

Article

# Effective Modulation of Optical and Photoelectrical Properties of SnS<sub>2</sub> Hexagonal Nanoflakes via Zn Incorporation

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**Abstract:** Tin sulfides are promising materials in the fields of photoelectronics and photovoltaics because of their appropriate energy bands. However, doping in SnS<sub>2</sub> can improve the stability and robustness of this material in potential applications. Herein, we report the synthesis of SnS<sub>2</sub> nanoflakes with Zn doping via simple hydrothermal route. The effect of doping Zn was found to display a huge influence in the structural and crystalline order of as synthesized SnS<sub>2</sub>. Their optical properties attest Zn doping of SnS<sub>2</sub> results in reduction of the band gap which benefits strong visible-light absorption. Significantly, enhanced photoresponse was observed with respect to pristine SnS<sub>2</sub>. Such enhancement could result in improved electronic conductivity and sensitivity due to Zn doping at appropriate concentration. These excellent performances show that Sn<sub>1-x</sub>Zn<sub>x</sub>S<sub>2</sub> nanoflakes could offer huge potential for nanoelectronics and optoelectronics device applications.

Keywords: SnS<sub>2</sub> nanoflakes; semiconductor; zinc doping; photoelectronics

#### 1. Introduction

Metal sulfides have received considerable interest due to their unique optoelectronic properties while processed at micro-nano level [1–4]. In particular, two-dimensional (2D) metal sulfides nanostructures such as nanoplates, nanoflakes and nanosheets have received much attention for their potential application in photodetectors, photovoltaic devices and light-emitting diodes [5–20]. 2D form of the material offers high specific surface area, making it advantageous for electrochemical, catalytic and photoelectrical activities. Another advantage in 2D materials is that they are more compatible and can easily be integrated into nano-microscale structures for developing new optoelectronic devices [21–24].

Meanwhile,  $SnS_2$  is considered as one of the promising layered materials with excellent visible light absorption and electrical properties. It possesses band gap (2.1–2.3 eV), n-type characteristics, high sensitivity and high surface activity for applications in Li-ion batteries [25], photovoltaic devices [26] and photodetector [27,28]. Variety of nanostructures such as nanoflakes, nanosheets and nanoplates through physical and chemical techniques including chemical vapor deposition, solvothermal and hydrothermal methods have been reported by several groups [29,30]. Among them, nanoflakes preparation via hydrothermal method have attracted considerable interest due to its low cost and large-scale production at low temperatures. Similarly, many efforts have also been made in controlling morphology and enhancing the photoelectrical, chemical and physical properties for improving the device performance. Moreover, dopants in semiconductor could lead to reduction in particle size,



narrowing of band gap and enhance the photoelectrical properties of  $SnS_2$  [31]. Recently, V and Ti doped  $SnS_2$  was reported to be an intermediate band material for application in wider solar absorption [32,33]. Recently doping  $SnS_2$  with Fe resulted in room temperature ferromagnetism [34]. Similarly, in our previous work, we reported enhanced optical and electrical properties of  $SnS_2$  nanoflakes via Cu doping [35]. More recently, Liu et al. reported enhanced photoresponsivity in Sb doped  $SnS_2$  monolayer [36]. Based on the above literatures we test the ability of doping Zn ions in  $SnS_2$  to significantly enhance conductivity and sensitivity favorable for its performance in photoelectronics.

The present work reports on hydrothermal synthesis of Zn doped SnS<sub>2</sub> nanoflakes at low temperatures. The properties of  $Sn_{1-x}Zn_xS_2$  nanoflakes have been intensively studied through structural, optical and photoelectrical methods. The results show that the Zn doping results in enhanced sensitivity, conductivity and efficiency of charge transfer kinetics. As a proof of concept,  $Sn_{1-x}Zn_xS_2$  nanoflakes were integrated into a patterned indium tin oxide (ITO) substrate (as active material) for photoelectronic device architecture. The results showcased excellent on-off ratio and photoresponse properties than that of pristine counterpart. Our investigations presents Zn doped SnS<sub>2</sub> could be a potential candidate for future nano electronic and photoelectronic applications.

