Bias-Modified Schottky Barrier Height-Dependent Graphene/ReSe$_2$ van der Waals Heterostructures for Excellent Photodetector and NO$_2$ Gas Sensing Applications

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Abstract: Herein, we reported a unique photo device consisting of monolayer graphene and a few-layer rhenium diselenide (ReSe$_2$) heterojunction. The prepared Gr/ReSe$_2$-HS demonstrated an excellent mobility of 380 cm$^2$/Vs, current on/off ratio $\sim 10^{11}$, photoresponsivity ($R \sim 74$ AW$^{-1}$ @ 82 mW cm$^{-2}$), detectivity ($D^* \sim 1.25 \times 10^{11}$ Jones), external quantum efficiency (EQE $\sim 173$%) and rapid photoresponse (rise/fall time $\sim 75/3$ ms) significantly higher to an individual ReSe$_2$ device (mobility $= 36$ cm$^2$/V s, $D^* = 1.02 \times 10^6$, EQE $= 26.1$%, rise/fall time $= 2.37/5.03$ s). Additionally, gate-bias dependent Schottky barrier height (SBH) estimation for individual ReSe$_2$ (45 meV at $V_{bg} = 40$ V) and Gr/ReSe$_2$-HS (9.02 meV at $V_{bg} = 40$ V) revealed a low value for the heterostructure, confirming dry transfer technique to be successful in fabricating an interfacial defects-free junction. In addition, HS is fully capable to demonstrate an excellent gas sensing response with rapid recovery time ($39/126$ s for NO$_2$ at 200 ppb) and is operational at room temperature ($26.85$ °C). The proposed Gr/ReSe$_2$-HS is capable of demonstrating excellent electro-optical, as well as gas sensing, performance simultaneously and, therefore, can be used as a building block to fabricate next-generation photodetectors and gas sensors.

Keywords: graphene; ReSe$_2$; heterostructure; photodetector; NO$_2$ gas sensor; Schottky barrier height

1. Introduction

Graphene and other two-dimensional (2D) materials, particularly transition metal dichalcogenides (TMDs), have attracted much attention due to their unique electro-optical properties [1–3]. TMDs consist of smooth surfaces without any dangling bonds and possess significantly low surface states and trapping defects that cumulatively enable rapid charge speed and suppress charge scattering even in a few nanometer-thick layers [4]. Using these materials, the scientific community is able to develop many proof-of-concept devices such as field effect transistors (FETs) [5–7], photodetectors [8–10], supercapacitors [5,11], solar cells [12], gas sensors [13], electrochemical sensors [14] and biosensors [15–17], etc., for years. Amongst these, photodetectors and gas sensors are of significant interest as they possess the capacity of resolving energy and environmental concerns to a certain level [18]. Interestingly, in contrast to graphene (a zero bandgap material) [19], TMDs have finite bandgap values normally between 0.2 to 3 eV [20] depending upon the choice of material and its layer thickness and were found to be a potential substitute for traditional narrow bandgap materials for many electronic and optoelectronic applications. Moreover, their
properties are strongly influenced by the choice of metal contacts (either ohmic or Schottky), energy band alignment, and types of TMDs [21]. Additionally, their electro-optical and gas sensor characteristics can also be modified by the electrostatic backgate voltage as well as channel region doping [22,23].

Furthermore, heterostructures (HS) fabricated on either TMDs or with other low-dimensional electronic materials have been found to demonstrate outstanding optoelectronic and gas sensing performance in comparison to their counterparts [24–26]. For instance, PbS quantum dots (PbS-QDs)/MoS$_2$ heterostructure have shown a tremendously high photoresponsivity ($\sim 6 \times 10^5$ AW$^{-1}$) as compared to only an MoS$_2$ photodetector. Such remarkable photoresponse properties are associated with strong light absorption characteristics of PbS-QDs [27]. Previously, we have demonstrated ZnO-QDs drop cast over MoS$_2$ nanosheets to study their electro-optical characteristics. The calculated photoresponsivity was found to be $2 \times 10^3$ AW$^{-1}$ [28]. Despite excellent photoresponse, these photodetectors have demonstrated low response speeds (0.1–10 s). This limited performance is ascribed to low response rates as well as the environmental hazard nature (Zn or Pb leaching) of QDs [29].

Moving onward, 2D-materials-based gas sensors have also been found to be of significant interest. From the literature, the gas sensing response strictly depends upon the surface-to-volume ratio (SVR) of the material [33]. In this perspective, graphene was believed to outperform conventional sensors as its atomically thin layered structure possesses ultimately high SVR [34]. However, in addition to SVR, other factors that can influence gas sensing response are semiconducting properties and the density of available reactive sites for the occurrence of redox reactions [35,36]. Since individual graphene layers have no bandgap, however, stacking graphene to other TMDs can resolve this problem as the semiconducting properties of TMDs can easily be modified by the electrostatic gate bias or exposure to light and therefore, gas sensing response can be modulated/improved. Several 2D materials such as MoS$_2$, GaSe, GaS, hBN, WSe$_2$, etc. were investigated for gas sensing however, there is not much literature available on graphene-based TMDs heterostructures used as gas sensors [13].

Among various TMDs out there, rhenium diselenide (ReSe$_2$) has been found as an excellent 2D semiconducting material possessing a theoretically measured DFT-based direct narrow bandgap ($\sim 0.995$ (bulk)$–1.239$ eV (monolayer)) [37] which is significantly lower than conventional TMDs [38]. Recently, Kim et al. [23] investigated HCl-mediated p-doping of ReSe$_2$ and reported an improved photoresponsivity of $1.93 \times 10^3$ AW$^{-1}$ and photoresponse rise/decay time of 1.4/3.1 ms as compared to undoped ReSe$_2$ (photoresponsivity $= 79.99$ AW$^{-1}$, rise/decay time = 10.5 ms/291 ms). Bach et al. [39] have studied Gr/ReSe$_2$ barristor devices, however, with limited photoresponsivity of $42$ AW$^{-1}$ and rise/decay time of 33.9/20.8 ms under a high laser wavelength of 656 nm with a light intensity of 189 mW/cm$^2$. However, these reports demonstrated lower photoresponse time. Moreover, no gas-sensing performance was demonstrated in these devices. Therefore, it is of great interest to develop a heterostructure that can demonstrate good electro-optical and gas sensing characteristics simultaneously within a single device.

