Electrical characterization and solar light sensitivity of SnS$_2$/n-Si junction

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ABSTRACT: In this study, the SnS$_2$ thin film deposited by spray pyrolysis technique has been analyzed by XRD, SEM and UV-visible characterization techniques to investigate of structural, morphological and optical properties. The thin film has dominant (001) and (002) crystallographic planes, compact grain-like morphology with uniform and good coverage surface and 2.42 eV band gap. The Sn/SnS$_2$/Si/Au-Sb structure has been characterized by electrical measurement. The diode has ideality factor of 1.34 and barrier height of 0.762 eV with reverse-bias current temperature-dependent strongly. In addition, the ITO/SnS$_2$/Si/Au-Sb structure has been characterized by 1.5 AM solar simulator for determination of solar light sensitivity. The diode under 100 mW/cm$^2$ solar-light source has exhibited 0.24% PCE with $J_{sc}$ of 1.83 mA/cm$^2$, $V_{oc}$ of 0.46 V and FF of 0.28.

Keywords: Tin sulfide (SnS$_x$), Silicon, diode, sputtering, responsivity

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INTRODUCTION

The binary metal-chalcogenide (M_xV_y) semiconductor materials such as SnS, SnS_2, ZnS, CdS and In_2S_3 are important for today’s technological developments due to critical and specific properties. For example, some critical properties of the materials are high optical transparency with wide band gap, controllable carrier density with metal/chalcogenide ratio, high electrical conductivity with high mobility, low ionization potential with high valence band and peculiar optical- and electrical-properties thickness-dependent with two-dimensional (2D) growth feature (Pyeon et al., 2018). Furthermore, the wide band gap chalcogenide (WBC) semiconductors are of particular importance among others for future transparent-electronic technology such as solar cell, light emitting diode and transistor applications (Johny et al., 2018).

In particular, the SnS_2 has attracted considerable interest of researchers in recent years due to n-type electrical conductivity (Kim et al., 2018), non-toxic (Dong et al., 2018), wide band gap (Huanga et al., 2017), high absorption coefficient (Chalapathi et al., 2017), high surface activity (Kumar et al., 2019), earth-abundant and cost-effective properties (Hu et al., 2019). Therefore, this material with these properties is suitable some critical opto-electronic application such as optical and transparent gas sensor for sensing NH_3, H_2S and alcohols (Anitha et al., 2018) and an buffer layer in the n-CdS/p-SnS heterojunction solar cell instead of the CdS toxic-layer (Chalapathi et al., 2017). Furthermore, the Sn/S ratio allows change in conductivity type as p-type SnS and n-type SnS_2. Thus, the p-SnS/n-SnS_2 hetero junction solar cell or photo-sensor can be developed. A theoretical calculation revealed that the power conversion efficiency (PCE) of these solar cells can be reach 25% (Voznyi, Kosyak, Onufrijevs et al., 2016). In addition, magnetic properties at room temperature can easily be gained to 2D layered WBCs with doping magnetic atom such as Fe, Co and Ni (Li et al., 2017). These magnetic 2D layered WBC materials are suitable for applications of spintronic such as high-resolution and high-sensitivity magneto-optic microscopy. Vijayakumar et al. have studied on characterization of SnS_2 thin films prepared at different substrate temperature using spray pyrolysis technique (Vijayakumar et al., 2011). Interestingly, the film band gap has decreased from 2.80 eV to 2.6 eV with increasing substrate temperature. In addition, the electrical resistivity in dark and in light has shown significantly decrease from 5.95x10^3 Ωcm to 2.22x10^3 Ωcm and from 1.48x10^3 Ωcm to 0.55x10^3 Ωcm, respectively. This result suggests that SnS_2 thin film could be an alternative photo-active material for optical transistor channel as well as solar cell.

The SnS_2 thin films have been reported using various preparation process including thin film growth technic such as molecular beam epitaxy (MBE) (Schlaf et al., 1995), vacuum evaporation (VE) (Shi et al., 2012), spin-coating (Orletskyi et al., 2018), chemical bath deposition (CBD) (Li et al., 2011), chemical vapor-deposition (CVD) (Ye et al., 2017), plasma chemical vapor deposition (P-CVD) (Sanchez-Juarez et al., 2005) and spray pyrolysis technique (SP) (Kumar et al., 2017). Compared with other thin film deposition techniques, the SP technique allows some crucial advantages to obtain final desired material such as nano-film, clusters, porous-film and high density packaged film. In the non-vacuum SP system, controllable parameters as spray energy, gas flow pressure, sprayed drop size, substrate temperature allow the desired design and synthesis of various functional materials with composition and morphology (Leng et al., 2019).