#### 2. Experiment

#### 2.1. Synthesis of $Sn_{1-x}Zn_xS_2$ Nanoflakes

 $SnS_2$  and  $Sn_{1-x}Zn_xS_2$  nanoflakes were prepared via low cost hydrothermal route reported previously [35]. In brief, 0.1753 g  $SnCl_4$ ·5H<sub>2</sub>O (Tin (IV) chloride pentahydrate) and 0.15 g thioacetamide (TAA) were dissolved in 80 mL distilled water, stirred for 1 h to result in homogeneous solution. The prepared solution was transferred to 100 mL Teflon-line autoclave, sealed and heated up to 160 °C for 12 h and finally cooled to room temperature. The prepared  $SnS_2$  nanoflakes were then washed with ethanol and deionized water repeatedly and finally dried at 60 °C for 12 h in electric oven. For the synthesis of  $Sn_{1-x}Zn_xS_2$  nanoflakes, 1 and 3 mmol% of Zinc chloride was added to the precursor solution.

#### 2.2. Characterization

The morphological evolution of the sample was examined using field-emission scanning electron microscopy (FESEM, Philips, Model: XL-30, Amsterdam, The Netherland) and field-emission transmission electron microscopy (FE-TEM, JEM-2100F HR, Tokyo, Japan). The phase purity and crystal structure of SnS<sub>2</sub> and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes was inferred through X-ray diffractometer (SmartLab, Rigaku Corporation, Tokyo, Japan). The Raman measurements were performed in a micro-Raman spectrometer (DawoolAttonics, Model: Micro Raman System, Seongnam, Korea) using an excitation wavelength of 532 nm. The chemical composition of Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> was obtained using X-ray photoelectron spectroscopy (K-Alpha+, ThermoFisher Scientific, Waltham, MA, USA). In order to avoid charging effect, during the measurement, charge neutralization was performed with an electron flood gun (K-Alpha+, ThermoFisher Scientific, USA). The absorbance spectrum was recorded using a UV/VIS spectrophotometer (K LAB, Model: Optizen POP, Daejeon, Korea). A Keithley 617 semiconductor parameter analyzer (Tektronix, Beaverton, OR, USA; Model: Keithley 617) was employed to study the photo-response of the device under solar simulator (Newport, OR, USA; AM1.5) (SERIC, Model: XIL-01B50KP).

#### 2.3. Device Fabrication

Initially, 2 mg of samples  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  were added in 10 mL methoxy-ethanol solvent separately and magnetic stirred for 30 min followed by sonication of about 30 min to form colloidal suspension. The resulting suspension was then spin casted on cleaned and patterned ITO/glass substrate at 1000 rpm and dried at 100 °C for 5 min. Several cycles of spin casting process was repeated to obtain a continuous film.

The morphological features of SnS<sub>2</sub>, Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> (Figure S1) and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> products were examined with the aid of field-emission scanning electron microscope (FESEM) technique. The image seen from Figure 1a-c confirms hexagonal nanoflakes with smooth surface and homogeneous distribution in case of pristine SnS<sub>2</sub>. However, on doping with Zinc the morphology appears to be similar with that of pristine nanoflakes with some random aggregates on the surface of SnS<sub>2</sub> (Figure 1d,e). Additionally, transmission electron microscope (TEM) was employed to further investigate the detailed morphological information of  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  products. Figure 2 shows TEM images of pristine SnS<sub>2</sub> and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes with different magnifications. From the Figure 2a–c, it is clear that pristine SnS<sub>2</sub> possess typical nanoflakes like structures with hexagonal stacking. Similarly the  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes (Figure 2d–f) also possess indistinguishable hexagonal morphology of pristine SnS<sub>2</sub>. The inset of Figure 2c,f displays the selected area electron diffraction (SAED) pattern revealing polycrystalline structure of the obtained samples. Energy dispersive spectroscopy (EDS) analysis was further employed in TEM mode to study the homogeneous distribution of Zn element in Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes. Figure 3a–d displays the TEM image and TEM-EDS mapping of  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. As seen from Figure 3d, Zn element is distributed evenly throughout the whole structure of Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes.



**Figure 1.** Morphological and structural characterization of  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. (**a**–**c**) low magnification and high magnification scanning electron microscopy (SEM) image of  $SnS_2$ ; (**d**–**f**) low magnification and high magnification SEM image of  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes showing their hexagonal structure.



**Figure 2.** (**a**–**c**) Transmission electron microscopy (TEM) images of  $SnS_2$  and inset in Figure 2c shows selected area electron diffraction (SAED) pattern of  $SnS_2$  nanoflakes; (**d**–**f**) TEM images of a typical  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes with SAED pattern in inset of Figure 2*f*, revealing polycrystalline structure.



**Figure 3.** (a) TEM image of Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes and Energy dispersive spectroscopy (EDS) elemental mapping of Sn (b), S (c) and Zn (d) from selected area for 2D Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub>.

