of the FTO deposited on the porous silicon layer at two magnifications. It is clear in the inset the boundary of porous silicon region with circular shape. The highly magnified image reveals the FTO film deposited on entire porous surface with light brown color. As shown, the pores have different sizes.

Fig. 1: a) the set-up of homemade cell and b) thin film FTO on PSi/n-Si heterojunction

Fig. 2: Optical photograph images of the FTO deposited on the porous silicon layer at two magnifications.
Fig. 3 showed SEM photograph of FTO deposited on PSi. In Fig.3.a, the deposited film had grain with spherical shape of average grain size (26nm). The cross section of FTO-PSi interface presented in Fig.3.b. Fig.3.c reveals the film covered completely the porous.

The EDX spectrum of FTO film showed in Fig.4. It is obvious peaks related to oxygen, tin, and fluorine elements are observed.

The UV-Vis transmission and absorption spectrum of FTO film deposited on glass substrate as shown in Fig.5.a and b. The film thickness was 117 nm. As clear from Fig.5.a, the film had average optical transmittance of 75%.
The absorption edge that determined from Fig. 5-b was 330nm, which gives the energy gap of 3.75 eV. The optical gap of FTO film determined from the linear extrapolation of the most linear part of the \((\alpha h\nu)^2\) versus \((h\nu)\) plot as shown in Fig. 6. The intercept of the extrapolated line with photon energy axis is taken as the value for the energy gap \(E_g\). The absorption coefficient \(\alpha\) can be a function of photon energy \(h\nu\) when the density of states as a parabolic band at near the band edges [22]. With the aid of the following equation, the optical band gap of FTO film was 3.85 eV at room temperature [23].

\[
\alpha h\nu = A (h\nu - E_g)^m \\
\text{…………… (1)}
\]

Where \(m\) is the exponent with many values depending on the direct or indirect of the optical transition and \(A\) represents a constant.
From Fig.7, the dark current-voltage characteristic of FTO/PSi/n-Si structures at room temperature exhibit diode-like rectifying and Schottky contact between FTO film and porous silicon was formed. I–V characteristic of a practical Schottky diode was given by[24]:

\[ I = I_s \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \quad \ldots \ldots \quad (2) \]

Where (V) is the biased voltage, (I_s) is the saturation current in reverse biased, (n) is the ideality factor, (T) is the temperature, (q) is the electron charge and (k) is the Boltzmann constant. The presence of FTO/PSi contact results in the formation of Schottky type contact, due to the fact that the work function of FTO was lower than that of the porous Si. The saturation current I_s can be determined by extrapolating the semi log I versus V curve to V = 0. The barrier height $\phi_B$ of the FTO-PSi junction was calculated from the following equation [24] and found to be $\phi_B = 0.69 \text{ V}$

\[ \phi_B = \frac{kT}{q} \ln \frac{A^* A T^2}{I_s} \quad \ldots \ldots \quad (3) \]

Where $A^*$ is the effective Richardson constant and equals to 112 A/cm² K² for n-type Si , and A is the area of the heterojunction.

Fig. 7: Room temperature I-V characteristics under forward and reverse bias of FTO/PSi/n-Si/Al at dark

The range of the ideality factor value of ideal diode of (1-2). Sometimes a problem contacts or voltage dependent series resistance as shown in I-V curves which has ideality factors larger than 2 [25]. Fig.8 represented a semi logarithmic plot of current versus forward bias. The values of saturation current and ideality factor obtained for the FTO/PSi junction were found to be 40 $\mu$A and approximately 1.4 at low voltage by using following diode equation [24]:

\[ n = \frac{q}{kT} \frac{dV}{d\ln I_s} \quad \ldots \ldots \quad (4) \]

so that can be refer to the existence traps and of nonlinear MS contact as reported[26].
Fig. 8: Room temperature semi logarithm I-V plot