In this study, the SnS_2 thin film has been deposited by the SP technique. The structural, morphological and optically demonstrated SnS_2 thin film has been used to obtain Sn/SnS_2/Si/Au-Sb and ITO/SnS_2/Si/Au-Sb structures. The interlayer and solar light sensitivity performance of Sn/SnS_2/Si/Au-Sb and ITO/SnS_2/Si/Au-Sb structures has been analyzed respectively.
MATERIALS AND METHODS

First, a cleaning process was applied to purify the surface of the substrate from organic impurities. While the glass substrate was cleaned with ethanol, the n-Si substrate was cleaned by using the RCA cleaning procedure (in boiling NH₃+H₂O₂+6H₂O solution for 10 min and then in HCl+H₂O₂+6H₂O for 10 min at 60 °C). For the Si substrate, the ohmic contact was obtained by thermally evaporating Au-Sb alloy on the back side of Si. After the deposition, the substrate was annealed at 420 °C for 3 min in N₂ atmosphere.

Second, the SnS₂ thin film was deposited onto the Si substrate by spray pyrolysis technique. The solution was prepared using Sn (II) chloride dihydrate (SnCl₂·2H₂O) and thiourea (CS(NH₂)₂) powders from Sigma-Aldrich purchased. The thin film has been deposited using solution consist of the SnCl₂·2H₂O and the CS(NH₂)₂ in de-ionized water and 37% chloric acid, respectively. The molarities of both solutions were 0.1 M. The solution was sprayed at a 1.5 ml/min rate for 6 mins onto the pure side of Si at 350 °C. The pressure of the carrier gas (dry oxygen) is 0.7 bar and the distance between nozzle and substrate is 25 cm. The Sn metal was evaporated on SnS thin film to obtain the Sn/SnS₂/n-Si/Au-Sb structure. On the other hand, for testing solar light sensitivity, the indium tin oxide (ITO) was sputtered by RF magnetron sputtering system on the SnS₂/n-Si/Au-Sb as top transparent contact. The source material is a commercial 99.99% pure ITO target having a radius of 2 inch and thickness of 0.25 inch from Kurt J. Lesker Company. Throughout the sputtering process, 99.999% pure Ar was used as a plasma gas. The distance between target and substrate is 6 cm and RF power is 100 W. The contact area is 7.85x10⁻³ cm² for the both contact (Sn and ITO). The experimental process is given schematically in Figure 1.

The structural characterization was carried out by X-ray Diffraction (XRD) measurement system, Rigaku D/Max-IIIC diffractometer with Cu:Kα radiation. The surface morphology of the films was scanned by a Scanning electron microscope (SEM), Zeiss Sigma 300 instrument. Perkin-Elmer Lambda2S UV-visible spectrometer was used to obtain optical absorbance spectrum of the thin film. The I-V measurements of the device were carried out using Leybold Heraeus closed-cycle helium cryostat with KEITHLEY 487 Picoammeter/Voltage Source. In addition, the current density-voltage (J-V) characteristic under illumination were tested by a solar simulator system (Sciencetech SF300–100 mW/cm²) under AM 1.5G one sun illumination. It is calibrated using a certified silicon reference cell, with a Keithley 2400 source-meter unit inside the glove box.