The crystallographic pattern of as synthesized  $SnS_2$ ,  $Sn_{0.99}Zn_{0.01}S_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes are investigated by XRD analysis and presented in Figure 4a. Here, the strong diffraction peak observed at  $2\theta = 14.92^{\circ}$  belongs to (001) diffraction, is an indication of the hexagonal structure of  $SnS_2$  [37]. However, the diffraction peak (001) tends to shift towards smaller angle on Zn doping. This shifting indicates that Zn ions replace Sn sites in the  $SnS_2$  crystal matrix. Furthermore, no peaks related to other compounds namely, ZnS and ZnSnS<sub>3</sub> are observed in the XRD pattern. Additionally, Raman measurement was further analyzed to study detailed information about the structural properties of Zn doped SnS<sub>2</sub> nanoflakes. Raman spectrum for sample SnS<sub>2</sub>, Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes are displayed in Figure 4b. Here, in case of pristine SnS<sub>2</sub>, Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes, a strong signal was observed at 312 cm<sup>-1</sup>, which is related to A<sub>1g</sub> phonon vibration mode of SnS<sub>2</sub> [38–40].



**Figure 4.** Structure properties of SnS<sub>2</sub>, Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes. (a) X-ray diffraction pattern of SnS<sub>2</sub>, Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes; (b) Raman spectrum of SnS<sub>2</sub>, Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes at excitation wavelength of 532 nm.

To elucidate the chemical composition of pristine and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes, XPS measurements have been carried out and shown in Figure 5a. XPS full survey spectrum (Figure 5a) confirms the presence of Zn doping in SnS<sub>2</sub>. Figure 5b,c displays the XPS spectra of Sn 3d and S 2p peaks for  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. As observed in Figure 5b,c, the peaks of Sn 3d at 486.33 and 494.4 eV of Sn 3d is ascribed to  $Sn3d_{3/2}$  and  $Sn3d_{5/2}$  and peaks at 161.2 and 163.3 eV correspond to S 2p peaks of SnS<sub>2</sub>. These results are consistent with those reported for SnS<sub>2</sub> [41,42]. The binding energies of Sn  $3d_{5/2}$  peak corresponding to pristine SnS<sub>2</sub> was observed at 486.47 eV. Subsequently doping with Zn on SnS<sub>2</sub>, peaks of Sn  $3d_{5/2}$  shifts to lower energy position to 486.33 eV. The shifting in the binding energy value of Sn  $3d_{5/2}$  peak was about 0.14 eV compared to pristine SnS<sub>2</sub>. This shift might be due to Zn ion replace Sn sites in the SnS<sub>2</sub> crystal lattice. Figure 5d shows the XPS spectrum for Zn in SnS<sub>2</sub> nanoflakes. Besides, the Zn  $2p_{3/2}$  peak appeared at 1021.3 eV is attributed to Zn<sup>2+</sup> bonding state [43], confirming Zn<sup>2+</sup> ions have been incorporated into the SnS<sub>2</sub>.



**Figure 5.** (a) Full survey spectra of  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  sample. (b) X-ray photoelectron spectroscopy (XPS) core level Sn 3d spectra of  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. (c) S 2p core level spectra of  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. (c) S 2p core level spectra of  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. (c) S 2p core level spectra of  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. (c) S 2p core level spectra of  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$ .

Figure 6a shows UV–visible absorption spectrum of  $SnS_2$ ,  $Sn_{0.99}Zn_{0.01}S_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  in the range of 300–750 nm.  $SnS_2$  displays a strong absorption in visible part of the solar spectrum. However, in contrast the samples  $Sn_{0.99}Zn_{0.01}S_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  displayed a broad light absorption in 300 to

750 nm, which indicates that doping Zn ion can result in extending of absorption edge of SnS<sub>2</sub>. This results suggests that samples  $Sn_{0.97}Zn_{0.03}S_2$  possess greater potential than that of pristine sample SnS<sub>2</sub> to drive photo excited charge carriers under the light irradiation. The values estimated was found to be 2.24 eV for sample SnS<sub>2</sub> which is consistent with our previous result (Figure 6b). However, the values was found to be 2.19 and 2.09 eV for sample  $Sn_{0.99}Zn_{0.01}S_2$  and  $Sn_{0.97}Zn_{0.03}S_2$ . It shows band gap becomes narrower than pristine  $SnS_2$  as the Zn content increases [44,45]. This reduction in the band gap might be due to modification in the electronic structures of SnS<sub>2</sub> due to Zn doping, which results in creating energy levels in the band gap. This band gap could result in better absorption in visible region and can increase photo excited charge carriers under illumination.



