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Broadening spectral responses and achieving environmental stability in SnS2/Ag-NPs/HfO2 flexible phototransistors

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1. Introduction

Photodetectors are sensors that convert incident photons into electrical signals. The energies of the incident photons may span throughout the electromagnetic spectrum ranging from X-ray, ultraviolet (UV), visible, and infrared (IR) to the terahertz range for different applications. Commercially, silicon-based photodetectors are dominant in the visible to near-IR spectrum due to their small band gap (1.1 eV) and Earth abundance. UV detection is realized either by coupling silicon photodetectors with appropriate filters or replacing Si with wide band gap semiconductors such as GaN, AlN and SiC and bulk heterostructures. These techniques pose fabrication complexities and limit the miniaturization of photodetectors to meet the criteria for future scaled devices. UV detection is important in space sciences for satellite communication, in the healthcare field for biological imaging and disinfection of bio-agents, and in various chemical analyses and water purification fields.

Semiconducting two-dimensional (2D) materials are advantageous to bulk semiconductors for photodetection because of their atomically thin and flexible nature, dangling bond-free surfaces, and wide range of energy gaps covering the UV to mid-IR spectrum. Previously, most efforts have been dedicated towards visible and IR photodetection since majority of well-studied 2D semiconductors such as MoS₂, WSe₂, and black phosphorus possess energy gaps < 2 eV. Here, we inves-
tigate the broadband UV-visible-near IR photodetection based on wide bandgap (2–2.6 eV) tin disulfide (SnS₂). The large bandgap of SnS₂ is advantageous to realize a high current on/off ratio with a suppressed dark current, besides extending the spectral range of photodetection.

2D materials have shown strong light-matter coupling caused by the sharp peaks in their density of states at certain energy levels thanks to the confinement effect. Despite their strong interaction with incident photons, atomically thin 2D materials absorb a small portion of the incident light due to their optically transparent nature. Likewise, the optical and optoelectronic performances of 2D materials based photodetectors are compromised. To solve this issue, external photonic structures, such as optical cavities and waveguides, or metal NPs are integrated with 2D materials to improve their optical absorption.

Here, we report the high performance and broadband photodetection of multilayer SnS₂ by decorating it with metal nanoparticles. Our results show that the decoration of silver nanoparticles (Ag-NPs) over SnS₂ channels leads to extended photodetection capabilities from UV to NIR (250–1050 nm). This is attributed to the localization of the electromagnetic field via the surface plasmon-enhanced optical field in the SnS₂ devices. In addition, we passivated the SnS₂/Ag-NPs devices with HfO₂, which demonstrated environmental stability with improved performance for more than seven weeks. Lastly, we demonstrated a flexible SnS₂/Ag-NPs device which retains ~80% of its photoresponsivity up to 500 bending cycles. Our results open possibilities for investigating wide band gap 2D semiconductors for broadband optoelectronic and photonic applications.

2. Results and discussion

2.1 SnS₂ FET

Figs. 1a and b show the device schematic with a circuit diagram and an optical microscopic image of the back-gated SnS₂ field-effect transistor (FET) on a Si/SiO₂ substrate, respectively. Before electrical measurements, we performed atomic force microscopy and Raman spectroscopy on the SnS₂ channel to ascertain its thickness and material quality, and the results are provided in ESI Fig. S1.† Our representative SnS₂ channel is ~13 nm thick, and it exhibits single Raman mode at ~316.4 cm⁻¹ (A₁g mode), which is attributed to the relative vibration of Sn and S atoms in the out-of-plane direction.

We performed the basic electrical measurements (transfer and output curves) on the multilayer SnS₂ FET in the dark, which is followed by an optoelectronic response under continuous wave lasers of different wavelengths. Note that all the measurements were performed under ambient conditions throughout this study. Fig. 1c shows the transfer curve obtained by sweeping the gate voltages (V₉) from −60 to +60 V at a constant bias voltage (V_ds = 0.5 V) under dark. The I_ds−V_g trend shows typical n-type (electron dominant) characteristics of the SnS₂ device, indicating that the Fermi level is positioned in the vicinity of the conduction band of SnS₂. Similar to MoS₂, the electron-rich characteristics in SnS₂ are attributed to the presence of sulfur vacancies and the strong Fermi level pinning effect close to the conduction band edge in SnS₂.