Herein, we have successfully developed a Gr/ReSe$_2$ hybrid device that can demonstrate exceptional photodetector and gas sensing performance, simultaneously. In our device, graphene and ReSe$_2$ flakes work as transport and light absorption layers, respectively. We have drawn a comparative analysis of electro-optical performance between individual ReSe$_2$ and Gr/ReSe$_2$ devices. The results indicate that the Gr/ReSe$_2$ photodetector has considerable photoresponsivity (R $\sim 74$ AW$^{-1}$ at 82 mW cm$^{-2}$), detectivity
(D* \sim 1.25 \times 10^{11} \text{Jones}) and a high photoresponse (rise/decay \sim 75/3 \mu s) as compared to an individual ReSe_2 device (R = 11.2 \text{ AW}^{-1}, D* = 1.02 \times 10^{10}, \text{rise/fall time} = 2.37/5.03 \text{s}). Moreover, the photocurrent and photoresponsivity were calculated as a function of laser light intensity. Furthermore, Schottky barrier height (SBH) evaluation has revealed Gr/ReSe_2 devices demonstrating low SBH (9.02 meV at V_{bg} = 40 \text{ V}) which is the reason behind the high electro-optical performance of the HS. Finally, Gr/ReSe_2-HS was tested for NO_2 gas sensing (20–200 ppb). The exceptional performance of our devices is ascribed to high-quality graphene, a suitable choice of ReSe_2 flake, residual-free PDMS stamp supported transfer technique and choice of metal electrodes that eventually reveal low SBH.

2. Experimental Detail

2.1. Device Fabrication

Here, a vertical heterostructure (HS) composed of mono-layer graphene and few-layer ReSe_2 was prepared over SiO_2 (300 nm)/p^+-Si substrate. Figure SI illustrates step-by-step fabrication detail about HS formation. Briefly, CVD-grown monolayer graphene was transferred over SiO_2/Si substrate by employing the wet transfer method reported elsewhere [40]. As-transferred graphene layer was then patterned into a rectangular shape (hall bar) using photolithography and an oxygen plasma etching process. During O_2 etching, graphene was treated by power (~50 W) for a few minutes to etch undesired graphene. To make a large pattern around the graphene hall bar, a second photolithography process was carried out after which the defined electrodes were filled by Cr/Au (5/30 nm) deposition. On completion of the deposition, the devices were left in acetone for several hours to accomplish the lift-off process.

On another substrate (SiO_2 (300 nm)/p^+-Si), we used the scotch-tape method to mechanically exfoliate the ReSe_2 flake. An optical microscope was used to find a suitable ReSe_2 flake of a few-layers thickness which was later transferred to a pre-patterned graphene hall bar using a PDMS stamp and micromanipulator. In the end, the e-beam lithography process followed by Cr/Au (8/120 nm) deposition and subsequent lift-off in acetone were conducted to make final electrical connections to Gr/ReSe_2 HS. Additionally, a moderate temperature annealing process (200 \text{ °C for 4 h}) was also carried out in a tube furnace under Ar/H_2 (97.5%/2.5%) gas flow to improve adhesion between metal electrodes and flake surfaces.

2.2. Characterization

Raman analysis was examined using micro-Raman (Renishaw, Wotton-under-Edge, UK) for monolayer graphene, few-layer ReSe_2, and Gr/ReSe_2 HS. A laser wavelength (514 nm) of low-power intensity (511 \mu W) with a spot size of 0.7 \mu m was used to avoid any kind of structural deterioration due to the laser heating effect. Furthermore, to realize the exact thickness of graphene and ReSe_2 flakes, atomic force microscopy (AFM; n-Tracer, NanoFocus, Oberhausen, Germany) in tapping mode was used.

2.3. Electrical and Electro-Optical Measurement

For electrical measurement, Keithley 2400 and Keithley 6485 K (Keithley Instruments, Inc., Cleveland, OH, USA) were used as source meter and picoammeter, respectively. The complete electrical measurement was performed at room temperature and under vacuum (10^{-3} \text{ Torr}) conditions. Further, to estimate Schottky barrier height (SBH), the device’s electrical measurement was achieved in the low-temperature range (30–300 K) under high vacuum (10^{-4} to 10^{-5} \text{ Torr}). Moreover, to study electro-optical measurement, the devices were tested using the same systems (Keithley 2400 and Keithley 6485 K) under a vacuum in the dark and under laser light irradiation (532 nm) of varying power intensity (82–820 mW cm^{-2}).
2.4. NO₂ Gas Sensing Measurement

To further test the Gr/ReSe₂ heterostructure ability to sense NO₂ gas, an experimental setup illustrated in Figure S5 was utilized. The desired concentration was achieved by mixing NO₂ (2%) and N₂ (98%) before injecting them into the chamber. For this purpose, a mass flow controller (MFC) was employed which can control concentration and maintain a total gas flow rate of around 1000 sccm throughout the experiment. The gas is injected inside the chamber in such a manner that it reaches the Gr/ReSe₂ HS-based sensor device within a few seconds. Such an experimental arrangement is very effective as it can detect any environmental change quickly. All the measurement was conducted at room temperature (26.85 °C) under ambient atmospheric conditions. The device was also irradiated with light illumination of 532 nm with a power intensity of 310 mW cm⁻² to enhance the gas sensing response of the heterostructure.

3. Results and Discussion

Figure 1a,b illustrates a schematic diagram and an actual device optical image of graphene/ReSe₂ van der Waals heterostructure, respectively, fabricated at Si/SiO₂ substrate and after Cr/Au contacts deposition via e-beam lithography process (scale bar: 5 µm). Figure S1 represents the device fabrication detail and the various steps involved. In brief, CVD-grown monolayer graphene was first etched into a rectangular bar after which a pristine ReSe₂ flake of appropriate thickness was exfoliated over polydimethylsiloxane (PDMS) stamp, was transferred onto graphene and interacted through van der Waals forces using micromanipulation process. Of note, the photodetector devices based on individual ReSe₂ and graphene/ReSe₂ heterostructures have used the same ReSe₂ flake to avoid any discrepancy while measuring photodetector device performance, as different ReSe₂ flakes could have a different capacity for demonstrating photosresponse.

