Research article

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Enhanced photoresponse of highly air-stable palladium diselenide by thickness engineering

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Abstract: Recently, layered two-dimensional (2D) palladium diselenide (PdSe₂), with a unique low-symmetry puckered pentagon atomic morphology, has emerged as a promising candidate for next-generation nanoelectronics and optoelectronics because of its chemical stability and extraordinary electrical properties. Moreover, PdSe₂ possesses a strong thickness-dependent bandgap that varies from 0 eV for bulk to 1.3 eV for monolayer, which can further render its potential applications in optoelectronics. However, the layer-dependent optoelectronic properties of PdSe₂ are still lacking up to date. Herein, we studied the optoelectronics transport characteristics of high-quality PdSe₂-based photodetectors with different thicknesses. We demonstrated an enhancement of PdSe₂ photodetector performance owing to the band engineering via a thickness reduction. The highest responsivity of 5.35 A/W can be achieved with an external quantum efficiency of 1250% at the wavelength of 532 nm. We attribute such high performance in photoresponsivity to the high valley convergence in the conduction band of layered PdSe₂,

in agreement with first-principles calculation. Our results offer new insight into the layer-dependent optoelectronic properties of PdSe₂ and open new avenues in engineering next-generation 2D-based electronics and optoelectronics.

Keywords: palladium diselenide; photoresponsivity; photodetector; band convergence.

1 Introduction

Two-dimensional (2D) semiconductors such as transition-metal dichalcogenides (TMDs) and black phosphorous (BP) have attracted enormous research interest in the “postgraphene age” because of their widely tunable bandgap when targeting applications in nanoelectronics and optoelectronics [1–8]. In this regard, layered TMDs including MoS₂, WS₂, and WSe₂ with tunable bandgap ranging from 1 to 2 eV have shown extraordinary electronic and optoelectronic properties beyond graphene [2, 9]. Their moderate carrier mobility and high ON/OFF transistor ratio render TMDs as promising building blocks for future nanoscale electronic and optoelectronic devices [10–16]. In contrast to TMDs, BP has a strong puckered orthorhombic lattice structure with a much lower symmetry, which gives BP an exotic in-plane anisotropic transport behavior, such as anisotropic electronic [17], optoelectronic [18], and thermal properties [19]. Moreover, BP has larger bandgap tunability ranging from 0.3 to 2 eV [20]. The relatively small bandgap gives BP a higher ON/OFF ratio and carrier mobility as compared with most TMDs, thereby attracting enormous research efforts toward the development of optoelectronic devices [21–23]. However, BP is highly unstable in air, which has become a bottleneck and needs extra treatment and process in practical device applications [24–27]. Therefore, a material with a better bandgap tunability, high electronic performance, and high air-stability is far more desirable.

The recent introduction of palladium diselenide (PdSe₂) as a noble TMD with strong puckered structure

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much-like BP but with unique pentagon atomic units [28–30] differentiates PdSe₂ from most 2D materials, where the pentagons are usually considered as geometrical defects [31]. This low-symmetry pentagonal material exhibits interesting anisotropic properties according to the structure–property relationship in contrast to an isotropic planar hexagonal structure, thereby offering a new degree of freedom in designing devices with better performance and unprecedented functionalities. It has been reported that few-layer PdSe₂-based field effect transistors (FETs) exhibited a mobility up to $\sim 158 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ along with ON/OFF ratios as high as 10^6 [28]. The existence of a thickness-dependent bandgap in PdSe₂ that varies from metallic (bulk) to $\sim 1.3 \text{ eV}$ (monolayer) makes it an interesting material to further probe its optoelectronic properties [32, 33]. More importantly, PdSe₂ is highly stable in the air like graphene [28], demonstrating its potential for practical applications in optoelectronics such as sensing, imaging, and space communications.

