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**WSe<sub>2</sub> Homojunction p-n Diode Formed by Photo-Induced Activation of Mid-Gap Defect States in Boron Nitride**

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**ABSTRACT:** A single nanoflake lateral p-n diode (in-plane) based on a two-dimensional (2D) material can facilitate electronic architecture miniaturization. Here, a novel lateral homojunction p-n diode of a single WSe<sub>2</sub> nanoflake is fabricated by photo-induced doping via optical excitation of defect states in an h-BN nanoflake upon illumination. This lateral diode is fabricated using a mechanical exfoliation technique by stacking the WSe<sub>2</sub> nanoflake partially on the h-BN and Si substrate. The carrier type in the part of WSe<sub>2</sub> film on the h-BN substrate is inverted and a built-in potential difference is formed, ranging from 5.0 to 4.50 eV, which is measured by Kelvin probe force microscopy. The contact potential difference across the junction of p-WSe<sub>2</sub> and n-WSe<sub>2</sub> is found to be ~492 mV. The lateral diode shows an excellent rectification ratio, up to  $\sim 3.9 \times 10^4$  with an ideality factor of  $\sim 1.1$ . A typical self-biased photovoltaic behavior is observed at the p-n junction upon the illumination of incident light, a positive open-circuit voltage ( $V_{oc}$ ) is generated i.e. voltage obtained (at  $I_{ds} = 0$  V) and also a negative short-circuit current ( $I_{sc}$ ) i.e. current obtained (at  $V_{ds} = 0$  V). The presence of built-in potential in the proposed homojunction diode establishes  $I_{sc}$  and  $V_{oc}$  upon illumination, which can be implemented for a self-powered photovoltaic system in future electronics. The proposed doping technique can be effectively applied to form planar homojunction devices without photoresist for future electronic and optoelectronic applications.

## INTRODUCTION

The family of two-dimensional (2D) layered transition metal dichalcogenides (TMDs) shows a wide range of characteristics in terms of intrinsic doping and band structures, allowing their application in various electronic and optoelectronic nanodevices.<sup>1-4</sup> These ultra-thin 2D layered materials may replace the conventional Si-based complementary metal-oxide-semiconductors (CMOSs) and facilitate structural flexibility and miniaturization in the development of transparent electronic devices<sup>5</sup> for the next-generation applications.<sup>6</sup> Among the TMD-based 2D materials, tungsten diselenide (WSe<sub>2</sub>) is a popularly emerging material owing to its comparatively high hole mobility ( $\mu$ ), approximately 100–250 cm<sup>2</sup>/V s with an excellent on/off ratio of  $\sim 10^7$ .<sup>7-10</sup> WSe<sub>2</sub> can be exfoliated (into a monolayer or multi-layers) from its bulk form using a mechanical exfoliation technique with an adhesive tape. A monolayer of WSe<sub>2</sub> shows a direct bandgap of  $\sim 1.7$  eV, while its bulk form shows an indirect bandgap of  $\sim 1.0$  eV.<sup>11</sup>

The TMD family offers unprecedented design flexibility in creating p-n junction devices which is not possible using conventional bulk semiconductor materials.<sup>12-13</sup> Until now, TMD-based p-n diodes have been exclusively prepared by stacking 2D materials, forming homostructures or heterostructures. Many researchers have implemented various doping approaches such as surface charge transfer, chemical doping, substitutional doping, surface functionalization, electrostatic gating, and intercalation with complicated device structures to prepare lateral homojunction diodes.<sup>12, 14-19</sup> However, such devices contain non-abrupt interfaces due to the use of photoresist, also they experience degeneration of electrical properties due to chemical or environmental effects which confine the necessary operation.<sup>24-27</sup>

Charge conversion was demonstrated in graphene using electrostatic doping, but it could not establish diode-like behavior due to the zero-band gap with Klein tunneling.<sup>20</sup> Enabling n- and

p-type behaviors in the same nanoflake of 2D materials is difficult as it often requires doping engineering techniques, such as electrostatic gating, elemental effect, and unstable chemical treatment.<sup>21-23</sup>

An insulating 2D material, hexagonal boron nitride (h-BN) is recently receiving attention, owing to its properties like good mechanical strength, extraordinary thermal conductivity (due to the strong B-N covalent bonds in its plane), along with excellent thermal and chemical stability.<sup>5, 28</sup> It exhibits an extremely low value of permittivity ( $\epsilon$ ) of 3.6–5.3 due to the strong covalent nonpolar bonds.<sup>29</sup> Like WSe<sub>2</sub>, h-BN can also be exfoliated into a multi-layer from the bulk crystals and used as a dielectric substrate, which has been effectively confirmed from the so-called “graphene plus further TMD field-effect transistors (FETs).”<sup>30-31</sup> Under DUV light illumination h-BN exhibits a bright excitonic luminescence verified by photoluminescence measurements.<sup>32</sup> The existence of defect states or point defects in h-BN has been confirmed by a rich array of sub-band-gap luminescence lines originated from the recombination at impurities or native defects.<sup>33</sup>

In this research, we developed a lateral WSe<sub>2</sub> based homojunction p-n diode, where the p-type WSe<sub>2</sub> nanoflakes exhibit an efficient doping effect using the optical excitation of mid-gap donor-like states (or defect states)<sup>34</sup> in multilayered h-BN nanoflakes i.e., to exploit photo-induced electron transferred from defects in h-BN to adjacent WSe<sub>2</sub> and establish n-type doping effect. Lateral WSe<sub>2</sub> homojunction p-n diodes are fabricated by the vertical stacking of WSe<sub>2</sub> nanoflakes on the h-BN and silicon dioxide substrates (SiO<sub>2</sub>) partially, using dry transfer method. The mechanism of the electron carrier type modulation in WSe<sub>2</sub> nanoflake under photo-induced doping, is analogous to the carrier type modulation in those heterostructures, that are composed of graphene and h-BN or WSe<sub>2</sub>/SiO<sub>2</sub>.<sup>35-37</sup> This photo-induced effect of ultrafast carrier modulation in the heterostructures of WSe<sub>2</sub> and h-BN is due to the mid-gap of donor-like states in the h-BN

flakes. However, the photo-induced effect observed in graphene nanoflakes that were exfoliated on thick SiO<sub>2</sub> substrates, originating from the interfacial trapped states of charges in amorphous oxide.<sup>38</sup> We have confirmed that the FETs based on p-WSe<sub>2</sub> are inverted to the n-type conduction that preserves efficient electron carrier mobility in the heterostructures of h-BN and n-WSe<sub>2</sub>. To further verify the photo-induced doping mechanism, Kelvin probe force microscopy (KPFM) experiments were implemented and discovered that the Fermi level of p-type WSe<sub>2</sub> nanoflake was satisfactorily modified to that of an n-type WSe<sub>2</sub>. The proposed lateral WSe<sub>2</sub> homojunction diode shows outstanding electronic and optoelectronic characteristics.

