Tungsten Disulphide based Heterojunction Photodetector

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Abstract: Two-dimensional (2D) materials have realized significant new applications in photonics, electronics and optoelectronics. Among these materials, tungsten disulphide (WS2), which is a 2D material that shows excellent optoelectronic properties, tunable/sizable bandgap in the visible range and good absorption. A polycrystalline WS2 thin film is successfully deposited on a substrate using radio frequency magnetron sputtering at room temperature. X-ray diffraction pattern reveals two hexagonal structured peaks along the (100) and (110) planes. Energy-dispersive X-ray spectroscopy reveals a non-stoichiometric WS2 film with 1.25 ratio of S/W for a 156.3 nm thick film, while Raman shifts are observed at the E1g and A1g phonon modes located at 350.70 cm⁻¹ and 415.60 cm⁻¹ respectively. A sandwiched heterojunction photodetector device was successfully fabricated and illuminated within the violet range at 441 nm and 10 V of bias voltage. The maximum photocurrent values are calculated as 0.95 µA, while the responsivity was observed 169.3 mAW⁻¹ and detectivity 1.48 x 10⁸ Jones. at illuminated power of 0.6124 µm. These results highlight the adaptability of the present technique for large scale applications as well as the flexibility to promote the development of advanced optoelectronic devices.

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1. Introduction

Two-dimensional (2D) nanomaterials such as graphene have recently received significant attention from the semiconductor industry due to their unique optical and electrical properties, such as strong interaction with photons in a wide energy range and high carrier mobility in a broad spectrum [1]. However, graphene based field effect transistors (FETs) did not garner its projected market share because of low ON/OFF ratios arising from the lack of a bandgap in this material. These spurred research efforts into other 2D materials such as transition metal dichalcogenides (TMDCs) that would be able to overcome this limitation. TMDCs in particular are of interest due to their atomic structure of MX2 where M is a transition metal atom such as Mo or W and X is a chalcogenide atom such as S or Se [2,3]. The X-M-X layer materials are covalently bonded to the six chalcogenides neighbouring them within the same plane with a very weak van der Waals force. There gives 2D nanomaterials based on TMDCs its unique characteristics such as surfaces without any dangling bonds [4]. It is also possible to raise vertical hetero-structures using different 2D materials without the conventional lattice mismatch due to the sheets having different lattice constants that are only bonded by a weak van der Waals force as in layered materials. As a result, even atomically thin layers interact with light strongly such as monolayer tungsten disulphide (WS2) being able to absorb roughly 10 % at exitonic resonances, covering a very wide electromagnetic spectrum because of their assorted electronic properties [3]. Furthermore, recent research has demonstrated that WS2 has very strong absorption [5]. In this manner, WS2 has substantial potential for high-responsivity photo-detecting applications [6,7], acting as a sandwiching material between metal heterojunction contacts for the fabrication of high performance devices [8].
In this work, a WS$_2$ thin film is successfully deposited on top of soda lime glass by means of radio frequency (RF) magnetron sputtering. The structural properties of the thin film are analysed using X-ray diffraction (XRD) while the surface morphology is obtained using field emission scanning electron microscopy (FESEM). Energy dispersive X-ray (EDX) compositional analysis and Raman spectroscopy is used to fingerprint the phonon modes of the WS$_2$ thin film in order to investigate an in-depth profile analysis. Subsequently, the WS$_2$ thin film is sandwiched in the heterojunction structure of a SLG/WS$_2$-p-Si:B/SiO$_2$ photodetector and its optoelectronic properties device under different illumination powers analysed. The photocurrent, responsivity, directivity and external quantum efficiency (EQE) are also determined.