Further, Figure 1c represents a scanning electron microscope (SEM) micrograph (scale bar: 5 µm) which reveals a clear heterostructure without any deformation or contamination during the transfer process (yellow dotted line indicates the boundary of monolayer graphene). To further visualize the uniformity of the material and to evaluate the accurate thickness of the ReSe₂ flake, the atomic force microscopy (AFM) image and corresponding height profile are presented in Figure S2. The AFM scanning reveals ReSe₂ thickness to be around ~6.4 nm, approximately nine layers [41].

![Figure 1. Cont.](image-url)
Figure 1. (a) Schematic illustration and (b) real device optical image of graphene/ReSe$_2$ van der Waals heterostructure (scale bar; 5 µm). (c) SEM micrograph (scale bar; 5 µm), whereas yellow dotted line indicate graphene layer. (d) Raman analysis of ReSe$_2$ (black curve) and graphene/ReSe$_2$ heterostructure (red curve).

Raman analysis of ReSe$_2$ and graphene/ReSe$_2$ heterostructure have revealed several distinct peaks between the ranges 100–300 cm$^{-1}$, ascribed to the interlayer vibrational decoupling in ReSe$_2$ (Figure 1d). The prominent peaks related to ReSe$_2$ were observed at 124 and 158 cm$^{-1}$. These are associated with in-plane ($E_g$) and out-of-plane (Ag) vibrational modes, respectively [42]. Furthermore, in the case of graphene/ReSe$_2$ heterostructure, some additional peaks related to monolayer graphene were observed; G-peak positioned at 1580 cm$^{-1}$ and is related to in-plane phonon mode, and 2D-peak located at $\sim$2700 cm$^{-1}$ is ascribed to double resonance [39,43].

3.1. ReSe$_2$ Device Electrical Performance

To explore the device’s performance and to investigate the advantage of graphene in the heterostructure, the device’s electrical properties were realized from both pristine ReSe$_2$ channel and Gr/ReSe$_2$ heterostructure. Figure 2 illustrates the electrical performance of a few-layer ReSe$_2$ flake fabricated on a Si/SiO$_2$ substrate. The transfer characteristics ($I_{ds}$–$V_{bg}$) were studied at $V_{ds} = 0.2$–1 V and are presented both in linear-, and log-scale as shown in Figure 2a,b, respectively. A bias-dependent increase in on-current ($I_{on}$) has been observed on increasing $V_{ds}$ from 0.2 to 1 V which demonstrates usual ReSe$_2$ transistor characteristics, similar to work [22,44]. The field-effect mobility denoted as $\mu_{FE}$ can be evaluated by the following relation:

$$\mu_{FE} = \frac{L}{W} \left( \frac{dI_{ds}}{dV_{bg}} \right) \frac{1}{C_{bg} V_{ds}}$$  \hspace{1cm} (1)

In the above relation, the letters “L” and “W” indicate the length and width of the ReSe$_2$ channel, $\frac{dI_{ds}}{dV_{bg}}$ denotes slope related to transfer characteristics, and $C_{bg}$ (115 aF/µm$^2$) represents gate capacitance [45–47]. The calculated mobility for the ReSe$_2$ transistor was 36 cm$^2$/Vs. In addition, the $V_{bg}$-dependent trend of transconductance ($g_m(\mu S) = \frac{dI_{ds}}{dV_{bg}}$) of ReSe$_2$-based FET was presented (inset: Figure 2a) which demonstrate that the proposed devices possess promising potential of delivering larger gain. Furthermore, to find the suitability of the prepared ReSe$_2$ transistors for digital applications, the devices must possess a current on/off ratio ($I_{on}/I_{off}$) of at least $10^4$ [48]. Figure 2b presents log-scale $I_{ds}$–$V_{bg}$
characteristics and the corresponding calculated $I_{on}/I_{off}$ ratio as the inset. Interestingly, the calculated $I_{on}/I_{off}$ ratio ($-1.4 \times 10^5$–$1.8 \times 10^5$) demonstrates an increasing trend with $V_{ds}$ possibly due to an increase in on-current as observed in $I_{ds}$–$V_{bg}$ characteristics. The calculated mobility and $I_{on}/I_{off}$ are reasonably higher than the minimum requirement and surpass most of the previously reported TMDs on the Si/SiO$_2$ substrate. Moving further, the output characteristics ($I_{ds}$–$V_{ds}$) related to the ReSe$_2$ transistor were evaluated, as presented in linear scale (Figure 2c) and log-scale (Figure 2d), respectively. Almost linear $I_{ds}$–$V_{ds}$ characteristics in the low bias ($\pm V_{ds}$) region reveal that the Cr/Au contact established nearly ohmic contact with the ReSe$_2$ channel with low Schottky barrier height (see Section 3.3), as observed previously [49].

![Figure 2](image_url)

Figure 2. Transfer characteristics ($I_{ds}$–$V_{bg}$) of ReSe$_2$ at $V_{ds} = 0.2$–$1.0$ V (a) in linear scale, and (b) in log scale (inset: current on/off ratio measured at $V_{ds} = 0.2$–$1.0$ V). Output characteristics ($I_{ds}$–$V_{ds}$) in $V_{bg}$ range from $-20$ to $30$ V (c) in linear scale, and (d) in log scale.

