Substrate effects in high gain, low operating voltage SnSe₂ photoconductor

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Abstract

High gain photoconductive devices find wide spread applications in low intensity light detection. Ultra-thin layered materials have recently drawn a lot of attention from researchers in this regard. However, in general, a large operating voltage is required to obtain large responsivity in these devices. In addition, the characteristics are often confounded by substrate induced trap effects. Here we report multi-layer SnSe₂ based photoconductive devices using two different structures: (1) SiO₂ substrate supported inter-digitated electrode (IDE), and (2) suspended channel. The IDE device exhibits a responsivity of \( \approx 10^3 \) A W⁻¹ and \( \approx 8.66 \times 10^4 \) A W⁻¹ at operating voltages of 1 mV and 100 mV, respectively—a superior low voltage performance over existing literature on planar 2D structures. However, the responsivity reduces by more than two orders of magnitude, while the transient response improves for the suspended device—providing insights into the critical role played by the channel-substrate interface in the gain mechanism. The results, on one hand, are promising for highly sensitive photoconductive applications consuming ultra-low power, and on the other hand, show a generic methodology that could be applied to other layered material based photoconductive devices as well for extracting the intrinsic behavior.

Keywords: layered materials, photoconductivity, photoconductive gain, SnSe₂

(Some figures may appear in colour only in the online journal)

1. Introduction

Ultra-thin layered materials are promising candidates for low cost, flexible electronic and opto-electronic applications [1]. While transition metal dichalcogenides (for example, sulfides and selenides of Mo and W) have attracted a lot of attention, other layered materials including group IIA–IVA (sulfides and selenides of Ga and In) and group IVA–VIA (sulfides and selenides of Ge, Sn) compounds also exhibit excellent opto-electronic properties [2]. SnSe₂ is one such layered material, which has a very similar structure as that of transition metal dichalcogenides. In a monolayer, Sn atoms are sandwiched between the Se atoms, while multiple layers are weakly coupled through van der Waals interaction in the out of plane direction. SnSe₂ has been reported to be an air stable material, and can be deposited using MBE growth [3], spray pyrolysis [4] and mechanical exfoliation [5–7]. While several works report moderate carrier mobility [5–7] and weak gate tunability due to inherent large doping [7], large gate modulation of conductivity has also been reported [5].

SnSe₂ based photodetectors have been recently reported [7–9]. However, most of the photodetector devices reported on SnSe₂, and on layered materials in general, use large operating voltage to achieve better sensitivity—a major limitation for low power applications. Strong light absorption [10], coupled with excellent carrier transport properties of SnSe₂ provide an opportunity for building highly sensitive photodetection devices operating at small bias voltage—a regime which has not yet been explored. In addition, the photoresponse of layered material based devices is often dominated by carrier trapping at the channel-substrate interface. In this work, by using high quality contacts to multi-layer SnSe₂ in an inter-digitated electrode (IDE) structure, we achieve responsivity of \( \approx 10^3 \) A W⁻¹ at 1 mV external bias, and the responsivity increases to \( \approx 8.66 \times 10^4 \) A W⁻¹ at 100 mV. To investigate the origin of such high gain, we also compare the results with that of a suspended SnSe₂ device...
where the transient response is improved at the expense of suppressed gain—providing insights into the gain mechanism.

2. Experiment

2.1. Characterization of SnSe\textsubscript{2} flakes

Thickness of the exfoliated flakes was confirmed with atomic force microscopy (AFM), as shown in figure 1(a). The exfoliated crystals exhibit strong thickness dependence in Raman scattered signals \[11, 12\], as illustrated in figure 1(b). Two prominent peaks, namely $E_g$ and $A_{1g}$, are clearly observed. With an increase in thickness, the separation ($\Delta$) between $A_{1g}$ and $E_g$ peaks reduces, particularly when the thickness is less than 8 nm (inset of figure 1(b)), and can be used to identify thickness of SnSe\textsubscript{2} flakes. On the other hand, with an increase in laser power, we observe that both the peaks exhibit strong shift towards lower wavenumber, as shown in figure 1(c). Here zero corresponds to peak position at very small laser power. Such a shift can be attributed to the anharmonic effect \[13\] of SnSe\textsubscript{2} phonons resulting from an enhancement in local temperature of the sample due to increasing laser power \[14\].

2.2. Fabrication of substrate supported and suspended structure

Thin layers of SnSe\textsubscript{2} are exfoliated on 285 nm thick SiO\textsubscript{2} covered Si substrate. The flakes are identified by the observation under optical microscopy, followed by Raman spectroscopy. SnSe\textsubscript{2} flakes having thickness of 10–15 nm are selected to fabricate photoconductor using IDE structure, as schematically shown in figure 2(a). The electrodes are defined using electron beam lithography followed by the deposition of Ni (10 nm)/Au (50 nm) using electron beam evaporation technique, and subsequent lift-off. The top inset of figure 2(b) shows the optical image of the fabricated device.