**Figure 6.** Properties of  $SnS_2$ ,  $Sn_{0.99}Zn_{0.01}S_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. (**a**) UV–vis absorption spectrum of the  $SnS_2$ ,  $Sn_{0.99}Zn_{0.01}S_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. (**b**) Tauc's plot extracted from the absorption spectrum revealing their direct band gap.

Mott–Schottky (M–S) analysis was made to study the electrical properties of pristine SnS<sub>2</sub>,  $Sn_{0.99}Zn_{0.01}S_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. Generally, Mott–Schottky plot was employed to determine the donor density ( $N_d$ ) and flat band potential ( $V_{fb}$ ) of the materials. M–S analysis are generally expressed by [46–48]

$$1/C^2 = (2/\epsilon\varepsilon_o N_d)[(V_{\rm fb} - V) - k_{\rm B}T/e]$$
<sup>(1)</sup>

where e is the electronic charge,  $\varepsilon$  is the dielectric constant of SnS<sub>2</sub>,  $\varepsilon_0$  is the relative permittivity,  $N_d$  dopant density, V the applied potential, C the specific capacitance,  $k_B$  the Boltzmann constant and  $V_{fb}$  the flat band potential. The M–S plots of pristine SnS<sub>2</sub>, Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> (Figure S2) and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes are displayed in Figure 7. Here  $V_{fb}$  was determined from intercept between the extrapolated linear plot of the curve and was estimated to be ~0.67 V for pristine SnS<sub>2</sub> and 0.64 V for Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes. Additionally the difference in the slope reflects the variation in the carrier density ( $N_d$ ). The values of carrier density was estimated from the Equation (1) to be about 1.46 × 10<sup>19</sup> and 0.47 × 10<sup>19</sup> and in case of SnS<sub>2</sub> and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes.



Figure 7. Mott–Schottky plots of (a) SnS<sub>2</sub> and (b) Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes.

A photoelectronic device was constructed on samples  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  to study its potential for optoelectronics applications (Figure 8a), (for the details of fabrication process refer Expt. sections). I-V curves of pristine SnS<sub>2</sub> nanoflakes at various illumination intensities and dark condition is displayed in Figure 8b. Inset shows I-V curves of the pristine SnS<sub>2</sub> nanoflakes under dark and illumination. Here, the I-V curve shows a roughly symmetric behavior indicating Schottky-like junction established at ITO and SnS<sub>2</sub> contacts. The dark current was noted to be 0.29 µA at a bias of 3 V. In contrast, the enhancement of current was measured and the value reaches to  $0.98 \,\mu\text{A}$  under illumination, demonstrating excellent photosensitivity of the SnS<sub>2</sub> samples. I-V curves of Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes device under illumination and dark is displayed in Figure 8c. Here, the value of dark current was found to increase than that of pristine SnS<sub>2</sub>, which suggests reduction in resistance of SnS<sub>2</sub> after Zn doping. However, a notable enhancement in photocurrent under illumination was noted compared to that of dark current at same bias voltage in  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes device, indicating their excellent sensitivity. Moreover, photo to dark current (Ilight/Idark) ratio for Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> device (~10.1) tends to increase compared to pristine  $SnS_2$  (~3.37). The high sensitivity and enhancement in photocurrent of  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes reveal the effective separation of photoexcited carriers in samples, which are actually promoted after Zn-doping. Figure 8d shows I-V curves of the Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> device measured at room temperature under different light intensities. The photocurrent increases with increasing light intensities revealing strong and clear photon-induced currents phenomena, indicating excellent photoresponse ability of the device. Under illumination, photoexcited charge carriers are mainly generated in Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub>. Then the charge carriers are quickly separated and driven towards the nearby electrodes due to built-in electric field created at the interface, resulting in photocurrent generation.



**Figure 8.** (a) Schematic representation of the photoelectronic device. (b) I-V characteristics of  $SnS_2$  device under different illumination intensities (Inset shows the I-V characteristics under dark and illumination intensity 84.0 mW/cm<sup>2</sup>). (c) I-V characteristics of  $Sn_{0.97}Zn_{0.03}S_2$  device under illumination conditions. (d) I-V characteristics of  $Sn_{0.97}Zn_{0.03}S_2$  device under different light intensities (55, 61.8, 74.0, 84.0 mW/cm<sup>2</sup>).