After the electrical transport measurement of the ReSe$_2$ transistor, a detailed transport measurement was carried out to evaluate Gr/ReSe$_2$ heterostructure electro-optical performance. Figure 3a illustrates the transfer characteristics ($I_{ds}$–$V_{bg}$) of Gr/ReSe$_2$ van der Waals heterostructure both in linear- and log-scale at $V_{ds} = 1$ V. It is noteworthy that the heterostructure demonstrates similar transfer characteristics as of pristine ReSe$_2$ transistor (Figure 2a); however, a high on-current was observed in the heterostructure as compared to pristine ReSe$_2$. This is ascribed to the higher carrier mobility of graphene [24]. The detailed transport characteristics (transfer and output) of pristine graphene are also presented in Figure S3. A charge-neutral point (CNP) also known as a Dirac point (DP) was observed around $-8$ V at $V_{ds} = 0.1$ V (Figure S3a), which indicates the graphene is a kind of n-doped graphene [50]. It should be noted here that no intentional doping was performed during the synthesis or transfer process. Therefore, the present monolayer graphene is
regarded as pristine graphene. Further, the mobility was calculated using the relation \( \mu = (1/C_{bg}) (-\sigma/V_{bg}) \), where \( \sigma = 1/\rho \) represents sample conductivity. The measured value of electron mobility for monolayer graphene was around 1350 cm\(^2\)/Vs. In addition, the output characteristics (I\(_{ds}\)-V\(_{ds}\)) were also performed (Figure S3b) which shows a linear relation, revealing the ohmic nature of Cr/Au contact with monolayer graphene. Such remarkable performance of monolayer graphene is the key reason for the high-performing Gr/ReSe\(_2\) heterostructure where we have observed mobility of 380 cm\(^2\)/Vs and an on/off ratio ~ 10\(^4\). Here, Gr/ReSe\(_2\) heterostructure was prepared using CVD-grown monolayer graphene over which an exfoliated ReSe\(_2\) flake was transferred. Such heterostructure was also reported previously, however with a limited \( I_{on}/I_{off} \) ratio of ~10\(^2\) [39]. However, the present work has demonstrated an \( I_{on}/I_{off} \) ratio (10\(^4\)), revealing the potential of the studied heterostructure for switching applications. The limited \( I_{on}/I_{off} \) could be ascribed to graphene’s semi-metallic nature where the Fermi level of graphene and the related work function varies with bias voltage, resulting in controlled carrier transportation across valence/conduction bands. Moreover, the defects during the growth process of graphene and impurities through the transfer process could also play a significant role in controlling device electro-optical performance [51].

![Graphene/ReSe\(_2\) heterostructure characteristics](image)

**Figure 3.** Graphene/ReSe\(_2\) heterostructure characteristics: (a) transfer characteristics (I\(_{ds}\)-V\(_{bg}\)) both in linear (black curve) and log-scale (blue curve) measured at V\(_{ds}\) = 1 V showing on/off ratio of ~10\(^4\). (b) Output characteristics (I\(_{ds}\)-V\(_{ds}\)) in dark and under various light intensities (82–820 mW/cm\(^2\)) conditions measured at V\(_{bg}\) = −20 V and incident light wavelength of 532 nm. (c) Observation of linear relationship between \( \Delta L_{ds} = I_{ph} - I_{dark} \) and light power intensities evaluated at V\(_{bg}\) = −20 V, V\(_{ds}\) = 1 V, and \( \lambda = 532 \) nm (where \( R^2 = 0.9859 \)). (d) Measurement of photocurrent for five consecutive cycles without any biasing at V\(_{ds}\) = 1 V, power = 310 mW/cm\(^2\), and \( \lambda = 532 \) nm. (e) Corresponding measurement of photoresponse (rise time (75 µs) and fall time (3 µs)) of the graphene/ReSe\(_2\) heterostructure-based photodetector. (f) Responsivity versus power intensity trend follows relationship \( R = \alpha P^{-\beta} \) with calculated \( \beta = 0.844 \).

### 3.2. Gr/ReSe\(_2\) Photodetector Response

To evaluate the photodetector performance based on Gr/ReSe\(_2\) heterostructure, photocurrent measurement as a function of V\(_{ds}\) at a fixed V\(_{bg}\) = −20 V and \( \lambda = 532 \) nm was presented in Figure 3b. The measured photocurrent at various incident light intensities is significantly higher than what has been observed under dark conditions, revealing
the excellent photoresponse of active charge carriers inside the Gr/ReSe$_2$ heterostructure. Interestingly, a linear relationship between $\Delta I_{ph}$ and light power intensities has been observed (Figure 3c) which indicates that the larger the light intensity, the higher will be the electron-hole pair generation which leads to the generation of high photocurrent in these devices [52]. Further, a cyclic measurement was performed which measured photocurrent for five consecutive cycles without any bias voltage at a power intensity of 310 mW/cm$^2$, $V_{ds} = 1$ V and $\lambda = 532$ nm (Figure 3d). In this way, Gr/ReSe$_2$ heterostructure photoresponse stability and results repeatability was verified. Noteworthy, the devices were measured under vacuum conditions to avoid external oxygen or water molecules device degradation. Moreover, the photoresponse was estimated at $V_{bg} = 0$ V to remove gate dependency or current contribution. However, the supplied $V_{ds}$ was maintained at 1 V to facilitate drift to charge carriers in the channel region of the Gr/ReSe$_2$ heterostructure. Furthermore, the photoresponse, i.e., the rise and fall time of the photodetector as a function of time, was estimated as shown in Figure 3e. The rise time ($\tau_{rise}$) and fall time ($\tau_{fall}$) of the photodetector was calculated using the following fitting equations [28]:

$$I_{ph}(t) = I_{dark} + Ae^{\frac{t}{\tau_{rise}}}$$ (2)

$$I_{ph}(t) = I_{dark} + Ae^{-\frac{t}{\tau_{fall}}}$$ (3)

where "$I_{ph}(t)$" represents time-dependent photocurrent, "$I_{dark}$" indicate dark current under no light illumination, "$t$" denotes light switching time, and "$A$" is equation constant. Equations (2) and (3) were used to estimate the rise and fall time of the Gr/ReSe$_2$-based photodetector. The calculated values for rise/fall time were 75/3 $\mu$s, significantly higher than most of the studied TMDs-based photodetectors [53–55]. We have also evaluated photoresponse characteristics from only the ReSe$_2$ channel-based photodetector (Figure S4). The results indicate that Gr/ReSe$_2$ photodetector has higher photo characteristics compared to the ReSe$_2$-based photodetector. In addition to the response time, several other important photodetector performance parameters such as photoresponsivity ($R_{\lambda}$), external quantum efficiency (EQE%), and detectivity ($D^*$) were evaluated and are presented in Figures 3f and 4, respectively. The $R_{\lambda}$ is equal to photocurrent produced as a unit of light intensity incident on the effective channel area of the photodetector and is given by the relation [56]:

$$R_{\lambda} = \frac{\Delta I_{ph}}{PA}$$ (4)

where $\Delta I_{ph} = I_{ph} - I_{dark}$ is the produced photocurrent, "$P$" denotes light intensity (82–310 mW/cm$^2$) and "$A$" represents the device-effective area. The calculated $R_{\lambda}$ as a function of power intensity is presented in Figure 3f and has values between (50–75 A/W). Responsivity decreases as laser power increases. This trend was fitted by the equation $R_{\lambda} = aP^{b-1}$ where $a$ and $b$ are constants whereas $P$ corresponds to optical power. The calculated value of $b$ was around 0.844 at maximum fit with $R^2 = 0.9423$. The calculated value of $R_{\lambda}$ for Gr/ReSe$_2$ photodetector is almost 7 times higher than ReSe$_2$ photodetector (Responsivity ~11.2 AW$^{-1}$).

EQE is the number of charge carriers produced per incident photon and mathematically expressed as [22]:

$$EQE = \frac{hcR_{\lambda}}{e\lambda}$$ (5)

where, $h$, $c$, and $\lambda$ are plank’s constant, speed of light and wavelength of the incident light, respectively. Interestingly, the EQE value is highly dependent on incident light wavelength, and for a fixed value of wavelength, it depends upon the value of photoresponsivity as other factors are constant. Figure 4 demonstrates a decreasing trend of EQE as a function of laser intensity and follows a similar trend as responsivity. The estimated EQE value was between 117–173% higher than the ReSe$_2$ photodetector (EQE ~ 26.1%).
Detectivity (D*) and external quantum efficiency (EQE%) measured at V_{ds} = 1 V, V_{bg} = -20 V, and \( \lambda = 532 \text{ nm} \).

Detectivity (D*) is defined as the device’s ability to detect signals of a weaker strength. This is mathematically given by the relation [28,57]:

\[
D^* = \frac{R_{\lambda}A^2}{\sqrt{2\pi I_{\text{dark}}}}
\]  

(6)

D* is described in the unit of Jones, and one Jones = 1 cm Hz^{1/2} W^{-1} and \( I_{\text{dark}} \) represent current under no illumination. Figure 4 shows D* as a function of light intensity follows a decreasing trend just like responsivity and EQE. It has values between 0.8–1.2 \times 10^{11}, significantly higher than ReSe_2 photodetector (D* \sim 1.02 \times 10^{10} \text{ Jones}). All these results indicate Gr/ReSe_2 van der Waals heterostructure-based photodetector has superior performance compared to only the ReSe_2 material-based photodetector. This means graphene has a governing role in outperforming Gr/ReSe_2 photodetector as it enhances transport rates of photo-carriers produced in ReSe_2 due to the high carrier mobility provided by graphene. The photodetector performance was compared to previously published reports as presented in Table 1.

3.3. SBH Estimation

Next, we have estimated Schottky barrier height (SBH) denoted as \( \Phi_{\text{SBH}} \), and describe it as an energy barrier faced by the electrons while moving across the metal-semiconductor junction. Schottky–Mott’s rule was used to predict the value of \( \Phi_{\text{SBH}} \). It states that the \( \Phi_{\text{SBH}} \) varies proportionally with the difference between the semiconductor’s electron affinity and the metal’s work function. Interestingly, many semiconductors do not satisfy this rule due to the generation of metal-induced gap states which pin the bandgap close to the Fermi level. Such unwanted effect is regarded as Fermi-level pinning [58]. Therefore, it is highly desirable to select proper metal and semiconductors to minimize SBH value so that devices with ultimate electro-optical performance could be achieved. Here we chose Cr metal (work function \sim 4.5 \text{ eV}) [59] to deposit as electrodes over the semiconductor (i.e., ReSe_2).
devices) and Gr/ReSe$_2$ heterostructure to define the channel. Temperature-dependent transfer characteristics ($I_{ds}$–$V_{bg}$) for the ReSe$_2$ transistor and Gr/ReSe$_2$ heterostructure were determined and presented in Figure 5a,b. The curves were obtained at various temperatures (300, 250, 200, 180, 140, 120, 100, 80, 50 and 30 K). Noteworthy, in the transfer curve, the current values increase as the temperature increases contrary to previous reports which claim a kind of metal-to-insulator transition (MIT) around 200 K [22]. Since the devices prepared in the present work are realized over Si/SiO$_2$ substrate, which possesses several impurities or defect states, it therefore hinders MIT observation in these devices. From the literature, it has been studied that gate-dependent carrier transport in thin layers of TMDs located near to dielectric substrate is strongly affected by the impurities and various disorders from the dielectric substrate. Therefore, these devices do not demonstrate MIT, which is in agreement with what we have observed in the present study. Moving further, the SBH value was calculated considering standard thermionic emission theory and using the below relationship [60]:

$$I_{ds} = A_{area}A^*T^2\exp\left(\frac{-q\Phi_{SBH}}{kT}\right)\left[\exp\left(\frac{qV_{ds}}{\eta kT}\right) - 1\right]$$

(7)

where $A_{area}$ represents the device’s effective area, $A^*$ is Richardson’s constant, $I_{ds}$ source-drain current through the device channel, $V_{ds}$ indicate source-drain voltage, $\eta$ is the ideality factor, $q$ represents electron charge, $T$ is temperature and $k$ is the Boltzmann constants.