For the suspended structure, closely spaced metal pads are patterned by optical lithography, followed by deposition of Ni (10 nm)/Au (50 nm) using the electron beam evaporation technique, and subsequently lift-off. The SnSe\textsubscript{2} flakes are then transferred on top of these metal pads carefully such that the flake is completely suspended without touching the SiO\textsubscript{2} substrate. The schematic of the suspended device is depicted in figure 2(c). The cross section SEM of the suspended device is shown in the inset of figure 2(d) and clearly indicates that the SnSe\textsubscript{2} film is completely isolated from the substrate.

3. Results and discussions

3.1. Electrical transport properties of SnSe\textsubscript{2} under dark condition

The black triangles in figure 2(b) indicate the dark current ($I_{\text{dark}}$) of a representative substrate supported IDE device. The strong linearity suggests good quality ohmic contacts with a
dark current of $0.56 \mu A \mu m^{-1}$ at $V_{ds} = 1$ mV. On the other hand, the SnSe$_2$ channel being completely isolated from the substrate in the suspended structure, is expected to exhibit intrinsic behavior of SnSe$_2$ as a photoconductor. The dark current of the suspended device, as shown by the black triangles in figure 2(d), exhibits excellent linear characteristics as well. This indicated good contact quality for both the structures.

To understand the origin of the high conductivity of SnSe$_2$, we perform kelvin probe force microscopy (KPFM) measurements. We prepared a special test structure for KPFM measurement where parallel Au lines are first deposited on a SiO$_2$/Si substrate, followed by exfoliation of SnSe$_2$ multilayer on top, such that the flake partially resides on a metal line, and the rest on SiO$_2$. An AFM thickness mapping image and the corresponding KPFM mapping of the test structure is shown in figures 3(a) and (b). This ‘metal-bottom/flake-top’ structure provides an easy access of the probe tip to the SnSe$_2$ film and avoids the difficulty of characterization of the SnSe$_2$ layers hidden underneath the contact metal in a typical ‘metal-top/flake bottom’ structure used in the photoconductor device. The metal lines were grounded during KPFM measurement. The KPFM measurements in figure 3(c) indicate the contact potential difference (CPD) between the tip and the sample, which, in turn, allows us to predict the local work function differences $\Delta W = W_{tip} - W_{sample}$. Here, $W_{tip} = 5.3$ eV. A CPD of 400 mV between tip and SnSe$_2$ thus suggests that the work function of the SnSe$_2$ sample is around 4.9 eV. The electron affinity of SnSe$_2$ has been reported to be around 5.2 eV [15]. Hence, we conclude that the flakes are degenerately n-type doped, explaining high conductivity and low resistance ohmic contacts. Figure 3(c) also shows that the work function difference between SnSe$_2$ and Au is about 150 meV. Note that, the conduction band minimum occurs at the L point (figure 3(d)) in the bulk SnSe$_2$ Brillouin zone [16], which has a valley degeneracy ($g_v$) of 3. The electron density can be calculated as $n = \int_0^\infty \frac{1}{g_v^*} \frac{1}{1 + e^{E/E_o}} \frac{8 \sqrt{2m^*}^{3/2}}{h^2} \sqrt{E} dE$ where $\mu = 0.3$ eV from KPFM measurement, and $m^* = 0.4m_0$ [10]. This leads to an estimated electron density in excess of $10^{20}$ cm$^{-3}$. We also observe very weak gate dependence of the output current, in agreement with degenerate doping. The resulting band diagram of a metal–SnSe$_2$–metal structure is schematically illustrated in figure 3(e).
3.2. Photoresponse of substrate supported and suspended SnSe$_2$ device

The response to a 532 nm wavelength laser spot focused at one of the source edges of the substrate supported IDE device is shown in red in figure 2(b), indicating strong photoresponse. The suspended device, on the other hand, exhibits a weaker photoresponse (figure 2(d)). The responsivities \( R = \frac{I_{\text{out}}}{I_{\text{in}}} = \frac{I_{\text{out}} - I_{\text{dark}}}{I_{\text{in}}} \) of two different IDE photoconductors (namely, ID1 and ID2, with similar device dimensions) are plotted in figure 4(a), as a function of drain bias.
The measured responsivity of the suspended structure (DS) is ≈115 A W⁻¹ at 100 mV for both types of illumination (532 nm laser and white light), as shown in figure 4(a). This is lower than the IDE devices by more than two orders of magnitude, but still compares superlatively with, for example, graphene based photoconductors [17–19]. The corresponding D* values of the suspended device also exhibit a similar reduction compared with the substrate supported IDE devices (figure 4(b)).

Owing to the degenerate electron doping in the multilayer SnSe₂, electrons are the primary current carrying species responsible for photocurrent. Note that the gain G is the ratio of hole trapping time and electron transit time \( G = \frac{\tau_e}{\tau_h} \).