## RESULTS AND DISCUSSION

The ultra-thin h-BN and WSe<sub>2</sub> nanoflakes were prepared by the standard mechanical exfoliation technique with an adhesive tape. Stacked h-BN/WSe<sub>2</sub> heterostructures were fabricated using the dry transfer method. The optical microscopy image of the h-BN/WSe<sub>2</sub> heterostructure based FETs is shown in Figure 1(a). The WSe<sub>2</sub>/h-BN heterostructure was illuminated by DUV light (Figure 2(b)). The p-type WSe<sub>2</sub> flake on h-BN is altered to the n-type WSe<sub>2</sub>, upon the exposure to deep ultra-violet light (DUV) illumination with a photon energy of ~5.63 eV and an applied gate voltage of -40 V.

Figure S1 (a, b) in Supporting Information, shows the micro-Raman spectra for both h-BN and WSe<sub>2</sub> nanoflakes. We achieved the Raman spectroscopy of WSe<sub>2</sub> multilayered BN nanoflakes using a setup which has an excitation laser (514 nm, 2.41 eV). Typically, the Raman peaks for WSe<sub>2</sub> (A<sub>1g</sub> mode at ~261.2 /cm and E<sub>2g</sub><sup>1</sup> mode at ~250.6 /cm) and h-BN (E<sub>2g</sub> mode at ~1364.1 /cm) were observed. Figure S2(a) displays AFM images of the WSe<sub>2</sub> and h-BN nanoflakes

and the AFM profile height line scan is shown in Figure S2 (b, c). The h-BN and WSe<sub>2</sub> nanoflakes have thicknesses, ~15 and ~4 nm, respectively.

Figure 1 (a) shows the fabricated FET based heterostructures of the h-BN and p-type WSe<sub>2</sub> nanoflakes. The pristine p-type WSe<sub>2</sub> mostly exhibited the p-type behavior as confirmed from transfer characteristics as shown in Figure 1 (b). The metal contacts, Pd/Au attached to the source and drain exhibit pure ohmic behavior, which can be seen in the  $I_{ds}$ - $V_{ds}$  characteristics as shown in Figure S3 (a). When the h-BN/p-type WSe<sub>2</sub> heterostructure is illuminated under the photon energy of 5.6 eV for 5 minutes with an applied gate voltage of -20 V, a photo-induced doping effect is achieved. The applied gate voltage ( $V_g^{light}$ ) is a back-gate voltage, which is applied during the illumination of DUV or visible light to make the photo-induced doping effect. The doped WSe<sub>2</sub> flakes showed the n-type behavior as confirmed from the transfer characteristics (Figure 1 (b)), while the metal contacts (Pd/Au) attached to the source and drain exhibit a non-ohmic behavior, which is confirmed from the  $I_{ds}$ - $V_{ds}$  characteristics as shown in the Figure S3 (b) of supporting information. The n-type WSe<sub>2</sub> flake showed rectifying behavior with Pd/Au electrodes. The WSe<sub>2</sub> with metal (Pd) can display either a unipolar p- or n-type transport curve or an ambipolar type conduction.

To confirm the hypothesis of photo-induced doping mechanism, the KPFM experiments were conducted to find the exact values of work function before and after the photo-induced doping of WSe<sub>2</sub> flakes. The following equation is used to find the work function of p- or n-type WSe<sub>2</sub>:

$$e \times CPD = \phi_{sample} - \phi_{tip} \quad (1)$$

where  $\phi_{sample}$  and  $\phi_{tip}$  are the individual values of the work function of the sample and tip. The contact potential difference (CPD) of the reference HOPG (highly ordered pyrolytic graphite,

$\phi_{HOPG} = 4.6 \text{ eV}$ ) surface was  $-100 \text{ mV}$ , which confirmed that  $\phi_{tip} = 4.7 \text{ eV}$ . The CPD of p-WSe<sub>2</sub> was  $300 \text{ mV}$ , which made the work function of WSe<sub>2</sub> for its pristine state ( $\phi_{p-WSe_2} = 5.0 \pm 0.08 \text{ eV}$ ). For the n-type WSe<sub>2</sub>, the CPD was approximately  $-200 \text{ mV}$ . Therefore, the work function of n-type WSe<sub>2</sub> is  $\phi_{n-WSe_2} = 4.5 \pm 0.10 \text{ eV}$ .

The photo-induced mechanism of electron doping in the heterostructures of h-BN and WSe<sub>2</sub> flakes is caused by the optical excitation of mid-gap donor-like states (or defect states) in h-BN upon the illumination by light. The photons of deep UV light can excite the donor-like defect states<sup>39</sup> in h-BN (Figure 1 (c, d)), which demonstrates the physical mechanism of the photo-induced effect of carrier modulation in the heterostructures of WSe<sub>2</sub> and h-BN. Upon illumination by the deep UV light, the electrons of mid-gap defect states in the h-BN are excited (or triggered) to the conduction band by the energy of incident photons. The photon-excited electrons enter the WSe<sub>2</sub> flake under negative gate voltage. The positively charged localized ionized defects in h-BN reduce the influence of the external electric field (i.e.,  $V_g^{light}$ ) on h-BN during the photo-induced effect. This removal process continues till the external electric field across the h-BN disappears and the positively ionized defects remain inside the h-BN.<sup>39</sup> These positively charged defects are stored in the h-BN even after the removal of light and the  $V_g^{light}$ , which leads to the stable doping effect in WSe<sub>2</sub>. We have also studied the dependence of the doping effect of the photon energy of illumination. The heterostructures of h-BN and WSe<sub>2</sub> were illuminated by the visible light ( $\lambda = 600 \text{ nm}$ ,  $400 \text{ nm}$ ,  $20 \text{ mW/cm}^2$ ) and deep UV light ( $\lambda = 220 \text{ nm}$ ,  $11 \text{ mW/cm}^2$ ) with  $V_g^{light} = -40 \text{ V}$  for 5 minutes. In all these cases, the doping effect was established in WSe<sub>2</sub>, which revealed that the mid-gap defects could be excited upon the illumination by visible light, but we found that better



doping effect was achieved by the DUV light of photon energy, 5.63 eV with  $V_g^{light} = -40$  V and 5 min of illumination (Figure S4).

