Effect of SnS thin film on the performance of porous silicon photodiode

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Abstract. In this study, Al/SnS/PS/n-Si/Al photodiode was fabricated and investigated. SnS thin film were prepared by thermal evaporation technique on porous silicon layer which prepared by anodization technique at 32mA/cm² etching current density and etching time 15min. The characteristics of porous silicon and SnS were investigated by using x-ray diffraction XRD, atomic force microscopy AFM, Fourier transformation infrared spectroscopy FT-IR.

Dark and illuminated current-voltage I-V characteristics, spectral responsivity, specific detectivity of photodiode were investigated after depositing. Significant improvement in photosensitivity and detectivity of porous silicon photodiode after SnS deposition on porous silicon was noticed.

1. Introduction

SnS thin films with band gap energy of 1.3 eV have great potential use in many applications. SnS films are highly suitable for a number of solid state devices, such as photovoltaic [1–5], photo-electrochemical (PEC) [6], photoconductive cells [7], and intercalation battery systems [8]. In addition, SnS thin films have a large optical absorption coefficient ($>10^4$ cm⁻¹) and high photoelectric conversion efficiency ($>24\%$) [9] for the fabrication of heterojunction solar cells. Recently, a survey on the ores of tin sulphide have been done by Reddy *et al.* [10] indicates that SnS compound could be used for photovoltaic application as an alternative material. These films can be prepared by different techniques, such as plasma enhanced chemical vapour deposition (PECVD) [11], vacuum evaporation [12], chemical bath deposition [13], spray pyrolysis [14], electrodeposition [15]. In this paper, we report on the preparation and characterization of thermally evaporated SnS thin films on porous silicon PS in order to study their suitability for the device application.

2. Experimental work

Samples used in this study are boron doped crystalline silicon (c-Si) wafers (thickness 508 ± 15 μ m and resistivity 1.5-4 Ω .cm grown by Czochralski (CZ) method in (100) orientation. The wafer was first dipped in 10 % HF to remove the native oxide. The back side of the wafer was covered with wax. The porous layer was formed by Photoelectrochemical etching (anodization) in ethanoic hydrofluoric acid solution at a current density of 32mA/cm for 15 min in dark conditions at 300K. Ethanol was often added to evacuate the H bubbles.

High purity (99.99%) SnS thin film was deposited on the n-PSi substrates by thermal evaporation system type (Edwards) at 10⁻⁶ mbar, thickness 200 nm. The bottom of PSi and above of SnS electrodes is coated with thick aluminum layer to measure the electrical properties as shown in figure 1:

Fig 1: Images for PS/Si and Al/SnS/PS/n-Si/Al photodiode

The structural, morphological and optical properties of porous silicon and SnS were investigated separately by means of (CuK α) XRD-6000, Shimadzu x-ray diffractometer, Fourier transformation infrared spectroscopy, JEOL (JSM-5600) scanning electron microscopy, Philips CM10 pw 6020 transmission electron microscopy, Angstrom AA 3000 atomic force microscopy and Cary 100 Conc plus UV-Vis spectrophotometer. The spectral photosensitivity of the doped and undoped photodetectors was measured in the range of 400-950 nm by using a monochromator, and a Sanwa silicon power meter was used for monochromator calibration. For capacity measurements, a 5 Hz-13 MHz impedance analyser was used. The (I-V) measurements, two electrometers and a 25 V power supply were used. The spectral responsivity of *Al/SnS/PS/n-Si/Al photodiode* was investigated by using a monochromator after making power calibration with standard silicon power meter. All the above characteristics are investigated at room temperature.

3. Results and discussion

3. a porous silicon studies

Figure 2 shows X-ray diffraction of crystalline silicon and PS samples. A peak of PSi at 32mA/cm² current density shows a splitting peak at $2\theta = 33.5^\circ$ oriented only along the (211) direction is observed confirming the monocrystalline structure of the PS layer which belongs to the (211) reflecting plane of Si of cubic structure (according to ICDD N 1997 and 2011 JCPDS).