Using \( \tau_h = \frac{L^2}{\mu_e V_{th}} \) we obtain

\[
R = \frac{g_\eta \lambda}{h c} \left( \frac{\tau_e}{\tau_h} \right) = \frac{q \lambda \eta \mu_e}{h c L^2} V_{th}
\]

where \( L \) and \( \mu_e \) are the length of the device channel and electron mobility, respectively. This explains the strong linearity obtained between \( R \) and \( V_{th} \) in figure 4 for a given wavelength of excitation. If we take \( \eta \approx 1 \), using equation (1), the responsivity at 555 nm wavelength translates to \( G \approx 2.24 \times 10^3 \) at \( V_{th} = 1 \) mV for the IDE devices.

3.3. Gain mechanism and role of substrate

To understand the origin of such high gain, we perform scanning photocurrent measurements in an IDE photoconductive device. As schematically illustrated in figure 5(a), a 532 nm laser is scanned across the device, and the corresponding photocurrent is recorded at \( V_{th} = 1 \) mV. The results are summarized in figure 5(b). We observe a strong non-uniformity in the spatial distribution of the photocurrent with a maximum at the source metal edges, while the minimum occurs inside the channel. Similar observations of non-uniform photocurrent have been made in other layered material based photoconductive devices as well [20]. Strong inherent doping allows efficient band bending at the SnSe₂/metal junction. The strong photocurrent at the source and drain edges can be attributed to a combined effect of band bending induced carrier separation and metal induced hot photo carrier injection. Larger photocurrent when the laser spot is at the source edge compared with the drain edge can be understood by noting that photo-generated electrons are the
primary charge carriers in the n-doped channel of the device. When the laser spot is at the drain contact edge, the holes being the minority carriers, recombine with electrons before being collected by the source end.

The high gain suggests that the lifetime of the photogenerated holes is much larger than the electron transit time, that is $\tau \gg \tau_e$. To obtain a quantitative understanding about the trapping time $\tau$, we performed a time dependent laser excitation, as shown in figure 5(c). The laser spot is focused at the source contact edge, turned on for a while and then turned off. The slow decay of the photocurrent shows an exponential behavior, suggesting slow de-trapping of holes. Once the laser is turned off, the slow decay of the photocurrent (after a sharp fall for a very short period) can be fitted well with single exponential decay expression as $I = I_0 + I_1 e^{-t/\tau_1}$, as shown by the black dashed line in figure 5(c). Here $I_0, I_1,$ and $\tau_1$ are fitting parameters. The time constant $\tau_1$ obtained from the fitting is found to be 66 s for this substrate supported photoductor. This slow process allows sufficient time for successive recombination of electrons in the system [21], providing high gain. This mechanism is more efficient when the laser spot is at the source metal edge, rather than inside the channel. Due to self-consistent electrostatics, the positive charge of the trapped holes at the source edge forces the bands to be pushed down, in turn, reducing the barrier height existing between the contact and SnSe$_2$ [20]. This is schematically shown in figures 5(d)-(f). A reduced barrier allows for more efficient injection of electrons from the source into the channel, in turn increasing the photocurrent.

However, this data does not clearly explain whether the holes are trapped in the SiO$_2$ substrate, or confined in the SnSe$_2$ film itself. To segregate the contributions of the substrate and the intrinsic film, we carry out similar transient response in the suspended structure, and the result is summarized in figure 6(a). Two different decay time scales are clearly observed, and this can be fitted with two different exponential decay rates as $I = I_0 + I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2}$, as shown by the black dashed line. The two decay time constants $\tau_1$ and $\tau_2$ are 2.27 s and 53.2 s, respectively. The fast decay with time constant $\tau_1$ immediately after turning off the laser, which is almost absent in the substrate supported device, corresponds to the faster component of the photocurrent, with relatively small gain. The slow decay with time constant $\tau_2$ at the longer time scale corresponds to the slow de-trapping of holes, likely trapped in the defect centers in the SnSe$_2$ film, as schematically depicted in figure 6(b). The differences in the observations of transient response (figures 5(c) and 6(a)) and responsivity (figure 4) between the substrate supported and suspended devices indicate that the interfacial traps between SnSe$_2$ and SiO$_2$ substrate play a crucial role in the photoconductive characteristics of substrate supported devices.

The input optical power dependent responsivity of the suspended device is shown in figure 6(c). Such a decrease of responsivity with increasing optical power can be attributed to the larger photo induced carrier density at higher optical power, resulting in (i) reduced drain field in the SnSe$_2$ layer due to screening, (ii) enhanced recombination of photo-generated electron–hole pairs, and (iii) saturation of trap filling in the SnSe$_2$ film by photo-generated holes, suppressing gain.

4. Conclusion

In conclusion, we demonstrate high gain photoconductive devices with impressive responsivity and specific detectivity using IDE structure in multi-layer SnSe$_2$, operating at ultra-low
voltages. Such devices will find applications in sensitive photodetection applications, consuming ultra-low electrical power, where speed is not the primary requirement. The gain is found to be suppressed in a suspended device, due to complete decoupling of the channel from the SiO2 substrate, avoiding hole traps. The comparison of gain and transient response between the suspended and substrate supported devices allows us to segregate the substrate effects in photoconductivity. The methodology is applicable to other layered material systems as well to extract the intrinsic photoconductive behavior.

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