Figure 5c,d illustrates individual ReSe$_2$ and Gr/ReSe$_2$ heterostructure device’s Richardson plot, i.e., ln ($I_s/T^2$) versus $q/kT$ in the reverse bias saturation regime where the obtained data was linearly fitted for each $V_{bg}$ value. Based on the concept of thermionic emission theory, the slope of linearly fitted curves gives the value of Schottky barrier height ($\Phi_{SBH}$) as presented in Figure 5e,f. Interestingly, the calculated values of $\Phi_{SBH}$ are lower/higher at positive/negative $V_{bg}$ values and do not vary linearly with the gate voltage. Moreover, there could exist three different transport regimes based on applied $V_{bg}$ [61]. At low $V_{bg}$, the device was considered in a switch-off state with the highest value of $\Phi_{SBH}$ and the only transport existed due to the thermal agitation of electrons crossing the barrier. Upon increasing $V_{bg}$, the $\Phi_{SBH}$ decreases and the conduction band of ReSe$_2$ started moving downward resulting in an exponential rise of current as obvious from the transfer characteristics of Figure 2b. Upon further increase in $V_{bg}$, a flat band condition ($V_{bg}$ = $V_{FB}$) reaches which exists in the subthreshold region of transfer characteristics. Moving on, for $V_{bg}$ > $V_{FB}$, the device underwent a Schottky band regime as obvious by the bent downward part of $I_{ds}$–$V_{bg}$ Characteristics, revealing a combination of thermionic and field emission transport. Finally, with more increase in $V_{bg}$, there exist a tunneling current through Cr/ReSe$_2$ barrier which became the major transport mechanism leading to the linear region in $I_{ds}$–$V_{bg}$ characteristics. As the devices are prepared over Si/SiO$_2$ substrates, therefore, a lot of charge impurities and surface traps are expected from the substrate surface that could significantly affect the transport mechanism. It is interesting to note that SBH value is significantly lower for Gr/ReSe$_2$ heterostructure ($\Phi_{SBH} = 179 - 9$ meV for $V_{bg}$ = 0–40 V) as compared to the individual ReSe$_2$ device ($\Phi_{SBH} = 274 - 45.4$ meV for $V_{bg}$ = 0–40 V). Such low SBH value is dominated by thermionic field emission and could be attributed to the graphene layer which, in the case of Gr/ReSe$_2$ heterostructure devices, acts as an impurity buffer layer. This will lead to a lesser amount of charge trapping in these devices which is evident from improved electro-optical performance in Gr/ReSe$_2$ devices as compared to individual ReSe$_2$ devices.
\[ I_{ds} = A_{area} A^* T^2 \exp \left( -q \Phi_{SBH} k T \right) \left[ \exp \left( q V_{ds} \eta k T \right) - 1 \right] \] (7)

where \( A_{area} \) represents the device’s effective area, \( A^* \) is Richardson’s constant, \( I_{ds} \) is the source-drain current through the device channel, \( V_{ds} \) indicates the source-drain voltage, \( \eta \) is the ideality factor, \( q \) represents the electron charge, \( T \) is the temperature, and \( k \) is the Boltzmann constant.

Figure 5. (a) Temperature-dependent transfer curves \((I_{ds}-V_{g})\) of ReSe\(_2\) and (b) Gr/ReSe\(_2\) transistors for temperature range 30–300 K and \( V_{ds} = 1\) V. No MIT evidence is visible. Richardson plot between \( \ln \left( I_{ds}/T^2 \right) \) and \( 1000/T \) at various \( V_{bg} \) for (c) ReSe\(_2\) device, and (d) Gr/ReSe\(_2\) heterostructure device. (e) Extracted SBH values versus \( V_{bg} \) for the ReSe\(_2\) device. (f) Extracted SBH values versus \( V_{bg} \) for Gr/ReSe\(_2\) device.

3.4. Energy Band Diagram

To further understand, we have presented the energy band diagram of the Gr/ReSe\(_2\) heterostructure as shown in Figure 6a,b. Interestingly, the substrate impurities induce p-type doping of monolayer graphene leading to an increased density of holes within the graphene layer which, in turn, shift the Fermi level lower as compared to what was observed in the case of pristine graphene. Furthermore, from transfer characteristics (Figure 2), ReSe\(_2\) appears to be an n-type semiconductor; therefore, its Fermi level will be situated close to the conduction band. Moving further, as a result of ReSe\(_2\) transferred over CVD-grown monolayer graphene, a band bending occurs across the valence/conduction bands of ReSe\(_2\) to align the Fermi levels of both materials. This band bending is attributed to the work function difference between graphene and ReSe\(_2\). Upon biasing Gr/ReSe\(_2\) heterojunction, two types of band diagrams are possibly manifested in Figure 6b,c. It should be noted that the graphene layer is in direct contact with Si/SiO\(_2\) (300 nm) dielectric substrate; therefore, an externally applied electric field could significantly modify its Fermi
level and thus the associated work function [62]. To calculate the $\Phi_{\text{SBH}}$ between graphene and ReSe$_2$, a difference between graphene Fermi level and electron affinity of ReSe$_2$ was obtained, i.e., $\Phi_{\text{SBH}} = \Phi_{\text{Gr}} - \chi_{\text{ReSe}_2}$. From this relation, one can understand that $\Phi_{\text{SBH}}$ is strictly dependent upon $\Phi_{\text{Gr}}$ and can be modified if an external voltage is applied across graphene as it changes its work function in the heterostructure device. Figure 6b explains the band diagram under $V_{bg} \leq 0$ bias condition. In this state, graphene became more hole-doped as is obvious from the downward shift of the graphene Fermi level which eventually increases its work function and the $\Phi_{\text{SBH}}$. The value of $\Phi_{\text{SBH}}$ of Gr/ReSe$_2$ heterostructure keeps on increasing with an increase in negative $V_{bg}$. The highest value of $\Phi_{\text{SBH}}$ was observed at $\sim 300$ meV at $V_{bg} = -40$ V. Moving further, in the case of $V_{bg} > 0$, the electrons are generated in the graphene layer (Figure 6c). Under this condition, the Fermi level of graphene shifts in the upward direction resulting in a reduced $\Phi_{\text{SBH}}$ value. The lower value of $\Phi_{\text{SBH}}$ under forward biasing ($V_{bg} > 0$) facilitates easy transport of majority carriers across the junctions thus an increase in on-current was realized in the transfer characteristics (Figure 3a). As our heterostructure is composed of atomically thin flakes (i.e., monolayer graphene and few-layer ReSe$_2$), the possibility of incomplete electric field screening in both materials cannot be evaded. Thus, both components of the heterostructure are affected by the electric field modulation, as evident in previous reports [63]. The estimated values provide an accurate assessment of $\Phi_{\text{SBH}}$ at the Gr/ReSe$_2$ van der Waals interface via electric field modulation. Since the $\Phi_{\text{SBH}}$ demonstrates a strong gate modulation, one can speculate that the electric field-induced transport mechanism is the governing mechanism in the devices demonstrated here.