The photo-induced electron doping in WSe<sub>2</sub> nanoflakes eliminates the need for complicated device architectures (using various photoresists) to modulate the carrier type in 2D materials.<sup>40-41</sup> Furthermore, the photo-induced doping is simple to apply on the WSe<sub>2</sub> FETs based on mechanical exfoliation, since this process did not affect the properties of metal contacts in the device. Consequently, this approach of electron doping is superior to previous artificial doping methods, such as doping through electrostatic gating effect to amend the carrier type concentration,<sup>42</sup> with different metal contacts to enable unipolar p- or n-type conduction in a similar nanoflake, or electrostatic doping in a planar device.<sup>21-23</sup>

We have found that the electron doping effect in WSe<sub>2</sub> depends on  $V_g^{light}$ , which means that on-current on electron regime increased with a rise in  $V_g^{light}$ . The electronic carrier concentration  $n_{(n-WSe_2)}$  for the  $V_g^{light}$  can be calculated using the following relation:

$$n_{(n-WSe_2)} = -C_g (V_{bg} - V_{th})/e, \quad (2)$$

where  $V_{bg}$  is the back gate voltage,  $V_{th}$  is the threshold voltage for electron transport,  $e$  is the electronic charge, and  $C_g$  is the gate capacitance/unit area for thick SiO<sub>2</sub> film with 300 nm, its value is  $\sim 115 \times 10^{-10}$  F/cm<sup>2</sup>. The value of  $C_g$  for h-BN is calculated by  $C_g = \epsilon_0 \epsilon_r / d$ , where  $\epsilon_0$  = vacuum permittivity,  $d$  = thickness of h-BN, and  $\epsilon_r$  = dielectric constant of h-BN, which equals 4.<sup>43</sup> For h-BN nanoflake having a thickness of 15 nm, the  $C_g$  is  $\sim 2.36 \times 10^{-7}$  F/cm<sup>2</sup>, and the combined gate capacitance is  $\sim 1.09 \times 10^{-8}$  F/cm<sup>2</sup>. For example, at  $V_{bg} = -60$  V,  $n_{(n-WSe_2)}$  was calculated to be  $\sim 3.27 \times 10^{12}$  cm<sup>-2</sup>. The electron concentration is estimated to be  $2.05 \times 10^{12}$  cm<sup>-2</sup> after photo doping under  $V_g^{light} = -10$  V. Further increasing  $V_g^{light}$  to  $-60$  V, the electron concentration is

increased to  $3.28 \times 10^{12} \text{ cm}^{-2}$ . The larger value of  $V_g^{light}$  facilitates the formation of positively charged defects in higher concentration, localized in the mid-gap donor-like states (or point defects) in the BN flake,<sup>39</sup> which makes the electron-doping effect more efficient and enhances the electron concentration in the n-WSe<sub>2</sub>/BN FET device.

The field-effect mobility  $\mu_{(n-WSe_2)}$  of n-type WSe<sub>2</sub> FET can be found by the following equation,<sup>44</sup>

$$\mu_{(n-WSe_2)} = \frac{L}{W} \left( \frac{dI_{ds}}{dV_{bg}} \right) \frac{1}{C_g V_{ds}}, \quad (3)$$

where  $L$  and  $W$  are the dimensions of n-type WSe<sub>2</sub> flake, its length and width, respectively, and  $\left( \frac{dI_{ds}}{dV_{bg}} \right)$  is the slope of the transfer plot in the linear region. For example,  $\mu_{(n-WSe_2)}$  of n-WSe<sub>2</sub> based FET was estimated as  $\sim 77.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  after applying  $V_g^{light} = -60 \text{ V}$ . The photo doping effect in the n-WSe<sub>2</sub>/BN FET device exhibits the strong enhancement of electron mobility, from 9.7 to  $77.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with increasing the  $V_g^{light}$  from  $-10$  to  $-60 \text{ V}$ . The carrier concentration  $n_{(n-WSe_2)}$  and electron mobility  $\mu_{(n-WSe_2)}$  as a reference to varying  $V_g^{light}$  are shown in Figure 1 (f). Moreover, we found that our results regarding the carrier concentration and electron mobility are either better or on a par with the previous reports based on different doping mechanisms.<sup>45-49</sup>

Additionally, we did not notice any clear peak shift of WSe<sub>2</sub> after the photo-induced effect at varied  $V_g^{light}$ , and there was no added Raman peak, inferring that the photo-induced doping technique did not produce extra effects in the WSe<sub>2</sub> nanoflake (Figure S5). Also, we did not find any disintegration in the electrical characteristics of the device even after retaining it in an ambient environment for several days. The prepared WSe<sub>2</sub> flakes have shown a stable n-type doping effect in the ambient environments (Figure S6).

We have demonstrated the preparation of the lateral WSe<sub>2</sub> homojunction p-n diode using a mechanical exfoliation technique by stacking the nanoflakes of WSe<sub>2</sub> on a multilayered h-BN flake, where a portion of the WSe<sub>2</sub> flake was placed on an h-BN, and the remaining area was placed on an Si/SiO<sub>2</sub> as shown in the Figure 2 (a). Figure 2 (b) demonstrates the optical microscope image of the device. Figure 2 (c) shows the difference between WSe<sub>2</sub>/SiO<sub>2</sub> and WSe<sub>2</sub>/h-BN parts of a single WSe<sub>2</sub> flake before the doping process. The CPD of WSe<sub>2</sub> flakes on the SiO<sub>2</sub> and h-BN substrates is ~46 mV before photo doping as shown in Figure 2 (d), which is probably caused by the interface trap charges on the SiO<sub>2</sub> substrate. The work function difference between the WSe<sub>2</sub>/SiO<sub>2</sub> and WSe<sub>2</sub>/h-BN before doping was 0.06 eV. The difference between pristine WSe<sub>2</sub>/SiO<sub>2</sub> and doped WSe<sub>2</sub>/h-BN parts of a single WSe<sub>2</sub> flake can be seen in the Figure 2 (d).