Figure 1. The schematically illustration of the experimental processes.
RESULTS AND DISCUSSION

Figure 2(a) shows XRD pattern of SnS$_2$ films deposited on the Si. In addition, the Figure 2(b) shows XRD pattern of the film deposited on the glass. According to the patterns, dominant peaks at 14.89° and 31.81° (at 31.69° in the film deposited on glass) correspond to reflections from the (001) and (002) crystallographic planes of hexagonal phases, respectively (Seo et al., 2017; Voznyi, Kosyak, Opanasyuk et al., 2016). The values of Full Width at Half Maximum (FWHM) of the dominant peaks have determined to obtain average grain size. The FWHM values are determined to be 2.16 and 0.17. The average crystal size is calculated from well-known Scherrer’s equation,

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  

(1)

where $\lambda$ the x-ray wavelength, $\beta$ the value of FWHM and $\theta$ the diffraction angle of the dominant peak. The calculated average grain sizes are 3.82 nm and 50.12 nm, respectively. On the other hand, the weak peaks have been also observed at 30.64°, 38.94°, 44.51°, 47.64°, 54.43°, 56.13° and 66.29° correspond to reflection from (011), (311), (411), (112), (312), (321), (411) and (800) planes belong to orthorhombic structure of the SnS crystal (Reddy and Kumar, 2016, Ju et al., 2019). Besides, the (202) plane of the orthorhombic phase of Sn$_2$S$_3$ has been observed in the film deposited on glass (Voznyi et al, 2016). Furthermore, diffraction peak of (310) crystallographic plane belong to the SnO phase (Janardhan et al., 2018) has been observed at 61.66 in the films deposited on the Si. The SnO may be form in interface between Si and SnS$_2$ due to oxides surface of Si and/or high amount of Sn in the solution. The Sn element has high reaction potential with oxygen and thus the excess elements are reacted with oxygen to form the SnO phase (Chen et al., 2008).

![Figure 2. XRD patterns of the SnS$_2$ thin film deposited on the Si (a) and glass (b) substrates.](image)

The morphology of the top surface of the SnS$_2$ thin film is presented with SEM image in Figure 3. The image shows a compact grain-like growth with uniform and good coverage surface morphology. In the solution based process, substrate, solution and annealing temperatures are crucial parameters for crystallinity and morphology. For example, the surface morphology features of as-deposited and annealed SnS$_x$ thin films have been reported (Reddy et al., 2018) and the cross-sectional view and SEM image showed that the annealing temperature has caused changing morphology with increasing temperature from 300 °C to 400 °C. The morphology has a hexagonal flake-like structure at 300 °C, a
completely covered hexagonal flakes at 350 °C and cylindrical nanorod-like structures at 400 °C. Furthermore, increasing temperature has also caused phase transition from SnS$_2$ to SnS after 500 °C. In another report, the SnS$_2$ thin films have been prepared in two different solvent (ethanol and isopropyl alcohol) and investigated effect of annealing temperature (Johny et al., 2018). While the effect of solvent has been observed to be morphological defects such as porosity and pinholes, the effect of temperature is caused different surface morphology such as compact nanocolloid and nanoparticle. Clearly, the SEM image and the XRD patterns are quite compatible with each other due to the hexagonal crystal structure of SnS$_2$ with average grain size of 50.12 nm observed in the XRD patterns.

Figure 4 shows the plot of $(\alpha h \nu)^2$ versus photon energy $(h \nu)$ obtained by optic-absorption spectrum of the SnS$_2$ thin film in range of 300 nm and 900 nm, as seen in inset figure. The film has an optical absorption onset at 550 nm with sharp absorption edge. The band gap $(E_g)$ value has been determined to be 2.42 eV for direct allowed transition. Furthermore, the thin film has exhibited an absorption coefficient $(\alpha)$ of $10^4$ cm$^{-1}$. The $E_g$ value has been reported around 1.3 eV for SnS and 2.4 for SnS$_2$ thin film (Seo et al., 2017; Wang et al., 2017). Therefore, the $E_g$ and $\alpha$ values of the SnS$_2$ thin film are in good agreement with those reported previously (Reddy et al., 2018). On the other hand, in order to be used as window layer or transparent charge-carrier transport layer in solar cells, the SnS$_2$ thin film has an advantage that the band gap can be adjusted to application-specific values. For example, Neodymium (Nd) doped SnS$_2$ thin films have been reported that the band gap has increased from 2.75 eV to 2.95 eV with increasing doping concentration (Arulanantham et al., 2019).