Fig. 2: XRD spectra of c-Si and PSi samples anodized for 15 min etching time and 32mA/cm² anodization current density.

The intensity of the porous silicon peak decreases when the crystal size is reduced toward nanometric scale, then a broadening of diffraction peaks is observed, as compared with c-Si peak, and the width of the peak is directly correlated to the size of the nanocrystalline domains. This result is ascribed and listed in Table (1).

Table 1: Calculated crystallite size, average grain size, dislocation density and strain for PSi prepared at 15min etching current .

Current density (mA/cm ²)	2 Θ (deg)	FWHM (deg)	D (nm)	Dislocation density (lines.m ⁻²) $\times 10^{14}$	Strain $\times 10^{-3}$ lines ² m ⁻⁴
32	33.5	0.217	39.93	6.27	9.06

AFM image of PS prepared on n-Si wafer give the formation of uniform porous structures on the silicon wafer. The topographical properties of the PS samples prepared with current density 32mA/cm² at 15min etching time are shown in figure (3), which shows 3D images and Granularity accumulation distribution charts of the anodized PS. We can observe from this figure that the average diameter is about 41.08 nm. The surface morphology of the n-PSi layer investigated by the AFM analyses is shown very smooth and homogeneous structures .The average roughness is 0.7nm and the RMS is 0.842nm, while the Porosity equal to 62%.

Fig. 3: 3D AFM images of n-PS surface and Granularity accumulation distribution chart of PS prepared at 15min and different etching current densities

Surface chemical composition of PSi is best probed with Fourier Transform Infrared (FTIR) spectroscopy. Figure (4) shows the FTIR spectra for PS layer. A strong broad band is observed at about 1071 cm⁻¹ and 1080.17 cm⁻¹ due to Si-O-Si asymmetry stretching vibrations mode in PSi , which are dependent on the oxidation degree of porous silicon. The transmittance peak at 624.94 cm⁻¹, 638.46 cm⁻¹ , 873 cm⁻¹ , 2088.98 cm⁻¹, 2114.05 cm⁻¹and 2260.65 cm⁻¹ Si-H bending in (Si₃SiH), 908.47 cm⁻¹ Si-H₂ scissor mode. The transmittance peak at 1705.07 cm⁻¹ related to C-O.

Fig. 4: FTIR spectra of the sample prepared at 15 min for 32mA/cm2 etching current density.

PL spectrum of the PSi/p-Si heterojunction formed at the current density $32\text{mA}/\text{cm}^2$ at 15min etching time indicating emission peak 744nm as shown in figure (6), the PL peak are related to the S-band emission, an emission for the fixed excitation wavelength at 380nm.

Fig. 5: PL spectra for p-PSi prepared at 15 min etching time and $32\text{mA}/\text{cm}^2$ current density.

Increase of current density $32\text{ mA}/\text{cm}^2$ leads to increase the porosity and thereby produces large porous structures, which leads to brighter PL at shorter wavelengths, and this may be attributed to the luminescence from the confined silicon structures. The silicon structure size on the surface clearly decreases by increasing the porosity. Size dependency of the PL energy, which explains the efficient luminescence[10].

3.b SnS thin film studies

X-ray diffraction patterns of SnS thin film prepared at 200°C temperatures are given in Figure 6. The figure shows crystalline peak at $2\theta=31.6^\circ$, corresponding to the (111) plane of orthorhombic crystal structure, compared to JCPDS card 33-1375 for herzenbergite SnS [16]. The spectrum reveal the presence of traces of other phases along with predominant SnS phase. Degree of crystallinity was also found at 200°C temperature. The XRD spectrum of films grown at lower 200°C temperatures showed presence of both SnS_2 and Sn phases, along with dominant SnS phase.