In this study, we investigate the optoelectronic properties of few-layer PdSe₂-based phototransistors through photocurrent measurements. As we know, 2D materials are extremely sensitive to the environment because of their 2D nature [34]. Hence, we employed *h*-BN as the substrate for our PdSe₂ phototransistor to provide atomically flat support, as well as to minimize charge inhomogeneity in order to probe its intrinsic optoelectronic properties [35]. Upon illumination of 532-nm laser, the few-layer PdSe₂-based phototransistor exhibits excellent photodetector performance up to few A/W photoresponsivity, comparable to or even better than most of the 2D material-based devices [2]. More interestingly, by measuring electronic transport properties of PdSe₂ with different thicknesses, a higher current is observed in thinner flakes, which is in contrary to the electrical resistivity equation, where a smaller cross section will give a higher resistance. Consistently, an enhancement of photodetector performance is also demonstrated in a thinner PdSe₂ phototransistor. The highest photoresponsivity of 5.35 A/W is achieved with an external quantum efficiency (EQE) of 1250% in our 3.8-nm-thick PdSe₂ phototransistor. We believe such anomalous electrical transport behavior together with its high performance in photoreponsivity is attributed to the higher valley convergence [36] in the conduction band of thinner PdSe₂, in agreement with our first-principles calculation [37, 38]. Our work offers new insight into the layer-dependent optoelectronic properties of PdSe₂ and opens new avenues in engineering next-generation 2D-based electronics and optoelectronics.

2 Materials and methods

2.1 Synthesis of bulk PdSe₂ crystal

Standard self-flux method was employed here to grow bulk PdSe₂ single crystal. The elements of Pd powder (99.99%) and Se (99.94%) from Sigma-Aldrich (Singapore) were mixed in an atomic ratio of 1:6 and then sealed in a quartz ampule under high vacuum of 10^{-6} torr in a thermal furnace. The synthesis process started from slowly heating up the furnace to 850°C and maintained for 50 h. Then, it was allowed to cool to 450°C at a cooling rate of 3°C/h. The furnace is finally cooled down to room temperature, where shiny single crystals of PdSe₂ can be obtained by cleaving an ingot product.

2.2 Device fabrication and measurement

Palladium diselenide and *h*-BN flakes were separately mechanically exfoliated onto SiO₂/Si substrates. The flakes are then examined by optical microscope and atomic force microscopy (AFM) to ensure clean surface with well-defined shape and uniform thickness. Then poly(methyl methacrylate) was employed as supporting layer for standard wet-transfer technique [39] to transfer PdSe₂ flakes onto a *h*-BN flakes to fabricate PdSe₂/*h*-BN devices. After which, electrodes were patterned by standard electron-beam lithography procedures, followed by thermal deposition of titanium/gold (Ti/Au) with thickness of 5 nm for Ti and 80 nm for Au. The FET characteristics and photoresponsivity of PdSe₂-based photodetectors were carried out by Keithley 6430 and 2400 SourceMeters (Keithley, Tektronix Southeast Asia Pte Ltd., Singapore) at room temperature. The samples were illuminated by a 532-nm laser with a tunable power density.

2.3 First-principles calculation

First-principles calculations were performed using Vienna *ab initio* Simulation Package [40] with the projector-augmented plane-wave (PAW) method [41]. The kinetic energy cutoff of PAW potentials is 350 eV, the exchange–correlation interactions is described by Perdew–Burke–Ernzerhof functional [42], and the weak dispersion force is described by the TS (Tkatchenko–Scheffler) + SCS (self-consistent screening) [43] method. Monkhorst–Pack [44] *k*-point mesh of $9 \times 9 \times 1$ was used to sample the Brillouin zone for relaxations. The accurate position of conduction band minimum (CBM) of PdSe₂ layers is obtained from a $45 \times 45 \times 1$ self-consistent

calculation. In the nonperiodic direction, we add a large vacuum region of 25 Å to avoid unphysical interactions. The convergence criterion for total energy is 10^{-8} eV, and atomic force is 10^{-4} eV/Å for our calculation.