Figure 6. (a) Band diagram of graphene and ReSe$_2$ before contact, (b) after contact when $V_g < 0$, and (c) after contact when $V_g > 0$.

3.5. Gr/ReSe$_2$ Heterostructure as NO$_2$ Gas Sensor

To demonstrate the NO$_2$ gas sensing experiment, the prepared devices were placed in a mass flow controller (MFC) setup as illustrated in Figure S5. Individual Gr, ReSe$_2$, and Gr/ReSe$_2$ heterostructure devices were evaluated at room temperature under different gas concentrations (20–200 ppb). During the gas sensing experiment, the samples were continuously irradiated by a light illumination of 532 nm as it improves gas sensing response [26]. Additionally, the samples were irradiated by visible light instead of UV to avoid any damage from the light source. Figure 7a illustrates the gas sensing dynamic response of Gr/ReSe$_2$ heterostructure under various NO$_2$ concentrations at $V_{ds} = 1$ V and incident light illumination of 532 nm with the intensity of 310 mW cm$^{-2}$. The gas sensing response was determined by the following relation:

$$\text{Response(\%)} = \frac{|R_g - R_a|}{R_a} \times 100\%$$

(8)

where “$R_g$” and “$R_a$” indicate device resistance under NO$_2$ gas environment and in air. Noteworthy, since two-dimensional materials (2D) bestow a large surface-to-volume ratio, their heterostructure could demonstrate a relatively high NO$_2$ gas sensing response despite being under low NO$_2$ concentration. It is obvious from Figure 7a that the Gr/ReSe$_2$
heterostructure demonstrates a monotonically increasing gas sensing response with rising NO$_2$ concentration from 20 to 200 ppb. Compared to previous reports on 2D materials-based gas sensors, our heterostructure demonstrates a large response of ~36% even at a low NO$_2$ concentration of 20 ppb [64-66]. Moving further, we have explored our heterostructure gas sensing response for various light intensities. Under NO$_2$ gas flow (200 ppb) and light wavelength (532 nm) exposure, the gas sensing response of heterostructure was evaluated with increasing light intensities as illustrated in Figure 7b. The gas sensing response rises from ~10% to ~200% as the light intensity increases from 0 to 310 mW cm$^{-2}$. This is ascribed to the fact that more electrons are produced by increasing light intensity and made their way from the heterojunction to the NO$_2$, subsequently leading to improved gas sensing response. Here, it is also noted that only Gr (black curve), and individual ReSe$_2$ (blue curve) devices have demonstrated lower gas sensing performance of about ~20%, and ~41% as compared to Gr/ReSe$_2$ heterostructure (~200%; red curve) under similar conditions as illustrated in Figure S6. This is attributed to enhanced electron-hole pairs generation at heterojunction interface under light exposure and agrees well with previous reports [67,68]. To further evaluate the NO$_2$ gas response efficiency of the prepared Gr/ReSe$_2$ heterostructure, the transient response was determined for 200 ppb NO$_2$ concentration and under light illumination (532 nm) with intensity 310 mW cm$^{-2}$ as displayed in Figure S7. As-calculated room temperature NO$_2$ response/recovery time for the heterostructure was found to be 39/126 sec which is comparable with the top gas sensors based on 2D materials so far [69,70]. Next, the Gr/ReSe$_2$ heterostructure was tested for gas sensing stability as illustrated in Figure 7c. The freshly prepared heterostructure (0-day) was placed under NO$_2$ (200 ppb) and light wavelength (532 nm) with an intensity of 310 mW cm$^{-2}$ exposure. The resultant NO$_2$ gas sensing response was around ~200%. The device was tested again after a month under ambient conditions. The resultant gas sensing response was ~180% which is only 20% less than the original value, revealing the highly stable nature of Gr/ReSe$_2$ heterojunction. Furthermore, to see the stable working potential of prepared sensor, relative humidity effect on response factor was tested as demonstrated in Figure S8. The results reveal similar sensing response under various humidity conditions, i.e., relative humidity (RH: 20–80%). The minor degradation was observed for RH = 20% and RH = 80%, however, no significant change was observed for RH: 40%, 60%, which is typical working conditions in most of the laborites. The results indicate that humidity is not the main factor for consideration to demonstrate consistent NO$_2$ gas sensing behavior. Other parameters, such as NO$_2$ gas exposure, light wavelength and intensity and exposure duration are the main factors that influence sensor properties.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** (a) Dynamic response of Gr/ReSe$_2$ heterostructure under NO$_2$ exposure with different concentrations at $V_{ds} = 1$ V and laser light (532 nm) of power intensity 310 mW cm$^{-2}$. (b) NO$_2$ (200 ppb) gas sensing response of heterostructure under light wavelength (532 nm) exposure with increasing power intensity. (c) Heterostructure stability assessment under NO$_2$ (200 ppb) with laser light (532 nm) intensity of 310 mW cm$^{-2}$. The black curve (0-day) indicates the gas sensing performance of freshly prepared heterostructure, whereas the red curve demonstrates heterostructure performance after one month under ambient conditions.
Table 1. Comparison of photodetector performance of as-prepared FL-ReSe$_2$ and Gr/ReSe$_2$-HS with other reports from the literature.