Fig. 6: XRD spectra of SnS thin film.

The SnS films deposited on glass by thermal avaporation and annealed at 200°C . XRD spectra relieve the the surface has a good crystallinity. The height of (111) peak in X-ray diffraction pattern for SnS thin films prepared at annealing temperature of 200°C are found to have sharper peaks with small FWHM data. The average crystallite size has been calculated the Debye–Scherrer formula [16]:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where D is the mean crystallite size, β is the full width at half maximum (FWHM) of the diffraction line, θ is the diffraction angle, and λ is the wavelength of the X-ray radiation. The dislocation density δ can be evaluated from Williamson and Smallman's formula, δ [lines/m²] :

$$\sigma = \frac{1}{D^2} \quad (2)$$

The microstrain ε can be obtained using the relation:

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

The crystallite size, dislocation density and microstrain were 65.44 nm, 2.3×10^{14} (lines/m²) and 18.56×10^{-4} respectively.

The SEM picture of SnS thin film deposited at 200 °C for 1 h is shown in Figure 7. It was seen that the film had a needle shape grain structure without cracks on the surface. The grains crystallization was relatively good, grain sizes were almost near and the surface was uniformly covered. Surface properties observed have a strong effect on the optical properties of the thin film such as transition, absorption, and reflection. When such a surface morphology is formed on the surface of gas sensor or solar cell, it provides an extensive surface area for reaction[7].

Fig.7 : SEM micrograph of SnS thin film.

Figure 8 shows AFM images of SnS thin film deposited on glass substrate at 200 °C. The SnS film shows a granular morphology with good pyramid-like crystal structure and tightly bonded well formed dense network. These grains are oriented uniformly with nearly equal size. The composition analysis of the SnS film showed that the average diameter, roughness density and RMS were 55 nm, 0.534 nm 0.556 nm respectively.

Fig. 8: 2D and 3D AFM images of SnS thin film .

Hall measurements that reveal that the resistivity for the deposited SnS films have high resistivity. However, we managed to obtain resistivity of the sample, which is $4.02 \times 10^5 \Omega \text{ cm}$. It is much higher than the resistivity for solar cell applications, which ideally should be around $(1-10) \Omega \text{ cm}$.

The values of optical transmittance in the range from 300-900nm and a plot of $(\alpha h\nu)^2$ against $(h\nu)$ of SnS thin film were used to obtain direct band gap values. Figure (9) showed an increase in indirect band gap of SnS thin films. We conclude that the concentration of complexing agents has the effect on direct band gaps as they control the rate of release of Sn^{2+} ions and hence modify the structural properties.

The deposited SnS film had shown high absorption coefficient, $> 10^5 \text{ cm}^{-1}$, above the fundamental absorption edge. Single phase SnS thin films deposited at 200°C have shown the presence of direct optical band gap at 2.4 eV. These nearly stoichiometric, single-phase and highly absorbing SnS films with a direct optical band gap of 1.36 eV could be used as an absorber in the fabrication of thin film heterojunction photovoltaic devices.

Fig. 9: $(\alpha h\nu)^2$ versus photon energy plot and inset is transmission spectrum of SnS thin film.

3.c Al/SnS/PS/n-Si/Al Photodetector Properties

Figure 10 shows the dark current-voltage (I-V) characteristics in forward and reverse direction of Al/SnS/PS/n-Si/Al and Al/PS/n-Si/Al photodiodes. The current in forward direction has increased after deposited SnS thin film due to increase the charge which transfer between PS layer and Al electrode.

Fig. 10: Dark I-V characteristics of Al/SnS/PS/n-Si/Al and Al/PS/n-Si/Al photodiodes

Figure 11 shows the dark (I-V) characteristics in reverse direction of Al/SnS/PS/n-Si/Al and Al/PS/n-Si/Al photodiodes under 8mW/cm^2 light illumination. The photocurrent in reverse direction has increased after deposited SnS thin film due to increase the increase of absorption coefficient and carriers diffusion length [17] of the photo-induced carriers from SnS thin film to PS.