3 Results and discussion

Layered 2D PdSe₂ is a semimetal noble TMD in its bulk form and has much stronger interlayer coupling and layer binding energy compared to other 2D materials, making bulk PdSe₂ very challenging to thin down to monolayer [45]. Figure 1A shows the top view (top) and side view (bottom) of a monolayer PdSe₂, similar to puckered structures such as BP [17] but with pentagonal rings instead of hexagonal rings. Each Pd atom is bonded with four Se atoms in the same layer to form a vertical puckering distance ~ 1.6 Å [28]. From the first-order Raman spectrum of few-layer PdSe₂ as shown in Figure 1B, we observe a few prominent peaks around 143, 205, 221, and 255 cm⁻¹, which originate from the vibrational modes of PdSe₂ crystal lattice, namely, A_g^1 , A_g^2 , B_{1g} , and A_g^3 , respectively [46].

The inset in Figure 1C displays the optical image of the PdSe₂/h-BN phototransistor device fabricated on a highly p-doped silicon substrate with 285-nm-thick SiO₂ layer. Figure 1D presents the AFM image of this PdSe₂ phototransistor device, where its thickness is extracted to be ~ 8 nm along the white dashed line. All electronic measurements were performed using a two-terminal DC technique at room temperature under high vacuum of 10^{-7} mbar. Figure 1C demonstrates the typical transfer characteristics of this device with the gate voltage (V_g) sweeping from -70 to 70 V. The source-drain current (I_{sd}) increases with increasing gate voltage under a bias (V_{sd}) of 0.5 V. The ON/OFF ratio observed for this device is around 10^4 . From this typical gate-dependent transfer curve, the FET mobility can be extracted based on the following equation [47]:

$$\mu = \frac{L}{W} \frac{1}{C_g} \frac{dG}{dV_g} \quad (1)$$

where L and W are the length and width of the PdSe₂ channel, respectively; C_g is the capacitance per unit area of the substrate; and G is the conductance of the

Figure 1: Characterization of few-layered PdSe₂ flake.

(A) Puckered pentagonal atomic structure can be observed from the top view and side view of the crystal structure of monolayer PdSe₂. The dashed black line indicates the unit cell. (B) Raman analysis on few-layered PdSe₂ flake used to make phototransistor. (C) Typical FET transfer characterization of few-layered PdSe₂ phototransistor with $V_{sd} = 0.5$ V. Inset: Optical image of the measured PdSe₂ phototransistor. (D) AFM scan across the channel area of our device showing the thickness of the PdSe₂ flake to be 8 nm.

device channel. We obtain an FET mobility of $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature, which is comparable with previous studies in PdSe_2 [33] and other TMDs such as MoS_2 [48].

To study the optoelectronic properties of PdSe_2 -based phototransistors, we used a 532-nm laser with a tunable power density to excite the photocurrent as illustrated in Figure 2A. (Similar photocurrent measurement was also performed with a 660-nm laser for comparison, and the detailed results can be found in Supporting Information Figure S5.) Figure 2B shows the time-dependent photoresponse characteristics of PdSe_2 photodetector with gradually increased bias voltage at 0 V_g . As observed, the excited photocurrent was significantly increased by nearly an order of magnitude as the bias voltage increases from 0.5 to 2.5 V, which is similar to other 2D photodetectors [18]. The main critical parameters of photodetector performance, namely, photoresponsivity (R), were calculated from the measured photocurrent and plotted as a function of bias voltage in Figure 2C. The photoresponsivity (R) is defined as photoresponse current generated per unit power of excitation light on the effective area of the photodetector [49, 50]