![Figure 3. The surface SEM nanograph of the SnS$_2$ thin film.](image)

Figure 5(a) shows the ln(I)-V curves of the Sn/SnS$_2$/n-Si/Au-Sb diode at different temperatures. As seen in forward-bias current curve, the saturation current has increased from $10^{-6}$ A to $10^{-3}$ A with increasing temperature. However, the rectification ratio at $\pm 1$ V has not changed due to increasing reverse leakage current with increasing temperature. The directly proportional increase between reverse- and forward-bias current with increasing temperature is due to the suppressed trap-assisted tunneling current and dominant thermionic field emission current at low temperatures (Fang et al., 2009). This may be resulted that the SnO formed in interface between Si and SnS$_2$ as above mentioned.
Figure 4. The plot of \((\alpha h\nu)^2\) versus photon energy \((h\nu)\) of the thin film. Inset shows UV-visible absorption spectrum.

As shown in Figure 5(b) and (c), logarithmic current-voltage curves have changed with changing current-voltage mechanism at different temperatures. The three regions having different slope value are called as the ohmic current-voltage mechanism (Region I), space charge limited current (SCLC) mechanism (Region II) and trap-free SCLC mechanism (Region III) (Baltakesmez, 2019), as seen in Figure 5(c). In the region I, the ohmic current-voltage mechanism based on carrier mobility with proportional to the electric field has not been observed at low temperature and the mechanism has an onset from the SCLC \((I-V^2)\). The trap-free limit voltage \((V_{TFL})\) is given as Eq. (2) (Kumar et al., 2008).

\[
V_{TFL} = 0.5 \frac{qH_d' d^2}{\varepsilon \varepsilon_0} 
\]

where \(q\) is the elementary charge, \(d\) is the sample thickness, \(\varepsilon\) is the dielectric constants of the material, \(\varepsilon_0\) is the permittivity of the free-space and \(H_d'\) is the total filled trap density. According to the Eq. (2), the \(V_{TFL}\) value is directly related with total trap density. As can be seen in Figure 5(b) and (c), the voltage values have shifted from 0.49 V at 100 K to 0.38 V at 300 K. This alteration in the \(V_{TFL}\) values can be attributed that the fixed charge density in the traps depends on the temperature. Furthermore, these charges may be produce a reverse voltage in the material and thus voltage drop can be observed (Kumar et al., 2008). Therefore, in the low temperature, the presence of the SnO insulator-interface and insufficient thermal energy has caused almost zero current (~10^-9 A) with poor mobility up to 0.2 V.

The changes in turn-on voltage and leakage current with measurement temperature have been shown in Figure 6(a). The reverse leakage current temperature-dependent behaviour is attributed to change in electron tunneling rate from traps with temperature (Pipinys et al, 2006). On the other hand, the turn-on voltage has three different change ranges and first two ranges have increased with increasing temperature up to 240 K. However, at temperatures above 220 K, the voltage is almost constant. The presence of these three different ranges of variation is due to the strongly dependent temperature dependence of the reverse-bias character of the diode. Clearly, this is a result of the temperature
dependence of the leakage current. Figure 6(b) shows plot of change in ideality factor and zero-bias barrier height (SBH), which has been calculated by the TE theory, versus temperature.

\[ I = I_0 \exp \left( \frac{eV}{nkT} \right) \left[ 1 - \exp \left( -\frac{e(V - IR_s)}{kT} \right) \right] \]  

where \( n \) is the ideality factor, \( k \) is the Boltzmann constant, \( e \) is the electron charge, \( V \) is the forward bias voltage, \( T \) is the temperature, \( R_s \) the series resistance and \( I_0 \) is the saturation current. Besides, the saturation current is as given in Eq. (3).

\[ I_0 = A^*A T^2 \exp \left( -\frac{e\Phi_b}{kT} \right) \]  

\( A^*, A, \Phi_b \) are the effective Richardson constant of 112 A/cm²K² for \( n \) type Si, the area of the rectifier contact, the experimental zero bias barrier height, respectively. The value of ideality factor \( n \) is can be determined from Eq. (2) as,

\[ n = \frac{e}{kT} \frac{dV}{d(\ln I)} \]
According to the TE theory, the ideality factor has decreased with increasing temperature, changing range from 3.69 to 1.34. The calculated values have been given in Table 1. The temperature dependence of ideality factor has been frequently explained by presence of SBH inhomogeneity (Hudait and Krupanihi, 2001). In the diode, the presence of the SnS$_2$ interlayer and SnO interface may cause multi-surface polarity and also increases surface roughness with consist of crystal domain boundaries. Thus, these effects may cause the inhomogeneity of the SBH (Zhou et al., 2019). On the other hand, Zhou et al. have shown that the peak of bent conduction band increases with increasing forward-bias and shifts away from interface region towards the semiconductor (Zhou et al., 2019). Furthermore, these changes cause an increase in effective SBH with more uniform interface. Therefore, the change in barrier height has shown decreasing alteration with increasing temperature.