2. Methodology

The fabrication of the thin film WS$_2$ based heterojunction photodetector can be divided into two phases. In the first stage, WS$_2$ thin film is deposited onto a soda lime glass (SLG) substrate. The SLG substrate is cleaned in an ultrasonic bath in the sequence of methanol, acetone and then methanol again for 10 minutes each, then de-ionised (DI) water for 20 minutes and finally dried using pure nitrogen (N$_2$) gas to remove any undesired residual particles from the surface of the substrate. Subsequently, the thin WS$_2$ film is deposited on the surface of the cleaned SLG substrate using RF magnetron sputtering system at room temperature (RT). The deposition process was carried out over a period of 60 minutes at a power of 50 W under high vacuum conditions. At the same time, a boron doped p-type silicon (p-Si:B) wafer together with a thermally oxidised silicon dioxide (SiO$_2$) layer with thicknesses of 1000 microns and 1.5 microns respectively was prepared as a secondary substrate. The p-Si:B/SiO$_2$ substrate was cleaned ultrasonically with acetone for 30 minutes, followed by DI water for 20 minutes and then dried with N$_2$ gas as before to ensure a clean surface with no impurities. Afterwards, both the SLG/WS$_2$ and p-Si:B/SiO$_2$ films are placed on top of a hotplate for 15 minutes at a temperature of 100 °C and sandwiched tightly with each other using a paper clip to form a heterojunction photodetector device with a SLG/n-WS$_2$/SiO$_2$/p-Si:B structure. Figure 1 shows the schematic diagram of the fabricated device.

![Fig. 1. Schematic diagram of thin film WS$_2$ based heterojunction photodetector device](image)

XRD measurement of the WS$_2$ thin film was performed using a Bruker AXS Germany’s D8 Advance (Cu K-Alpha 1) equipment at RT with a wavelength of 0.15406 nm under 40 kV voltage and 40 mA current. The XRD pattern was recorded over a scan range of 20 from 20° to 80° with a step size of 0.025° over a 0.1 s exposure time. The morphology of the deposited film was studied by means of FESEM of JEOL brand with model number JSM7600F. Energy dispersive x-ray spectroscopy (EDX) was executed to investigate compositional analysis of
WS₂ thin film with Oxford instrument. Raman spectra was obtained at RT by using a laser of 532 nm equipped with Renishaw inVia at 25 mW laser power. The optoelectronic properties of the fabricated WS₂ based heterojunction photodetector was characterized within the violet range at 441 nm for illumination. The distance between laser source and the surface of the photodetector was maintained at 2 cm. The current – voltage (IV) measurement was performed using a Keithley’s 2410 – 1100 V – SourceMeter® between -20 V to +20 V. The power of the laser source was tuned by varying the input voltages from 0.0 V to 2.7 V as well as frequency modulation at 1 Hz, 5 Hz, 10 Hz, 100 Hz, 300 Hz and 500 Hz using a DS345 – 30 MHz synthesized function generator (SFG) from Stanford Research Systems. The time-based responses of the device are obtained using a Yokogawa DLM2054 mixed signal oscilloscope. All optoelectronic measurements are carried out at room temperature.

3. Results & Discussion

Fig. 2 provides the XRD pattern of the sputtered WS₂ thin film. From the figure, it can be seen that the crystallites of WS₂ maintain hexagonal crystal structure. The polycrystalline WS₂ film exhibits only two diffraction peaks corresponding to the (100) plane at 2θ = 34.28° and the (110) plane at 2θ = 60.82° which is in agreement with the JCPDS card number 84-1398. The lattice parameters of the sample are determined to be a=0.315 nm and c=1.227 nm with a hexagonal crystal structure of 2H [9,10]. The intensity of first peak along the (100) plane was observed to be 3 times higher than the second peak along the (110) plane [11]. No phases corresponding to impurities are seen at the current resolution, indicating the high purity of the sample.

![Fig. 2. XRD pattern of deposited WS₂ thin film](image)

The surface morphology image obtained by FESEM for deposited WS₂ thin film is shown in Fig. 3 (a), and shows the polycrystalline growth of WS₂ with a surface coverage of 80 %. The thickness of the deposited film is measured to be approximately 156.3 nm. The EDX spectrum of WS₂ thin film on the other hand is shown in Fig. 3(b), and clearly indicates the presence of tungsten (W) and sulphur (S) elements in the thin film. The normalized S/W ratio was calculated to be 1.25, confirming the non-stoichiometric nature of the WS₂ film. The deficiency of S is attributed to thermal decomposition [12].
Fig. 3. (a) FESEM surface image and (b) EDX spectrum of WS$_2$ thin film

Fig. 4. Elemental composition of sputtered WS$_2$ thin film

Fig. 4 shows the elemental composition of the sputtered WS$_2$ thin film as obtained via EDX analysis. The presence of C, O, Na, Mg, Si and Ca are attributed to the SLG substrate, while the presence of W and S confirms the deposited WS$_2$ layer.