The heterostructure of h-BN and WSe<sub>2</sub> was illuminated upon the exposure to the deep UV light ( $\lambda = 220$  nm,  $11 \text{ mW cm}^{-2}$ ). Only the part of the p-type WSe<sub>2</sub> flake on h-BN was inverted to the n-type WSe<sub>2</sub> by the DUV illumination for 5 minutes with the photon energy ~5.6 eV at  $V_g^{light} = -40$  V. After the doping process, we measured the CPD across the junction of n-WSe<sub>2</sub> and p-WSe<sub>2</sub>. The CPD value from the KPFM image is given by the line scan indicated in Figure 2 (e), which gives the value of CPD at  $\sim 492 \pm 8.48$  mV as shown in Figure 2 (f). In this case, the value of CPD is higher than the previously reported planar diode (~55 meV) achieved by helium ion irradiation,<sup>50</sup> and the MoTe<sub>2</sub>-based homojunction diode (~100 meV) achieved through deep UV light in an N<sub>2</sub> gas environment.<sup>51</sup>

To achieve low-resistance metal contacts, Pd/Au and Al/Au with the thickness of 6/100 nm were deposited on the p-WSe<sub>2</sub> and n-WSe<sub>2</sub> flakes, respectively. The work function of Pd (~5.2 eV)<sup>52</sup> is slightly greater than the valence band maximum or the Fermi level (5.0 eV) of p-WSe<sub>2</sub>. Conversely, the work function of Al electrodes is ~4.1 eV<sup>53</sup> which is smaller than the electron

affinity ( $\sim 4.21$  eV) of n-type WSe<sub>2</sub>. The  $I$ - $V$  characteristics of both p-WSe<sub>2</sub> with Pd/Au metal contacts and n-WSe<sub>2</sub> with Al/Au contacts show an ohmic behavior (Figure S7 (a, b)), and their transfer characteristics show the p- and n-type conduction, respectively (Figure 3 (a)). We evaluated the rectifying behavior of lateral WSe<sub>2</sub> p-n diode by varying the gate voltage ( $V_{bg}$ ) from +40 to  $-80$  V. As  $V_{bg}$  increases from  $-80$  to  $-30$  V, the diode current decreases rapidly in the reverse bias as shown in Figure 3 (b), yielding to an increase in the rectification ratio (forward to reverse currents,  $I_f/I_r$ , at  $\pm 2$  V) up to  $\sim 3.9 \times 10^4$  (Figure 3 (c)). We repeated the experiments and found that the uncertainty in the rectification ratio of devices remains  $39000 \pm 80$ . We compared the performance of our p-n diode with the previous reports (using other doping methods) such as elemental doping effect,<sup>54-55</sup> chemical doping,<sup>18, 45</sup> and doping due to electrostatic gating<sup>56-57</sup> as shown in Figure 3 (e). The rectification ratio of our device exhibits a better performance than the previously reported MoTe<sub>2</sub> based p-n diode.<sup>51</sup> When  $V_{bg}$  increases further from  $-30$  to  $+40$  V, the reverse current ( $V_{ds} < 0$ ) becomes nearly constant, but the diode current in the forward bias regime ( $V_{ds} > 0$ ) continues to decline, resulting in a decay of the p-n diode rectification ratio as shown in Figure 3 (c). We also examined the rectification ratio using different asymmetric contacts of the pristine WSe<sub>2</sub> flake without the photo-induced doping. The rectification ratio of (Pd/Au)-(p-WSe<sub>2</sub>)-(Al/Au) device was  $\sim 22.6$  at  $V_{bg} = 0$  V as shown in Figure S8. However, the WSe<sub>2</sub> p-n diode was properly formed after the photo-induced doping and the diode rectification ratio was  $\sim 1.22 \times 10^4$  at  $V_{bg} = 0$  V (Figure 3 (c)).

The ideality factor of the lateral WSe<sub>2</sub> p-n diode was extracted by the following equation:

$$I_D = I_0 \left[ \exp\left(\frac{eV}{nK_B T}\right) - 1 \right], \quad (4)$$

where  $I_D$  is the diode current (i.e.  $I_f$ ),  $I_O$  is the reverse saturation current (i.e.  $I_r$  at saturation),  $V$  is the applied voltage across the diode during its action,  $K_B$  = Boltzmann constant, and  $T = 300$  K. The lower value ideality factor  $n$  was 1.1 at  $V_{bg} = -30$  V (Figure 3 (d)). In our case, the ideality factor is better than the previously reported p-n junctions.<sup>18, 38, 58-60</sup> The rectifying behavior of the lateral homojunction p-n diodes regarding the gate voltages originates from the modification of the built-in potential at their homointerface of the p-WSe<sub>2</sub> and n-WSe<sub>2</sub> by an electric field. In Figure 4 (a), the transfer curve ( $I_{sd}$ - $V_{bg}$ ) can be categorized into four regions. This infers that the WSe<sub>2</sub> homojunction diode possesses the four junction types  $pp^+$ ,  $pn^-$ ,  $p^-n$ , and  $nn^+$ . In the  $pp^+$  regime, the Fermi level of both p-WSe<sub>2</sub> and n-WSe<sub>2</sub> channels shifts down to the valence band under the greater negative back gate voltage, such that the holes become dominant in both p-WSe<sub>2</sub> and n-WSe<sub>2</sub> channels as shown in Figure 4 (b, i), and the device exhibits p-type semiconducting characteristics. Further by increasing the back gate voltage (i.e. rise in voltage from negative to a positive value), the Fermi level shifts near the bandgap and forms either a  $pn^-$  or  $p^-p$  junction state, as a result of the built-in potential at their homointerface, causing an increase in the rectification ratio as shown in Figure 4 (b, ii, iii). When the gate voltage was greater enough, the Fermi level moved into the conduction band in both p-WSe<sub>2</sub> and n-WSe<sub>2</sub> channels, where the electrons dominate effect was established, and the device worked as an  $n-n^+$  junction state as shown in Figure 4 (b, iv).