The device shows a current ON/OFF ratio of ~10³. From the slope of the transfer curve, i.e., transconductance (g_m), we cal-

Fig. 1 Device architecture and electrical response of the SnS₂ FET. (a) Schematic diagram of the SnS₂ device. (b) Optical image of the back-gated SnS₂ device (L = 2 μm, W = 4.5 μm, and thickness = 13 nm) on a Si/SiO₂ substrate. Scale bar: 10 μm. (c) Current vs. back gate voltage (I_ds−V_g) plots in logarithmic scale at V_ds = 0.5 V. The inset shows the current vs. source-to-drain voltage (I_ds−V_ds) plots at V_g values ranging from −20 to 20 V with the step of 10 V. (d) I_ds−V_g trajectories of pristine SnS₂ under different light illuminations.
culated an effective field-effect mobility ($\mu_{\text{FE}}$) of $\sim 20 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ using eqn (1).26

$$\mu_{\text{FE}} = \frac{g_m L}{W V_d C_{\text{ox}}}$$  \hspace{1cm} (1)

where ‘$L’$ and ‘$W’$ are the SnS$_2$ channel length and width, respectively, and $C_{\text{ox}}$ is the gate oxide capacitance per unit area ($\sim 1.15 \times 10^{-12} \text{F cm}^{-2}$ for 300 nm thick SiO$_2$). The low-resistive electrical contacts between Cr/Au and the SnS$_2$ channel are confirmed by realizing the almost linear output characteristics at all the measured $V_g$ values of $\sim 20$ to 20 V with a step of 10 V, as shown in the inset of Fig. 1c. Furthermore, the optoelectronic response of SnS$_2$ at given laser wavelengths at a fixed laser power ($P_{\text{in}} = 10 \text{ mW cm}^{-2}$) and $V_d = 0.5$ V is compiled in Fig. 1d. The SnS$_2$ device exhibits robust photoactive performance under incident wavelengths with a large photo-current at shorter wavelengths due to the large photon energy. Under larger wavelength (over 540 nm) excitation, the device exhibits a very weak photocurrent as the incident photon energy is smaller than the optical band gap of multilayer SnS$_2$ ($\sim 2.3$ eV). This limits the applicability of large bandgap materials for broadband photodetection. To address this issue, we employed a subtle technique by decorating metallic nanoparticles over SnS$_2$ flakes. Silver, being relatively inexpensive compared to gold, has a higher refractive index at shorter wavelengths. Similarly, silver nanoparticles, Ag-NPs, exhibit plasmonic resonances at relatively shorter wavelengths.27

### 2.2 Ag-NPs-decorated SnS$_2$ FETs

We, therefore, decorated Ag-NPs with a density of 40–45 NPs $\mu\text{m}^{-2}$ over a fresh SnS$_2$ phototransistor, as shown in the field emission scanning electron microscopy image in the inset of Fig. 2a. Note that the following results are obtained from different devices compared to Fig. 1; therefore, the maximum current levels are different in Fig. 2a as compared to Fig. 1c due to the device-to-device variation. From the comparative plots in Fig. 2a, we realized an almost two times increase in the on-state current from 1.39 $\mu$A to 2.75 $\mu$A after Ag-NPs deposition over SnS$_2$. As a result, the SnS$_2$ device shows a two-times increase in $\mu_{\text{FE}}$ from $\sim 15$ to $\sim 32 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, a shift in the threshold voltage ($\Delta V_{\text{th}} \approx 5$ V) from $-23$ to $-28$ V and an increase in the electron density concentration [$n_e = C_{\text{ox}}(V_g - V_{\text{th}})$] from $3 \times 10^{12}$ to $5.5 \times 10^{12} \text{ cm}^{-2}$, as shown in Fig. 2b and ESI S3.† These changes confirm the electron doping of SnS$_2$ with Ag-NPs deposition induced by the surface charge transfer doping from Ag-NPs to SnS$_2$ flakes.