Fig. 11: Illuminated I-V characteristics of Al/SnS/PS/n-Si/Al and Al/PS/n-Si/Al photodiodes.

Figure 12 shows a linear relation between inverse of square of capacitance ($1/C^2$) reverse bias voltage for Al/PS/n-Si/Al and Al/SnS/PS/n-Si/Al, indicating abrupt junction. The built-in potential V_b value were obtained after extrapolating the ($1/C^2$) point to the voltage axis. The built-in potential V_b for PS/n-Si was 1.1 volt but it was decreased to the 0.3 volt for SnS/PS/n-Si. The value of V_b are expected to depend on the Fermi level position in the conduction band at high concentrations for SnS thin film and this behavior is attributed to the increasing of depletion region width, leading to the decrease the capacitance at the junction sides.

Fig. 12 : $1/C^2$ versus reverse voltage of Al/SnS/PS/n-Si/Al and Al/PS/n-Si/Al photodiodes.

Figure 13 shows the spectral responsivity and spectral detectivity (inset) of Al/SnS/PS/n-Si/Al photodiode is investigated in the wavelength range from 400 nm to the 900nm with 5 volt bias, which is calculated by following equation :

$$R_{(\lambda)} = \frac{I_{ph}}{p_{in}} \quad (4)$$

Where I_{ph} is the photocurrent and p_{in} is the input power.

The spectral responsivity is an important function to know how much detector signal will be available for application [18].

Fig. 13: Spectral responsivity as a function of wavelength of SnS/PSi/n-Si photodiode .

The SnS/PS/n-Si sandwich structure (photodiode) has two peaks located at about 550 nm represented the absorption edge of SnS/PS as shown in figure 14(a) and the other one located at 750nm related to the PS/n-Si as in figure 14(b)

Fig. 14: Spectral responsivity as a function of wavelength of SnS/PSi/n-Si photodiode,(a) the absorption edge of SnS/PS and (b) the absorption edge of PS/n-Si .

Figure 15 shows spectral detectivity as a function of wavelength(400nm-900nm).this figure shows that it is depended directly to the spectral responsivity and calculated by the following equation [18]:

$$D_{(\lambda)} = R_{(\lambda)} \left(\frac{A^{1/2} \Delta f^{1/2}}{I_n} \right) \quad (5)$$

$$I_n = \sqrt{2q I_d \Delta f} \quad (6)$$

where Δf is the noise bandwidth, I_n is the noise current and A is the area of the detector. A detectivity of photodiode is about $9.8 \times 10^{12} \text{ cm} \cdot \text{Hz}^{-1} \cdot \text{W}^{-1}$ at 793 nm was obtained when detector was biased to -5V

Fig. 15: Spectral detectivity as a function of wavelength of SnS/PSi/n-Si photodiode .

4. Conclusion

A simple and efficient approach to improve the photo-detective of porous silicon PS prepared by photoelectrochemical method via deposited SnS layer on PS by thermal evaporation technique. Deposition of SnS on porous silicon (PS) gives suspensions photodetector characteristics enhanced the properties porous photodetectors and the spectral responsivity $R_{(\lambda)}$ of Al/SnS/PS/n-Si/Al photodetector is around 0.7 A/W at ≈ 750 nm wavelength due to the absorption edge of silicon and around 0.3 A/W at ≈ 400 nm wavelength due to the absorption edge of SnS thin film. The maximum value of the specific detectivity $D_{(\lambda)}$ is found to be $9.8 \times 10^{12} \text{ W}^{-1} \cdot \text{cm} \cdot \text{Hz}^{-1}$ located at 793 nm wavelength for Al/SnS /PSi/Si/Al photodetector prepared by 32 mA/cm² current density for 15 min aching time and the SnS thin film.

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