To explore the photovoltaic performance of the lateral WSe<sub>2</sub> homojunction, the p-n diode was illuminated under a laser light ( $\lambda = 530$  nm) with variation in the intensity of light. A typical self-biased photovoltaic behavior is observed at the p-n junction state upon illumination of incident light, a positive open-circuit voltage ( $V_{oc}$ ) is generated i.e. the voltage obtained (at  $I_{ds} = 0$  V) and also a negative short-circuit current ( $I_{sc}$ ) i.e. the current obtained (at  $V_{ds} = 0$  V). The presence of

built-in potential in the proposed homojunction diode establishes  $I_{sc}$  and  $V_{oc}$  upon illumination, which can be implemented for a self-powered photovoltaic system in future electronics that as shown in Figure 5 (a). The identified values of the  $I_{sc}$  and  $V_{oc}$  are consistent with the lateral homojunction p-n diode and comparable to the diodes based on mix-dimensional heterostructures<sup>61-64</sup> or photodetectors.<sup>65-66</sup> The existence of a built-in potential at p-n homojunction diode established  $I_{sc}$  and  $V_{oc}$  without an external electric field, which can be implemented for a self-powered photovoltaic system in future electronics. Figure 5 (b) shows the relation between  $V_{oc}$  and  $I_{sc}$  as a function of the light intensity.

## CONCLUSIONS

We established a single flake lateral WSe<sub>2</sub> p-n diode by photo-induced doping through optical excitation of donor-like states in a multilayered h-BN nanoflake upon illumination. This planar diode was fabricated using a dry transfer technique by stacking the WSe<sub>2</sub> nanoflake partially on the h-BN and Si substrate. The p-type WSe<sub>2</sub> nanoflake is converted to an n-type nanoflake by the photo-induced doping technique. KPFM experiments demonstrated the amendment of the Fermi level from 5.0 to 4.50 eV upon photo-induced doping. Also, the CPD across the junction of p-WSe<sub>2</sub> and n-WSe<sub>2</sub> was ~492 mV. The WSe<sub>2</sub> homojunction p-n diode showed a maximum rectification ratio of  $\sim 3.9 \times 10^4$  at the back gate of -30 V with the ideality factor of ~1.05. The presence of built-in potential in the proposed homojunction diode establishes  $I_{sc}$  and  $V_{oc}$  upon illumination, which can be implemented for a self-powered photovoltaic system in future electronics. This efficient photo-induced doping technique of carrier-type modulation may lead to the advancement of functional devices in the field of nanotechnology.

## EXPERIMENTAL SECTION

Natural bulk crystals of h-BN and WSe<sub>2</sub> were bought from HQ graphene. The mechanical exfoliation technique was implemented to obtain the ultra-thin nanoflakes of h-BN and WSe<sub>2</sub> from their bulk form, with adhesive tape in a cleanroom environment. A dry transfer method was employed to stack the h-BN and WSe<sub>2</sub> heterostructures using a micromanipulator with a transparent PDMS stamp. At first, the bottom h-BN flake was dry-transferred onto SiO<sub>2</sub>/Si substrate inside the window (90×90 μm<sup>2</sup>) of large pattern. The top WSe<sub>2</sub> nanoflake was transferred by making a vertical stack i.e. WSe<sub>2</sub>/h-BN heterostructure with the help of a micromanipulator moveable platform, we made sure that it was fit line up and partially stacked on the h-BN bottom flake and remained on the substrate. At the end of the transfer process, the substrate was placed on a hot plate at 90 °C to remove the miniature water vapors from the exterior surfaces and interfaces. Throughout the transfer process, the samples were first washed with acetone and then with methanol and dried under N<sub>2</sub> gas flow after each step. The heterostructures of h-BN and WSe<sub>2</sub> were illuminated upon the exposure to deep UV light ( $\lambda = 220$  nm, 11 mW cm<sup>-2</sup>). For the nanofabrication of electrodes, the regular e-beam lithography procedure was accomplished to make patterns of the source/drain electrodes. Finally, the thermal evaporation process was used to deposit the metal contacts, Pd/Au, and Al/Au with the thickness of 6/100 nm for each case on the p-WSe<sub>2</sub> and n-WSe<sub>2</sub>, respectively. The WSe<sub>2</sub> nanoflakes were analyzed from beginning to end using optical microscopy as well as Raman spectroscopy and confirmed their thickness through atomic force microscopy (AFM). Electrical measurements were completed by placing the samples inside a vacuum box with a source meter (Keithley 2400) and Pico-ammeter (Keithley 6485). The photovoltaic measurements were done by a green laser having a wavelength of 530 nm varying the intensity of light. Commercial equipment (XE-100 and NX10 by Park System Inc.) in Kelvin

probe force microscopy (KPFM) mode was used for surface potential measurement in ambient air condition. A cantilever (NSC36) coated with Cr/Au tip was calibrated from the work function of HOPG ( $\phi_{\text{HOPG}} = 4.6$  eV), which is an electrically stable material, and the scan rate was 0.3 Hz. Freshly cleaved HOPG was used to calibrate the work function of the tip. The work function of HOPG is known for not changing significantly in the ambient environments, because it does not form the interface dipoles.

**ASSOCIATED CONTENT**

Supporting Information. The Supporting Information is available free of charge on the website. It contains Raman spectra of WSe<sub>2</sub> and h-BN, AFM image of h-BN/WSe<sub>2</sub>, *I-V* characteristics of p-WSe<sub>2</sub> and n-WSe<sub>2</sub> with Pd/Au metal contacts at various  $V_{\text{bg}}$ , transfer characteristics of the h-BN/WSe<sub>2</sub> FET device for the photon energy of incident light, Raman spectra of pristine and doped WSe<sub>2</sub>, transfer characteristics of n-WSe<sub>2</sub> after the photo-induced doping, *I-V* characteristics of p-WSe<sub>2</sub> with Pd/Au metal contacts, *I-V* characteristics of n-WSe<sub>2</sub> with Al/Au metal contacts and gate-dependent rectifying effect of the WSe<sub>2</sub> flake with Pd/Au and Al/Au source and drain electrodes.

**Notes**

The authors declare no competing financial interests.