Fig. 5. Raman spectra of WS$_2$ thin film. The shift in the vibration mode indicates the change in the material size

The Raman spectra of the WS$_2$ thin film sample is given in Fig. 5. From the figure, it can be seen that there are two dominant peaks arising from the weak van der Waals interlayer
forces which distressed lattice vibration and bonding between layers. The two peaks originate from optical phonon E'_{2g} and A_{1g} modes. The E'_{2g} phonon mode is an in-plane optical mode while the A_{1g} mode is caused by the out-of-plane vibrations of the S atoms. It is apparent from Fig. 5 that both the E'_{2g} and A_{1g} phonon modes of WS2 are located at 350.70 cm^{-1} and 415.60 cm^{-1} respectively, confirming the growth of the WS2 layer [13], and augur well with the findings of previous literature [14]. In certain cases, a blue-shift in the in-plane mode of WS2 is observed [15,16], and could be a result of the strain encountered during the growth process [17].

The optoelectronic characteristics of the WS2 based SLG/n-WS2/SiO2/p-Si:B heterojunction photodetector is investigated using IV measurement under dark and illuminated conditions. The laser powers are varied at 0.6124 µW, 13.54 µW, 115.8 µW and 277.9 µW to obtain the IV curves as shown in Fig. 6. The bias voltage is maintained at 10 V and the frequency is set to 1 Hz. The IV curve was measured between a voltage range of -20 V to 20 V and shown in Fig. 6 (a) with logarithmic coordinates on the bottom right. It can be observed that under increasing illumination from dark conditions, the device expressively acts as photodetector with the 441 nm light source. Good Schottky barrier function between the n-WS2 and p-Si layers can be observed, even though the IV curves are non-linear. An increasing trend can be observed from the partially magnified logarithmic IV curves in Fig. 6 (b) with the increase in laser power from its dark current to 0.6124 µW, 13.54 µW, 115.8 µW and 277.9 µW at bias voltage. These IV curves also indicate a unique feature of the heterojunction SLG/n-WS2/SiO2/p-Si:B photodetector, which is its ability to respond positively in the forward bias region and negatively in the reverse bias region when under illumination.

![Figure 6](image)

**Fig. 6.** (a) IV curves of SLG/n-WS2/SiO2/p-Si:B heterojunction photodetector under dark and illuminated conditions at various powers with the curves in logarithmic coordinates at bottom right, (b) Partially magnified logarithmic IV curve of SLG/n-WS2/SiO2/p-Si:B heterojunction photodetector with voltage bias from 5 V to 11 V with normal curve on top left

The photocurrent used to weigh the photo-response characteristics of heterojunction SLG/n-WS2/SiO2/p-Si:B photodetector under various conditions can be calculated from Equation 1:

\[
I_{ph} = I_{illuminated} - I_{dark} \quad (1)
\]

where \( I_{ph} \) is photocurrent, \( I_{illuminated} \) is the current under illuminated conditions and \( I_{dark} \) is the dark current. Significant changes in the photocurrent can be observed from Fig. 7 (a), where the laser power heavily influences the photocurrent by the rise in power. Increment in the laser power indicates a narrowed depletion region at the p-n junction, which allows most of the incident photons to be converted into a photocurrent [18]. The responsivity is another interesting characteristic used to evaluate the performance of photodetector and can be
measured as in Equation 2, where $R$ is responsivity, $P_{\text{illuminated}}$ is the laser power and $A$ is the area of light incident [19]:

$$R = \frac{I_{\text{ph}}}{P_{\text{illuminated}} \times A}$$

(2)

Fig. 7. (a) Power dependent photocurrent and responsivity of heterojunction photodetector SLG/n-WS$_2$/SiO$_2$/p-Si:B under illumination at 441 nm, (b) Power dependent detectivity and EQE of heterojunction photodetector SLG/n-WS$_2$/SiO$_2$/p-Si:B under illumination at 441 nm