| Photodetector (Material) | Responsivity (AW$^{-1}$) @ Wavelength | Internal or External Quantum Efficiency (%) | Detectivity (Jones) | Rise/Fall Time (s) OR Response Time | Refs. |
|--------------------------|---------------------------------------|---------------------------------------------|---------------------|------------------------------------|-------|
| Graphene                 | $5 \times 10^{-4}$                    | 6-16%                                       | -                   | -                                  | [71]  |
| Few layer ReSe$_2$       | 13 (220 nm)                           | 0.73                                        | -                   | 6/21                               | [22]  |
| 1D Se–2D InSe heterojunction | $3.2 \times 10^{-2}$ (460 nm)          | 8.7                                         | $1.7 \times 10^{11}$| $3.0 \times 10^{-2}$/$3.7 \times 10^{-2}$ | [72]  |
| BP/InSe                 | $1.17 \times 10^{-2}$ (455 nm)         | 3.2                                         | -                   | $2.4 \times 10^{-2}$/$3.2 \times 10^{-2}$ | [73]  |
| Se-ReSe$_2$             | 36 (370 nm)                           | -                                           | $8 \times 10^{12}$  | $<1 \times 10^{-2}$/$<1 \times 10^{-2}$ | [74]  |
| CVD monolayer ReSe$_2$  | 13 (532 nm)                           | -                                           | -                   | 30-50 s                            | [75]  |
| ReSe$_2$/WSe$_2$        | 0.28 (520 nm)                         | -                                           | $1.1 \times 10^{12}$| $4.7 \times 10^{-2}$/$4.1 \times 10^{-3}$ | [76]  |
| ReSe$_2$/ReSe$_2$       | 126.5e (350 nm)                       | -                                           | $1.76 \times 10^{11}$ | $6.0 \times 10^{-6}$/$8.9 \times 10^{-6}$ | [77]  |
| Sb$_2$Se$_3$/WS$_2$     | 1.51 (520 nm)                         | -                                           | $1.16 \times 10^{10}$| $8.0 \times 10^{-3}$/$8.0 \times 10^{-3}$ | [78]  |
| ReSe$_2$ bi-layer film  | $4 \times 10^{-3}$ (500 nm)           | 0.99                                        | -                   | $10^4$                             | [79]  |
| FL-ReSe$_2$             | 11.2 (532 nm)                         | 26.1                                        | $1.02 \times 10^{10}$| 2.37/5.03                          | This work |
| Gr/ReSe$_2$-HS          | 74 (332 nm)                           | 173                                         | $1.25 \times 10^{11}$| $75 \times 10^{-6}$/$3.0 \times 10^{-6}$ | This work |

4. Conclusions

We have successfully fabricated Gr/ReSe$_2$ van der Waals heterostructure (vdW-HS) using CVD-grown monolayer graphene (patterned into a rectangular bar), mechanically exfoliated few-layer ReSe$_2$ and all-dry PDMS stamp-assisted transfer method. The prepared HS has been used to evaluate electro-optical properties and gas sensing performance. By exploiting narrow bandgap features of ReSe$_2$, the prepared Gr/ReSe$_2$-HS demonstrated an excellent mobility of 380 cm$^2$/V·s, current on/off ratio ~ $10^4$, photoresponsivity ($R \sim 74$ AW$^{-1}$ @ 82 mW·cm$^{-2}$), detectivity ($D' \sim 1.25 \times 10^{11}$ Jones), external quantum efficiency (EQE ~ 173%) and rapid photoresponse (rise/fall time ~ 75/3 µs) as compared to individual ReSe$_2$ device (mobility = 36 cm$^2$·V$^{-1}$·s$^{-1}$, $I_{on}/I_{off}$ ratio = 1.4 $\times 10^5$–1.8 $\times 10^5$, $R = 11.2$ AW$^{-1}$, $D^* = 1.02 \times 10^{10}$, EQE = 26.1%, rise/fall time = 2.37/5.03 s). Such remarkable performance is due to the combined result of strong light absorption of ReSe$_2$ and high carrier transport of graphene. Moreover, low value of Schottky barrier height (SBH) for Gr/ReSe$_2$-HS (9.02 meV @ $V_{bg}$ = 40 V) confirms that graphene is somehow working as a defect (due to Si/SiO$_2$ dielectric substrate) suppressing layer. Furthermore, the HS was subjected to NO$_2$ gas environment under various humidity conditions to test its aptitude for the gas sensor at room temperature (26.85 °C). The results demonstrated a high response, good reversibility, and gas selectivity under light irradiation of 532 nm. Interestingly, the proposed HS has illustrated an excellent response even toward low ppb-level NO$_2$ exposure (20 ppb), revealing the proposed HS is superior to most of the reported literature. To conclude, our Gr/ReSe$_2$-HS is capable of demonstrating excellent electro-optical as well as gas sensing performance simultaneously and, therefore, can be used as a building block to fabricate next-generation photodetectors and gas sensors to further enhance optoelectronics research domain and internet of things (IoT) devices. Moreover, it offers a potential sensing platform for cost-effective environmental monitoring systems.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12213713/s1, Figure S1: Gr/ReSe$_2$ heterostructure fabrication step-by-step detail; Figure S2: (a) AFM image (scale bar: 3 µm), and (b) corresponding height profile to accurately assess ReSe$_2$ flake thickness; Figure S3: (a) Transfer characteristics ($I_{ds}$–$V_{bg}$) of monolayer graphene measured at $V_{ds} = 0.1$ V reveals CNP = −8 V. (b) Output characteristics ($I_{ds}$–$V_{ds}$) calculated at various $V_{bg}$ from −40 to 50 V reveal ohmic behavior of monolayer graphene; Figure S4: Photocurrent measurement of ReSe$_2$-based photodetector at mentioned conditions; Figure S5: MFC (mass flow controller) setup to test individual flakes (Gr, and ReSe$_2$) and Gr/ReSe$_2$ heterostructure-
based NO\textsubscript{2} gas sensing performance; Figure S6: Room temperature comparative analysis of Gas sensing responses from individual Gr (black), individual ReSe\textsubscript{2} (blue), and Gr/ReSe\textsubscript{2} heterostructure (red) for NO\textsubscript{2} (200 ppb) under laser power of 310 mW cm\textsuperscript{-2} with a wavelength of 532 nm; Figure S7: Room temperature transient response of Gr/ReSe\textsubscript{2} heterostructure for NO\textsubscript{2} (200 ppb) under laser power of 310 mW cm\textsuperscript{-2} with a wavelength of 532 nm; Figure S8: (a) Response factor of Gr/ReSe\textsubscript{2}-HS for 200 ppm NO\textsubscript{2} exposure under different values of relative humidity. (b) Corresponding column bar representation of the maximum value of response factor of Figure S8a.

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