$$R = I_{ph} / P A_s \quad (2)$$

where I_{ph} is the photocurrent excited by incident light; P is the intensity of the light power, which is tunable in our setups; and A_s of $1.68 \mu\text{m}^2$ is the effective area under illumination, respectively (detailed power-dependent photoresponsivity behavior is shown in Supporting Information). By sweeping the bias voltage from 0.5 to 3 V at 0 V_g , the responsivity of PdSe_2 photodetector increased almost linearly from 0.06 to 0.74 A/W, which is comparable with other 2D-based photodetectors [2, 51–53] (Table 1 in Supporting Information). Exploiting the advantage of 2D materials, the charge carrier concentration can be easily modulated by the application of back gate voltage [54–57]. Here, we also investigated the photoresponsivity dependence on back gate voltage. Figure 2D shows that the photocurrent increases with increasing back gate voltage from 0 to 70 V and an enhancement in photoresponsivity of PdSe_2 to 3 A/W. The mechanism of such gate-dependent photoresponse for PdSe_2 photodetector can be explained by the modulation of the Schottky barrier [18, 21] formed between the metal contacts and PdSe_2 flake. As shown in Figure 2E and F, without any application of back gate voltage, the realignment between the fermi level of PdSe_2 and work function of metal contacts will form a nonnegligible Schottky barrier. When a positive back gate voltage is applied, the fermi level of PdSe_2 is effectively pushed

Figure 2: Optoelectronic characterization of few-layered PdSe_2 flake.

(A) Three-dimensional illustration of the device structure used to measure photo current. (B) Time-dependent photocurrent under different bias voltage V_{sd} . (C) Photoresponsivity as function of V_{sd} . (D) Time dependence of photocurrent measured at different gate voltages. (E and F) Qualitative energy band diagrams of PdSe_2 device through gating effect.

toward the conduction band, thereby reducing the effective Schottky barrier height by compressing the barrier region, which acts to reduce contact resistance as well. This significantly improves the electrical transport of photoinduced carriers that contribute to the large enhancement in photocurrent.

Exhibiting strong thickness-dependent band structure by tuning the thickness, PdSe₂ provides many interesting and important opportunities for applications in optoelectronics [32, 46, 58]. As shown in previous studies, the bandgap varies from 0 to 1.3 eV as PdSe₂ is thinned down from bulk to monolayer. To further study the effect of thickness on its optoelectronic property, we fabricated another phototransistor using a thinner PdSe₂ flake with a thickness of 3.8 nm. Figure 3A shows the sheet conductance ($G_s = G \cdot L/W$, where G , L and W is the conductance, width, and length of sample channel, respectively) as function of back gate voltage. Surprisingly, a much higher sheet conductance is observed in the 3.8-nm phototransistor device in contrary to the electrical resistivity equation.

Considering a smaller cross section of a thinner flake, the electrical conductivity of 3.8 nm PdSe₂ is even higher than that of 8 nm PdSe₂, implying a different band structure. The time-dependent photoresponse characteristics of PdSe₂ photodetectors with different thicknesses at $V_g = 70$ V were plotted in Figure 3B. As expected from the electrical transport property, the photoresponse current of 3.8 nm PdSe₂ is also higher than that of the 8-nm PdSe₂ device under the same condition. We also compared gate-dependent photoresponsivity between two devices. As shown in Figure 3C, at $V_g = 0$ V, the photoresponsivity increased from 0.5 to 3.1 A/W as the PdSe₂ thickness reduces from 8 nm to 3.8 nm, which demonstrates the outstanding enhancement in the photodetection through band engineering by varying the thickness of PdSe₂. The highest photoresponsivity reaches 5.35 A/W in the 3.8-nm PdSe₂ device, which is around two times higher than the 8-nm device and also higher than the current reported PdSe₂ photodetector in the visible light range [33]. It is worth to notice that the photoresponse time of different-thickness PdSe₂

Figure 3: Layer-dependent optoelectronic properties in PdSe₂ phototransistor.

(A) Sheet conductance as function of back gate voltages for PdSe₂ phototransistors with different thickness. (B) Time dependence of photocurrent measured at $V_g = 70$ V, $V_{sd} = 3$ V for PdSe₂ phototransistors with different thickness. (C) Comparison of photoresponsivity for the measured PdSe₂ phototransistors as function of back gate voltage. (D) Back gate-dependent EQE of 3.8-nm-thick PdSe₂ phototransistor.