It can be observed from Fig. 7 (a) that the responsivity decreases with the increasing power of the laser. The maximum value of $R$ is estimated as 169.3 mAW$^{-1}$ for an illumination power of 0.6124 $\mu$W. This is a property of the sandwiched photodetector to detect the response at 441 nm without any external power source. The in-built electric field causes the separation of electron-hole pairs (EHP) from charge carrier recombination [20]. When the light is illuminated at the surface of photodetector, the incident photons generate EHPs in the p-Si and n-WS$_2$ regions. In the forward bias region, the photo-generated holes in the p region are accelerated towards the n region and contribute to photocurrent [18]. The detectivity symbolizes the ability of the detector to detect a weak optical signal, assuming that the actual impact to the total noise comes from Poisson noise from the dark current [21]. The detectivity can be understood from Equation 3 as follows:

$$D^* = R \sqrt{\frac{S}{2q I_{\text{dark}}}}$$

(3)

where $D^*$ is the detectivity and is directly proportional to $R$, $S$ is the effective photosensing area and $q$ is the charge of an electron. The maximum value of $D^*$ is premeditated to 1.48 x 10$^6$ Jones for an incident light intensity of 0.6124 $\mu$m.

The EQE of the SLG/n-WS$_2$/SiO$_2$/p-Si:B heterojunction photodetector is obtained from the IV curves under forward bias conditions [22] and given as:

$$EQE = \frac{hc}{e\lambda}R$$

(4)

where $h$ is Planck constant, $c$ is the velocity of light, $e$ is charge of an electron and $\lambda$ is illumination wavelength at 441 nm. A high EQE value is an indicator of a highly sensitive heterojunction photodetector device. Fig. 7 (b) shows the power dependence of the EQE of the fabricated device where a low laser illumination power demonstrates a high EQE as compares to higher illumination powers. This suggests inadequate absorption of photon energy and carrier recombination due to the low EQE value (<1).

Figure 8 shows the time-dependent current response of sandwiched heterojunction photodetector under 441 nm laser illumination at various laser powers of 0.6124 $\mu$W, 13.54
µW, 115.8 µW and 277.9 µW at 10 V bias voltage. The rise times and fall times is tabulated in Table 1.

![Graph showing current response](image)

**Fig. 8.** Time dependent current response of photodetector within the violet range light illumination at 441 nm with different powers at bias voltage and modulation frequency of 1 Hz.

<table>
<thead>
<tr>
<th>Power (µW)</th>
<th>Frequency (Hz)</th>
<th>Rise Time (m.s)</th>
<th>Fall Time (m.s)</th>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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**Table 1** Rise and fall time of heterojunction photodetector illuminated under 441 nm

Figure 9 shows the time dependent current response of the photodetector within the violet range at 441 nm with various frequencies i.e., 1 Hz, 5 Hz, 10 Hz, 100 Hz, 300 Hz and 500 Hz at 10 V bias voltage and laser power 277.9 µW. The rise times and fall times at various frequencies is also tabulated in Table 1.

![Graph showing current response](image)
4. Conclusion

A WS2 thin film sandwiched SLG/n-WS2/SiO2/p-Si:B heterojunction photodetector is successfully fabricated by RF magnetron sputtering. XRD pattern reveals a polycrystalline WS2 film with two diffraction peaks corresponding to (100) plane at 20 = 34.28° and (110) plane at 20 = 60.82° with hexagonal structure. FESEM reveals nano-flake like structures in the 156.3 nm thick layer of non-stoichiometric WS2 film with S/W ratio of 1.25. Raman shifts are found at the E′2g and A1g phonon modes located at 350.70 cm⁻¹ and 415.60 cm⁻¹ respectively. The optoelectronic characteristics show evidence of Schottky barrier behaviour in the sandwiched photodetector with 10 V bias voltage and the ability to work in both the forward and reverse bias regions. The maximum Iph was obtained at higher laser power as 0.95 µA. The maximum value of R was calculated as 169.3 mAW⁻¹ and D* was observed 1.48 x 10⁸ Jones for an incident light intensity of 0.6124 µm. Overall, these results highlight the technological potential of TM DC sandwiched photodetectors for practical applications in next-generation high performance optoelectronics.

Funding


References