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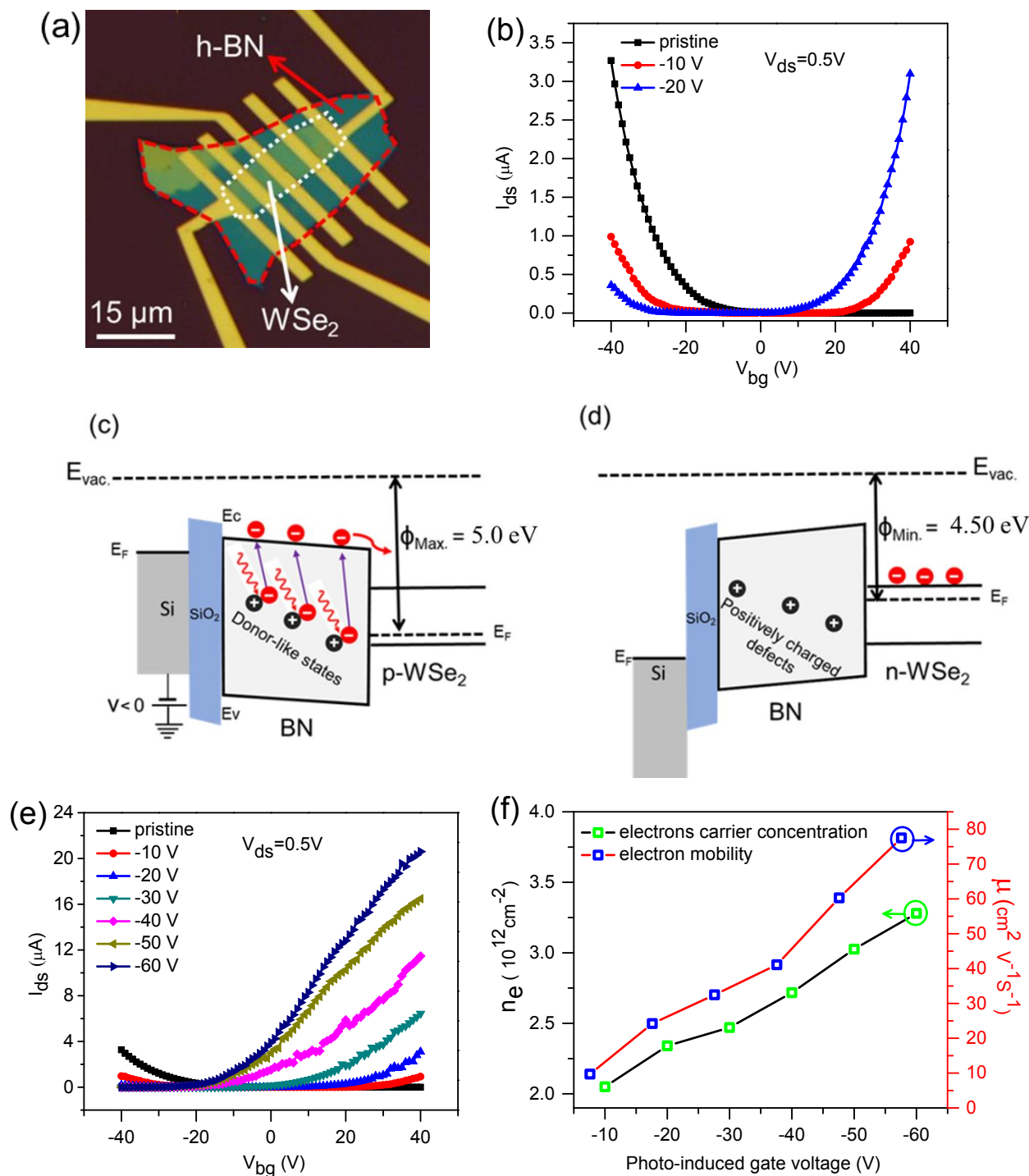
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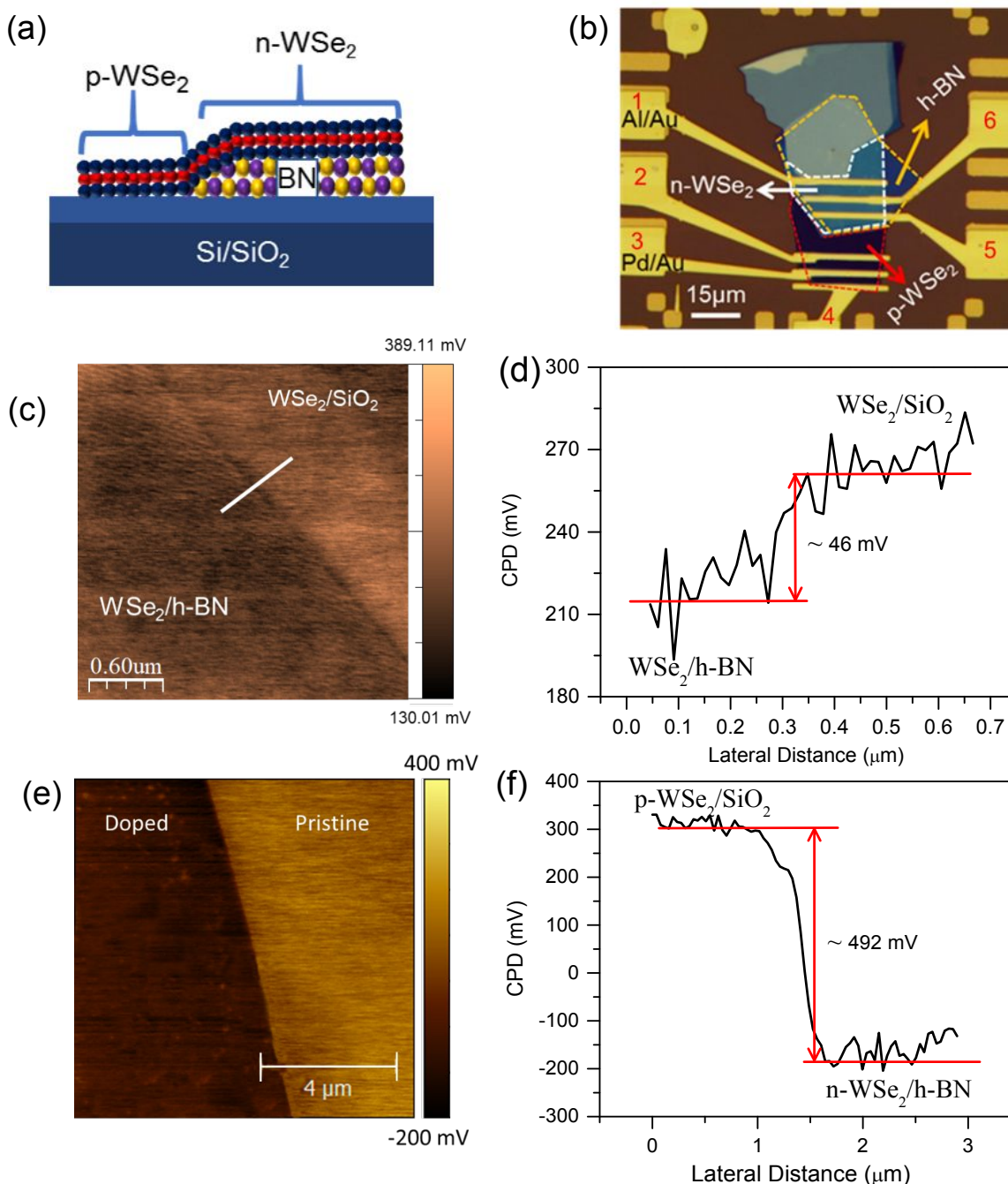
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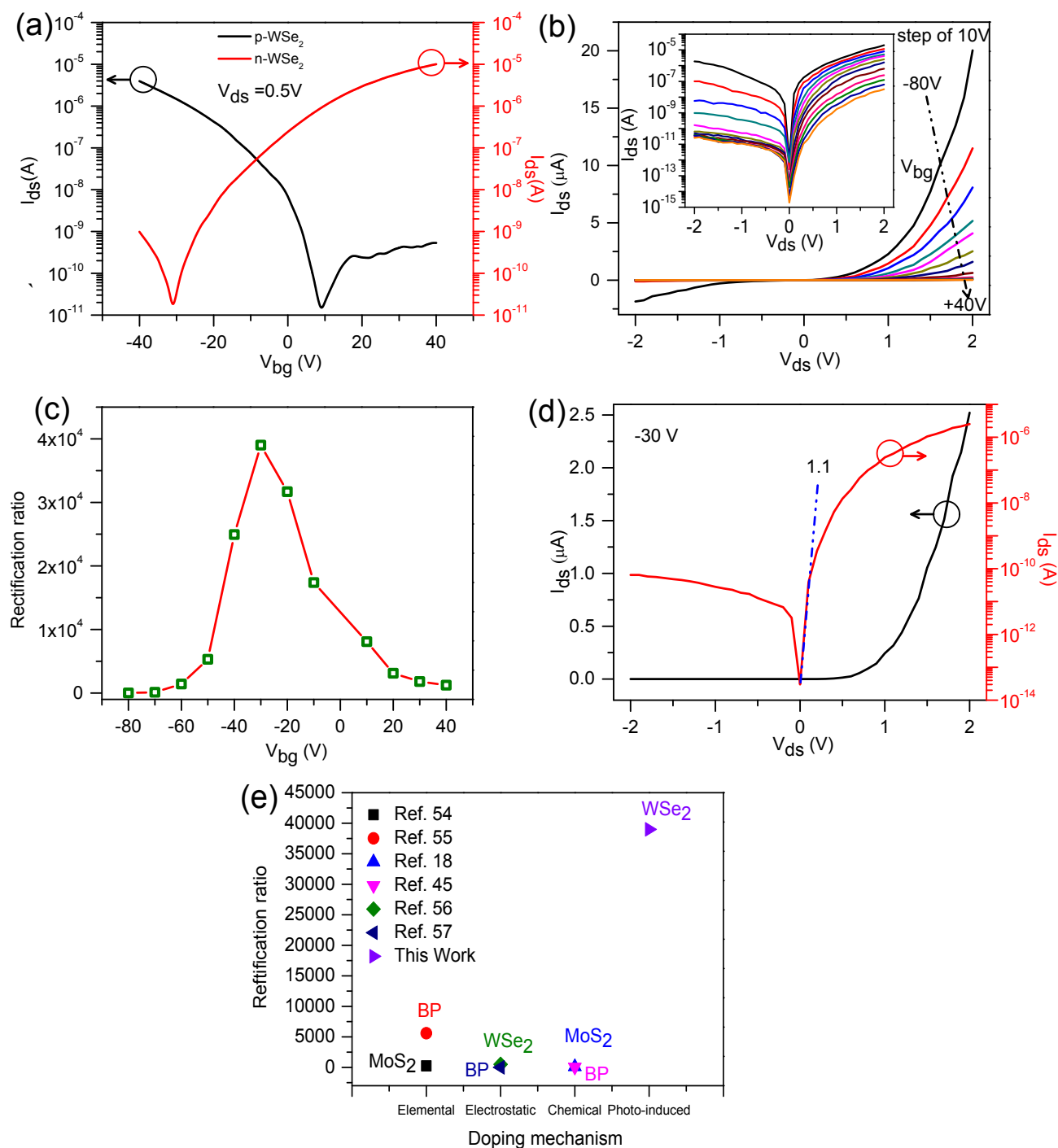
**Figure 1.** (a) Optical image of an h-BN/WSe<sub>2</sub> FET. (b) The transfer characteristics of pristine and doped h-BN/WSe<sub>2</sub> FET device with a light pulse of 5 minutes. The energy of incident photons is 5.6 eV. (c) The schematic of photo-induced doping mechanism, where incident light excites electrons from defect states in the h-BN. The excited electrons can enter into the WSe<sub>2</sub> flake under