Figure 9a shows light intensity-dependent photocurrent values of pristine  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  device. The observed photocurrent value to illumination intensities suggest that the charge carrier photo-generation efficiency is proportional to the number of photons absorbed by the pristine  $SnS_2$  and

 $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes. Reliable response speed and stability to illumination conditions are crucial for the photoelectronic device. To address this concern, time related photoresponse of pristine  $SnS_2$ and  $Sn_{0.97}Zn_{0.03}S_2$  device was measured with turning light on/off condition for a period of 10 seconds for multiple cycles. Figure 9b,c shows time related photoresponse of the pristine and Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> device under several switch on and switch off conditions. Here, the photocurrent of pristine SnS<sub>2</sub> was found to be 0.8  $\mu$ A. Interestingly the photocurrent is improved by two fold in case of Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> nanoflakes (1.75  $\mu$ A) compared to pristine SnS<sub>2</sub> (Figure 9c). The photoresponse enhancement could be related to Zn ions which acts as an effective dopant and enhance charge separation taking place at the interface. The rise/decay time was measured to be 0.2 and 0.2 s. The reason for the relative longer response speed in our case is probably related to the formation of interface states between the  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes and ITO substrate, which can block the photo-generated carriers, resulting in long life time of the photo-generated carriers. Meanwhile, the device shows no fluctuation under illumination for several repetitive cycles, inferring the excellent stability of the  $Sn_{0.97}Zn_{0.03}S_2$  device. The time related response of the  $Sn_{0.97}Zn_{0.03}S_2$  device under varied light intensities are displayed in Figure 9d. Here, the photocurrent value varies with different light intensities demonstrating excellent reproducibility of Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub> based device. Such high and stable photoresponse behavior may come from the fact that Zn ions act as an effective dopant and result in increased light absorption, which enhances photogenerated charge carriers and leads to an enhanced photocurrent of the device. Thus, photoelectrical studies on  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes illustrates that Zn doping in SnS<sub>2</sub> results in significant enhancement of their optoelectronic properties, which leads to improved conductivity and sensitivity.



**Figure 9.** (a) Light intensity-dependent photocurrent values of pristine  $SnS_2$  and  $Sn_{0.97}Zn_{0.03}S_2$  device. Time-dependent photocurrent response of (b)  $SnS_2$  device and (c)  $Sn_{0.97}Zn_{0.03}S_2$ . (d) Time-dependent photocurrent response of  $Sn_{0.97}Zn_{0.03}S_2$  device under different illumination intensities.

The mechanism involved in the enhanced photoresponse of  $Sn_{0.97}Zn_{0.03}S_2$ /ITO structure was explained through energy band diagram in Figure 10. Since the work function between ITO and  $Sn_{0.97}Zn_{0.03}S_2$  is different, a Schottky-type behavior is established at  $Sn_{0.97}Zn_{0.03}S_2$ /ITO interface

(Figure 10). Due to this behavior, an electric field was established at the  $Sn_{0.97}Zn_{0.03}S_2$ /ITO interface. This electric field then accelerates the separation of the photoexcited charge carriers without the application of any applied bias. When illuminated, photoexcited charge carriers produced in  $Sn_{0.97}Zn_{0.03}S_2$  are then separated at the  $Sn_{0.97}Zn_{0.03}S_2$ /ITO interface. This charge carriers separation which was induced due to the electric field results in band bending at the  $Sn_{0.97}Zn_{0.03}S_2$ /ITO interface. As a result, the photoexcited charge carriers are swept towards ITO electrodes, involving in enhancement of photocurrent (Figure 10b).



**Figure 10.** Energy diagram of the Sn<sub>0.97</sub>Zn<sub>0.03</sub>S<sub>2</sub>/ITO Schottky junction under (**a**) dark and (**b**) illumination conditions.

### 4. Conclusions

In summary,  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes were prepared via low temperature hydrothermal synthesis. The modulation of the structural and photoelectrical properties in  $SnS_2$  via doping Zinc have been discussed in detail. A shift in XPS peak of Sn  $3d_{5/2}$  and S  $2p_{3/2}$  has been observed in  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes due to Zn ion replaced Sn sites in the SnS<sub>2</sub> crystal lattice. Optical properties studies show that  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes possess higher visible-light absorption than that of pristine SnS<sub>2</sub>. Photoelectrical properties based on  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes reveal that Zn doping leads to significant improvement in conductivity and sensitivity to illuminations compared to pristine SnS<sub>2</sub>. Such an excellent performance of  $Sn_{0.97}Zn_{0.03}S_2$  nanoflakes may endow it as a potential candidate for emerging 2D materials in optoelectronic applications.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2079-4991/9/7/924/s1, Figure S1: SEM image of Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> nanoflakes, Figure S2: Mott–Schottky plot of Sn<sub>0.99</sub>Zn<sub>0.01</sub>S<sub>2</sub> nanoflakes.

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