Fig. 9 showed the capacitance- voltage at room temperature measured at 50 kHz frequency. Through plotting $1/c^2$ versus $V$ under reverse bias, a straight line obtained indicates the fabricated heterojunction is one-sided abrupt junction. By using the following, the built-in-potential $V_{bi}$ was estimated$[27]$:

$$\frac{1}{c^2} = \frac{(2\varepsilon_0 \varepsilon_r V_{bi} - V)}{q\varepsilon_r \varepsilon_0 N_d A^2}$$

Where, $N_d$: carrier density concentration, $V_{bi}$: built in potential, $\varepsilon_r$: relative dielectric constant, $\varepsilon_0$: space dielectric constant, $C$: capacity and $A$ represent area.

It found that the extrapolation to linear curve of $C^2$ versus plot to $1/c^2 = 0$ gives the $V_{bi} = 0.7V$. The linear behavior indicates the junction was abrupt type$[28,29]$.

Fig. 9: Square of the inverse capacitance versus the applied voltage for a FTO/PSi/n-Si heterojunction
The photocurrent responses of the device were produced by the photo generation of both electrons and holes in bulk silicon for photon energies greater than 1.11 eV and in porous silicon for energies greater than 1.9 eV due to the higher porosity of layers [30]. It was clear from Fig. 10, the maximum absorption was observed at 1.9eV and it was related to absorption occurred in porous silicon region and this value called energy gap. The surface of the nanoporous silicon layer acts as film enhanced illumination absorption in the short wavelength region and also play as optimum devices for Schottky contact and as resulting that get a large photocurrent [31,32].

![Fig. 10: Photocurrent vs wavelength to FTO/PSi/and-Si heterojunction](image)

The saturation current variation with reciprocal operating temperature was given in Fig.11. The saturation current increased as temperature increase due to excitation of many electrons from valence band to conduction band.

![Fig. 11: Plots of Log (I_s) vs. the reciprocal of T](image)
The values of band offsets $\Delta E_{c}$ and $\Delta E_{v}$ determined from the following equations [20]

$$
\Delta E_{c} = x_{\text{PSi}} - x_{\text{FTO}} \quad \text{......... (6)}
$$

where $x_{\text{PSi}}$ and $x_{\text{FTO}}$ were the electron affinities of Si and FTO respectively and there value about (4.05eV and 4.55eV) from Eq.(6). $\Delta E_{c}$ was calculated to be 0.5 eV. The valence band offset can be determined from Eq.(7)[20]

$$
\Delta E_{v} = E_{\text{gFTO}} - E_{\text{gPSi}} - \Delta E_{c} \quad \text{......... (7)}
$$

where $E_{\text{gFTO}}$ and $E_{\text{gPSi}}$ represent the energy gap of FTO and Si respectively. When porous silicon formed, so the band gap energy increased [32]. Fig.11 showed the energy band diagram for FTO/PSi heterojunction.

![Energy-band diagram of FTO/PSi heterojunction](image)

**Figure 11:** Energy-band diagram of FTO/PSi heterojunction (A) and (B), Schottky Barrier High model indicated are the Fermi levels and built in voltage (C), and cross section of metal semiconductor metal MSM (D)

### 4. Conclusion

In this study, it was successfully prepared FTO/PSi heterojunction by deposition of FTO thin film prepared by spray pyrolysis on the porous silicon prepared by laser-assisted electrochemical etching techniques. The electrical, optical, and structural properties of FTO were inspected. The I-V and C-V characteristics of the FTO/PSi heterojunction were measured. The barrier height and ideality factor of FTO-PSi contact were found to be 0.69eV and 1.4, respectively. The energy band diagram of FTO/PSi was constructed after determining the values of $\Delta E_{c}$ and $\Delta E_{v}$.
References:

[1] Adrian K, Xiao S 2019 Adv. Mater. Technol. 4 1800334
[2] Raid A. Ismail, Effect of etching time on the characteristics of low resistivity porous Si devices, 2013 Mod. Phys. Lett. B 27, 1350217
[3] Hasan A. Hadi, Raid A. Ismail , and Nahida J. Almashhadani 2019 Journal of Inorganic and Organometallic Polymers and Materials, doi.org/10.1007/s10904-019-01072-9.
[4] Severiano F, García G, Castañeda L , Gayou V. L 2017 Journal of Nanomaterials 2017 1629702 , doi.org/10.1155/2017/1629702 .
[5]. Michael J. Sailor: Porous Silicon in Practice: Preparation, Characterization and Applications: Wiley-VCH Verlag GmbH & Co. KGaA 2012.
[6] Utpal Saha, Control of Pore Characteristics of Porous Silicon Using Non-toxic Electrochemical Etching for Photovoltaics and Supercapacitor Applications. 2017, A thesis Master of Science,South Dakota State University.
[7] David M, Sánchez, Salvador P-A and Jaime G-R 2019 Proceedings 4, 14-20
[8] Yu.P Bliokh 2006 Optics Communications 259 436-444
[9] Yuan M. Huang, Fu-fang Z, Bao-gai Z. , Lan-li C 2008 Solid State Ionics 179 1194-1197
[10] Golan G, Axelevitch A 2000 Microelectronics Journal 31 469-473
[11] Khan M.S.R. , Reza A 1992 Appl. Phys. A 54 204-207.
[12] Axelevitch A, Gorenstein B, Golan G, 2012 Physics Procedia 32 1 -13
[13] Bilgin V , Akyuz I., Ketenci E., Kose Atay S. 2010 Applied Surface Science,256 6586–6591.
[14] Arca E., Fleischer K 2012 ,Thin Solid Films 4 23 , doi: 10.1016/j.tsf.2011.09.016
[15] Yadav A. A., Masumdar E.U., Moholkar A.V., Rajpure K.Y, Bhosale C.H 2009 Physica B 404 1874-1877
[16] Ait Aouaj M. , Diaz R., Belayachi A., Rueda F., Abd-Lefdl M 2009 Materials Research Bulletin 44 1458-1461.
[17] Felipe A Garc´es, Raul Urteaga, Leandro N Acquaroli, Roberto R Koropecki,, Roberto D Arce 2012 Nanoscale Research Letters 7 419.
[18] S. M. Sze and K. N. Kwok : Physics of Semiconductor Devices: Wiley & Sons, Inc., Hoboken, New Jersey (2007)
[19] Sheng S. Li: Semiconductor Physical Electronics: Springer Science Business Media, LLC2006.
[20] Dieter k. Schroder : semiconductor material and device characterization: wiley & sons, inc., publication2006.
[21] Hasan A. Hadi 2018 International Letters of Chemistry, Physics and Astronomy 80 30-39
[22] Jai S :Optical Properties of Condensed Matter and Applications: John Wiley & Sons Ltd, England2006
[23] S. M. Sze : Physics of Semiconductor devices : Wiley eastern limited New Delhi. 1979
[24] Hasan A. Hadi,2014, Materials Focus, 3,1–6
[25] Angus R : the Materials Science of Semiconductors:Springer Science- Business Media, LLC2008.
[26] Hea J. H, Ho C. H 2007 Applied Physics Lett. 91 233105
[27] Hasan A. Hadi1 and Intesar H. Hashim (2014), Journal of Electron Devices, 20, 1701-1710
[28] Raid A. Ismail, Khawla S. Khashan Rana O. Mahdi 2017 Materials Science in Semiconductor Process. 68 252-261.
[29] Ismail R 2010 e. J. Surf. Sci. Nanotech. 8 388-391
[30] Ismail R., Abdulrazzaq O. Yahya K 2005 Surface Review and Lett. 12, 515-518
[31] Kuen H. Wu, Chong-Wei L 2015 *Materials* 8, 5922-5932, doi:10.3390/ma8095283
[32] Seyyedeh M Banihashemian, Hassan H, Alireza E, Majidreza A, Mansor M, Seyed M Mosakazemi 2010 *Sensors* 10, 1012-1020, doi:10.3390/s100201012