Figure 6. The plots of (a) the turn-on voltage and leakage current versus temperature and (b) the plots of ideality factor and barrier height versus temperature.

Table 1. The basic parameters of the diode.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>n</th>
<th>$\Phi_b$</th>
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<tbody>
<tr>
<td>100</td>
<td>3.69</td>
<td>0.313</td>
</tr>
<tr>
<td>120</td>
<td>3.56</td>
<td>0.377</td>
</tr>
<tr>
<td>140</td>
<td>3.00</td>
<td>0.433</td>
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<tr>
<td>160</td>
<td>2.45</td>
<td>0.490</td>
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<tr>
<td>180</td>
<td>2.05</td>
<td>0.542</td>
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<tr>
<td>200</td>
<td>1.82</td>
<td>0.586</td>
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<tr>
<td>220</td>
<td>1.70</td>
<td>0.633</td>
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<tr>
<td>240</td>
<td>1.46</td>
<td>0.671</td>
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<tr>
<td>260</td>
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<td>0.717</td>
</tr>
<tr>
<td>280</td>
<td>1.34</td>
<td>0.741</td>
</tr>
<tr>
<td>300</td>
<td>1.34</td>
<td>0.762</td>
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</table>
Recently, Wang et al. have reported effect of the SnS$_2$ secondary phase on surface of Cu$_2$ZnSnS$_4$ (CZTS) thin film in solar cell having SnS$_2$/CZTS structure and also CdS/CZTS structure for comparatively investigation (Wang et al., 2017). In this study reported, the SnS$_2$ layer is not suitable for this solar cell configuration and thus, Wang et al. have introduced mechanical exfoliation (ME) as a promising method for eliminate the detrimental effect of sheet-like SnS$_2$ films. However, Joshi et al. have presented synthesis of SnS$_2$ thin film by simple arrested precipitation technique for solar cell application and the photo-electrochemical solar cell performance of SnS$_2$ thin films has been given to be 0.053% (Joshi et al., 2018). In another study, Chu et al. have reported locally gated SnS$_2$/hBN thin film transistors with a broadband photo-response (Chu et al., 2018) and demonstrated a high photo-responsivity of ~0.7 mA/W in the SnS$_2$ channel transistor. Clearly, the SnS$_2$ thin film has an important application potential in suitable device fabrication. Therefore, to investigation of the performance of solar light sensitivity, the ITO/SnS$_2$/n-Si/Au-Sb structure has been measured under 1.5 AM light spectrum. The I-V characteristic of the diode has shown a solar cell character as seen in Figure 8. The device has exhibited a short-circuit current density ($J_{sc}$) of 1.83 mA/cm$^2$, an open-circuit voltage ($V_{oc}$) of 0.46 V and a fill factor (FF) of 0.28 and then PCE of 0.24%. Although low efficiency has been obtained due to high series resistance and low shunt resistance, as seen in I-V character, this promising performance may be improved with investigation detailed SnS$_2$ and contact properties.

**Figure 8.** The current density-voltage characteristic of the diode under 1.5 AM solar light.

**CONCLUSION**

Consequently, the SnS$_2$ thin film having large grain size (>200 nm in the SEM image) and wide band gap (~2.4 eV) has been deposited by spray pyrolysis technique on the Si and glass substrates. The predominant growth plane and average grain size has been determined to be (002) and ~50 nm from the XRD pattern. The Sn/SnS$_2$/Si/Au-Sb diode structure prepared by thermally evaporated metal contact has been achieved with ideality factor of 1.34 and barrier height of 0.762 eV. The ITO/SnS$_2$/Si/Au-Sb structure prepared by RF sputtered ITO contact has solar light sensitivity. The diode under 100 mW/cm$^2$ solar-light source has been exhibited 0.24% PCE with $J_{sc}$ of 1.83 mA/cm$^2$, $V_{oc}$ of 0.46 V and FF of 0.28.
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