devices show almost the same value of around 200 ms, which means that the conventional band-to-band recombination is dominated by the photon absorption with the excited electron hole pairs. Meanwhile, the EQE, another critical performance parameter for photodetectors, can be obtained by the following equation [49]:

$$\text{EQE} = hcR / (e\lambda) \quad (3)$$

where h , c , and e represent the Plank constant, speed of light, and the charge of electron, respectively. R and λ are the calculated responsivity and the wavelength of incident light, respectively. The value of EQE represents the number of carriers circulating a phototransistor per absorbed photon per unit time as described in the equation. As shown in Figure 3D, our 3.8 nm PdSe₂ photodetector demonstrates an EQE ranging from 700% to 1250% as the back voltage increases from 0 to 70 V, which is also larger than our 8-nm devices with maximum 726% EQE at the same condition (detailed results in Supporting Information Figure S3). Our results demonstrate the ability to modulate photoresponsivity and EQE by an external gate voltage to enhance the overall performance of PdSe₂-based photodetectors.

To better understand the mechanism of the layer-dependent electronic and optoelectronic properties of PdSe₂, the band structures of monolayer and 5-layer PdSe₂ were calculated using first-principle calculation and are shown in Figure 4. It can be found that PdSe₂ is an indirect bandgap semiconductor, and the CBM is not located at the high symmetry point like the other 2D semiconducting

materials [59]. The CBMs for monolayer and 5-layer PdSe₂ are both located at the Λ point. As the layer number of PdSe₂ increases from 1 to 5, its bandgap reduces from 1.38 to 0.33 eV. Interestingly, an extra valley in the conduction band is observed at $\Lambda + 1$ point in addition to the CBM at Λ point. The distance between CBMs at Λ point and $\Lambda + 1$ point for monolayer PdSe₂ is around 29 meV, which is smaller compared to a thermal energy of 52 meV ($2k_bT$, where k_b is Boltzmann constant, and T is the absolute temperature) at room temperature. This makes it possible that both Λ and $\Lambda + 1$ valleys contribute to the total density of state and thus enhance the electrical conductivity [36]. While the layer numbers increase, the distance between Λ point and $\Lambda + 1$ point also increases. For example, a 5-layer PdSe₂ with $|E_{\Lambda} - E_{\Lambda+1}| = 56$ meV is slightly higher than the thermal energy at room temperature, resulting in less contribution to electrical transport from the extra valley as compared to a monolayer PdSe₂. In addition, our results of the 6-nm PdSe₂ device show maximum photoresponsivity of 3.7 A/W at 70-V gate voltage further confirmed our calculations (details are in Supporting Information Figure S4). Although the first-principle calculated values cannot fully represent the real case in our room temperature measurement [28]. This provides a valuable clue to explain why thinner PdSe₂ FET exhibits better electrical performance than its thick counterpart, which we believe is also the key aspect to the enhancement of photoresponsivity in thinner PdSe₂ coming from band engineering with extra density of states induced by its stronger band convergence.

Figure 4: Comparison of the electronic band structure of monolayer and five-layer PdSe₂ calculated by first-principles method.

4 Conclusion

In this study, we demonstrated a high-performing PdSe₂-based photodetector through electrical transport and photoresponsivity measurement. By supporting PdSe₂ on atomic flat *h*-BN substrates, we are able to probe the intrinsic optoelectronic properties of PdSe₂ by minimizing the interface impurity effect. We also show a strong manipulation of the photodetector performance by an external back gate voltage through modulation of Schottky barrier formed between the metal contacts and PdSe₂ flake. Thickness-dependent electrical transport and photoresponsivity also demonstrated an enhancement in electronic and photodetector performance in thinner PdSe₂ devices due to band engineering by changing the device channel thickness. The highest responsivity of 5.35 A/W can be achieved with an EQE of 1250% upon the illumination of a 532-nm laser. We attribute such high performance

in photoresponsivity to a stronger valley convergence in the conduction band in thinner PdSe_2 , which is supported by our first-principles calculation. Our results show that air-stable unique pentagonal PdSe_2 may find potential applications in next-generation optoelectronics, and its layer-dependent photoresponsivity behavior offers a new avenue in the design and understanding of high-performance photodetectors.

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