We next focus on optoelectrical characteristics of pristine and Ag-NPs-decorated SnS$_2$ phototransistors that were investigated at different wavelengths. The pristine SnS$_2$ device demonstrated the photoresponse across a narrow spectral range (250–540 nm). Interestingly, the photocurrent of the same device increases by two times after depositing Ag-NPs, and the cut-off wavelength is extended to $1050$ nm, as shown in Fig. 2c, which is attributed to the enhanced absorption and the photoluminescence effect in 2D materials by Ag-NPs.28,29

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![Fig. 2](https://example.com/fig2.png)

**Fig. 2**  Optoelectronic performance before and after Ag-NPs deposition. (a) Comparative transfer curves of the SnS$_2$ device ($L = 2.2$ $\mu$m, $W = 4.1$ $\mu$m, and thickness = 4.8 nm) before and after Ag-NPs deposition. (b) Comparison of the extracted field effect mobility and threshold voltage from (a). (c) Photocurrents of pristine SnS$_2$ and Ag-NPs-decorated SnS$_2$ devices at $V_d = 0.5$ V and $V_{\text{gs}} = 0$. The light intensity was kept at 10 mW cm$^{-2}$ during all the incident wavelengths. (d) Rise (green shaded) and decay (brown shaded) times of SnS$_2$ and SnS$_2$/Ag-NPs photodetectors obtained from temporal photocurrent measurements. (e) The generated photocurrent of SnS$_2$ and SnS$_2$/Ag-NPs devices as a function of illumination power density at $V_{\text{gs}} = 0$ V, where the dashed lines represent power-law fitting.
The extension in the detection range of the SnS$_2$ device to near IR is mainly caused by the enhanced and broadband optical absorption in the NPs-decorated SnS$_2$ devices.

2.3 Passivated SnS$_2$/Ag-NPs/HfO$_2$ photodetector

Compared to other noble metal-based NPs, Ag-NPs are reported to be oxidized under ambient conditions, and this effect can be exaggerated under illumination conditions. As a result, the performance of the Ag-NPs-coated SnS$_2$ device may degrade over time. To circumvent this, we deposited a ~15 nm thick high-$k$ dielectric, HfO$_2$, by atomic layer deposition, as indicated in Fig. 3a schematic. The stabilities and performances of the pristine SnS$_2$, SnS$_2$/NPs, and SnS$_2$/Ag-NPs/HfO$_2$ devices were monitored under ambient conditions for the first seven weeks (Fig. 3b). For more details, see ESI S5 and S6. Among these three different device configurations, SnS$_2$/Ag-NPs/HfO$_2$ demonstrated the highest photoresponsivity ($R_{ph} = I_{ph}/I_{dark} \times A$; where $P_{op}$ is the illuminated laser power and $A$ is the active device area) of ~12 500 A W$^{-1}$ at $\lambda = 250$ nm. Moreover, from the aging test result, we realized that the $R_{ph}$ is reduced by ~20%, ~36%, and 6% for the SnS$_2$, SnS$_2$/Ag-NPs, and SnS$_2$/Ag-NPs/HfO$_2$ photodetectors after seven weeks under similar storage and operation conditions, as shown in Fig. 3c. This phenomenon is ascribed to the direct impact of oxygen on bare SnS$_2$, leading to the deterioration of material quality. In the case of SnS$_2$/Ag-NPs, the degradation is more pronounced due to surface oxidation and the consequent deprecation of the interface between SnS$_2$ and Ag-NPs. However, the introduction of HfO$_2$ passivation emerges as a pivotal mitigating factor. This passivation layer effectively impedes the interaction of oxygen with SnS$_2$ and Ag-NPs, thereby resulting in a mere 6% degradation and ensuring the stability of the devices with consistent performance. In a nutshell, the passivated SnS$_2$/Ag-NPs/HfO$_2$ photodetectors exhibit more stable performance for several weeks.

2.4 Mechanical flexibility of the SnS$_2$/Ag-NPs photodetector

Among other advantages, 2D materials are mechanically robust, thus they can be incorporated for flexible applications. Therefore, we investigated the mechanical endurance of the Ag-NPs-coated SnS$_2$ photodetectors by bending polyethylene naphthalate (PEN) substrates with different radii, as shown schematically in Fig. 4a. The photoreponses as a function of time characteristics of the SnS$_2$/Ag-NPs photodetectors were...
investigated at $\lambda = 250$ nm while holding the device at the bending position of various radii (0–flat, 20 mm, and 10 mm). Furthermore, we also illuminated at different light wavelengths ($\lambda = 250$, 540, and 1050 nm) at three different bending curvatures.