$V_g^{light}$ . (d) The donor-like states in the middle of h-BN become positively charged defects after the photo-induced doping at  $V_g^{light}$ . (e) Transfer characteristics of the h-BN/WSe<sub>2</sub> FET device after photo-induced doping at  $V_g^{light}$  for 5 minutes of illumination. (f) The plot of electron mobility ( $\mu$ ) and electron carrier concentration ( $n_e$ ) as a function of  $V_g^{light}$ .

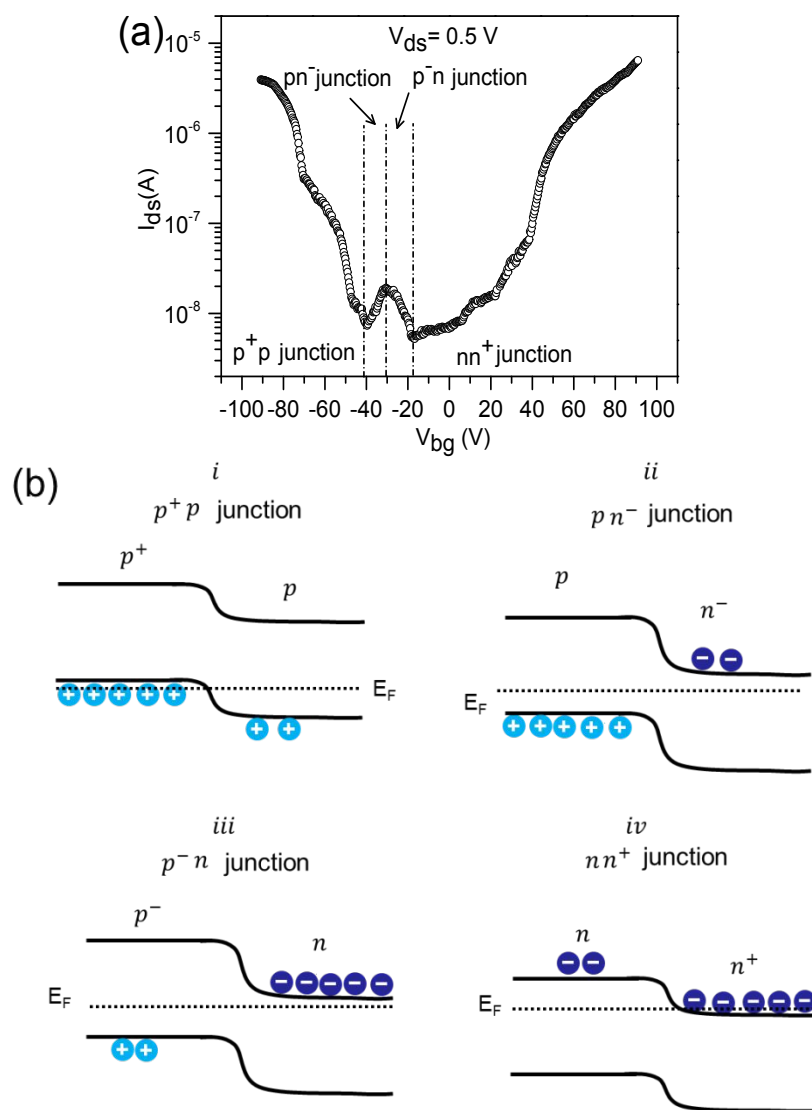




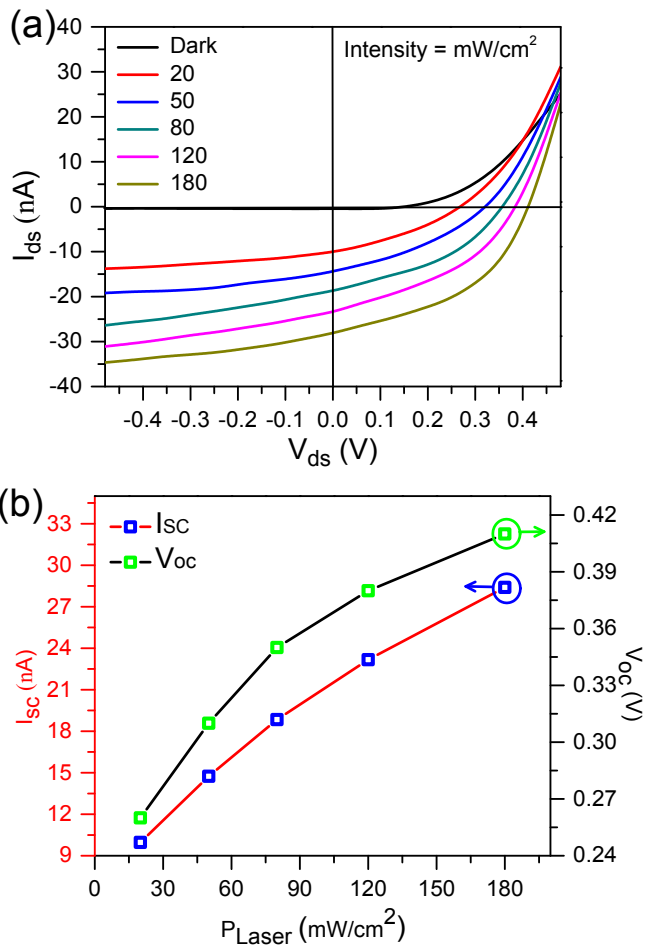
**Figure 2.** (a) An illustration of the lateral WSe<sub>2</sub> p-n diode. (b) The optical image of WSe<sub>2</sub> homojunction p-n diode. (c) KPFM image of the WSe<sub>2</sub> flake before the doping process. (d) The corresponding step height profile from the KPFM line scan is indicated. The value of contact potential difference across WSe<sub>2</sub>/h-BN and WSe<sub>2</sub>/SiO<sub>2</sub> is approximately ~46 mV. (e) A KPFM image of the WSe<sub>2</sub> flake for doped and undoped regions at a  $V_g^{light} = -40$  V. (f) The corresponding step height profile from the KPFM line scan is indicated. The value of the contact potential difference across h-BN/n-WSe<sub>2</sub> and SiO<sub>2</sub>/p-WSe<sub>2</sub> is approximately ~492 mV.



**Figure 3.** (a) Transfer curves of p-WSe<sub>2</sub> from probe (2, 3) and n-WSe<sub>2</sub> from probe (1, 6) as a function of  $V_{bg}$ . (b) Gate-dependent rectifying effect of the WSe<sub>2</sub> homojunction p-n diode with probe (5, 2) in a linear scale. Inset of (d) shown in log scale. (c) The rectification ratio of WSe<sub>2</sub> homojunction p-n diode as a function back gate voltage ( $V_{bg}$ ). (d) The ideality factor of the device at  $V_{bg} = -30$  V. (e) Rectification ratio as a function of different doping mechanisms in 2D materials.



**Figure 4.** (a) Transfer characteristics of the  $WSe_2$  diode with probe (5, 2) for four doping regimes as a function of back gate voltage ( $V_{bg}$ ). (b) Energy band diagram showing four different junctions with tuning the back gate.



**Figure 5.** (a)  $I_D$ - $V_D$  characteristics of the device under dark and light illumination at  $V_{bg}$ = 0 V. (b) The open circuit voltage ( $V_{oc}$ ) and short circuit current ( $I_{sc}$ ) is shown as a function laser power.

## TOC