Fig. 4c depicts that the photoresponsivity of the flexible photodetector at 0 (flat), 20, and 10 mm was found to be $\sim 4778$, $\sim 4575$, and $\sim 4332$ A W$^{-1}$ at $\lambda = 250$ nm, respectively. The results show that the photoresponse remains persistent at different curvature states, thereby indicating that the devices exhibit excellent mechanical flexibility and broadband photodetection which are hardly affected by bending conditions. Moreover, the bending stability and reliability are the key factors of flexible photodetectors. Therefore, we bent (20 mm) our devices several times and measured the endurance of the photocurrent. From Fig. 4d, it is observed that the photoresponsivity of the flexible photodetector is $\sim 4556$, $\sim 4523$, $\sim 4101$, and $\sim 3561$ after bending for 0, 50, 100, and 150 cycles, respectively. Importantly, after 150 cycles, the photoresponsivity of the device decreased by $\sim 21\%$, which endorsed the photodetection stability of the flexible SnS$_2$/Ag-NPs device under multiple bending cycles of 20 mm curvature. Furthermore, to observe the mechanical stability we calculated the response time of flexible the SnS$_2$/Ag-NPs device at $\lambda = 250$ nm at various bending curvatures. It is found that the response times are slightly reduced from 5.3 to 4.5 s (rise) and 6.7 to 6.1 s (decay) as the bending curvature is increased as shown in Fig. S8.$^{\dagger}$ The reduction of response may be attributed to the
defect states produced by stretching of the channel material SnS2. However, the flexible measurements clearly exhibit repeated bending, making it an attractive material for wearable photodetectors.

3. Conclusion

In summary, we have reported multilayer SnS2, SnS2/Ag-NP, and SnS2/Ag-NPs/HfO2 transistors to elucidate the light–matter interaction for broadband photodetectors. The light sensing capabilities of SnS2 are extended from the UV to near NIR (250–1050 nm) spectrum after decorating with Ag-NPs, which endorsed the extension of the cut-off wavelength in SnS2. These results suggest the enhanced light absorption with localization of the electromagnetic field via the surface plasmon-enhanced optical field and the wide band gap of SnS2 crystals. Furthermore, the photodetection performance, such as the photocurrent, photoresponsivity, and EQE, is significantly enhanced in the passivated Ag-NP-decorated SnS2 devices when compared to the bare SnS2 devices. In addition, we estimated the photo-performance deterioration of each device, where it was found that the SnS2/Ag-NPs/HfO2 device showed excellent stability with a meager reduction in photoresponsivity as compared to other devices. Moreover, we made a flexible SnS2/Ag-NPs photodetector, which showed a broadband light response having stability up to 500 bending cycles at a 20 mm curvature. Thus, our results provide an efficient approach to extend the optical and flexible sensing capabilities in wide bandgap 2D materials from UV to NIR for multifunctional photodetectors.

4. Materials and methods

To make large-scale patterns on Si/SiO2 substrates, we first performed photolithography. The chips were sonicated in acetone and isopropanol solvents, and later rinsed with piranha solution and washed with de-ionized water for 15 minutes to ensure the proper removal of contamination from the Si/SiO2 chips. The chips were soft-baked in a furnace at 125 °C to remove moisture. The 2D crystals of SnS2 were physically peeled off from the bulk crystals using a scotch tape and transferred to pre-patterned Au contact pads on Si/SiO2 wafers by the dry transfer method using the polydimethylsiloxane (PDMS) stamp technique. We used atomic force microscopy (AFM), XE-100 by Park Systems Inc., for precise thickness measurements of the SnS2 flakes. Subsequently, we performed electron beam lithography (EBL) to pattern metal electrodes. After EBL, we evaporated the Cr and Au metals of 5 and 80 nm thick, respectively, for metallization of the electrodes. Finally, the devices were immersed in acetone to lift-off the excess metal from the substrate. In addition, for flexible measurements, we used polyethylene naphthalate (PEN) substrates to fabricate the SnS2/Ag-NPs photodetector. Raman spectroscopy (Renishaw, In Via systems) was performed with a laser source...
of 514 nm under ambient conditions. Furthermore, atomic layer deposition (ALD) was used to deposit HfO₂ (~15 nm) at 250 °C at a rate of 0.1 nm per cycle. Electrical measurements were performed by employing a voltmeter (Keithley 2400) and a picoammeter (Keithley 6485).

Conflicts of interest
All authors have no conflict to declare.

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