Exploring the air stability of PdSe$_2$ via electrical transport measurements and defect calculations

Anna N. Hoffman, Yiyi Gu, Liangbo Liang, Jason D. Fowlkes, Kai Xiao and Philip D. Rack

In this work we investigate the effects of ambient exposure on CVD grown PdSe$_2$ and correlate density functional theory calculations of various physisorption and chemisorption binding energies and band structures to the observed changes in the electrical transport. Pristine PdSe$_2$ is n-type due to intrinsic selenium vacancies, but shows increased p-type conduction and decreased n-type conduction as a function of ambient aging during which various aging mechanisms appear to be operative. Short term aging (<160 h) is ascribed to an activated chemisorption of molecular O$_2$ at selenium vacancies; first-principles calculations suggest a ~0.85 eV activation energy and adsorption geometries with binding energies varying between 1.3–1.6 eV, in agreement with experimental results. Importantly, this chemisorption is reversible with a low temperature anneal. At long term aging (>430 h), there is a total suppression of n-type conduction, which is attributed to a dissociative adsorption/reaction of the O$_2$ molecules to atomic O and subsequent PdO$_2$ formation. XPS confirms the presence of PdO$_2$ in long term aged flakes. At these extended aging times, the low temperature anneal restores low n-type conduction and suppresses p-type conduction due to the low thermal stability of PdO$_2$, which, in agreement with XPS measurements, sublimates during the anneal. Thus PdSe$_2$ devices can be processed into device architectures in standard laboratory environments if atmospheric exposure times are limited to on the order of 1 week.

Palladium diselenide (PdSe$_2$) has recently been identified as a puckered 2D material, with the additional benefit of a low-symmetry pentagonal structure. Structurally, each layer is identical, but there are significant changes in electrical and optical behavior as these layers stack due to changes in symmetry and quantum confinement. Additionally, PdSe$_2$ is anticipated to be electronically anisotropic; mobility should vary depending on the crystal axis. The most notable and studied layer thickness dependent effect is the transition from an indirect band gap in some bulk TMD materials to a direct band gap in their monolayer counterpart. The MoS$_2$ band gap, for instance, varies from ~1.2 eV in the bulk to ~1.9 eV at the monolayer, while PdSe$_2$ varies from almost no gap (quasi-metallic) to 1.3 eV allowing for unique band gap control. This offers a promising path to logic junction devices processed in a single material by patterning various regions with thicker (contact and resisters) and thinner (semiconductor) regions. While some report PdSe$_2$ to be intrinsically ambipolar, as will be demonstrated, we tentatively attribute this behavior to adsorption at surface chalcogen vacancies and find PdSe$_2$ to be intrinsically n-type due to selenium vacancies.

Due to high surface to volume ratio, optoelectronic properties can be dramatically impacted by atmospheric surface adsorbents in 2D materials with strong layer number dependence. For this reason it is essential to understand the impact of exposure to ambient, which is often unavoidable during fabrication and characterization processes, on electrical properties. Electrical effects of ambient adsorbents and aging have been studied for MoS$_2$ and WSe$_2$. Studies on MoS$_2$ suggest that ambient molecules preferentially adsorb to chalcogen surface vacancies and act as both electron traps and p-type donors. While there is not a consensus on which specific adsorbents contribute to electron suppression and hole doping, most agree that oxygen produces the greatest effect. The effects of water adsorption and long term aging in WSe$_2$ was recently studied and the enhanced p-type conductivity and n-type suppression was associated with electron transfer to adsorbed water and O$_2$ molecules and a reduction of the selenium vacancies, respectively. Furthermore, selenides have been shown to be more affected by adsorbed atmospheric species and oxidation effects than sulfides.
Previous studies on 2D materials report significant electrical behavior variation after a vacuum or inert atmosphere anneal to drive off adsorbed species such as oxygen and water. Bartolomeo et al. recently explored the effects of external stimuli such as pressure, and optical and electron irradiation on the electrical properties of exfoliated thick (~25 layer) PdSe$_2$ field effect transistors. Notably they observed a transition from strongly p-type at atmospheric pressure to ambipolar behavior when pumped to ~$1 \times 10^{-6}$Torr. In this work we explore the effects of short term (90 min) ambient exposures and long term (~1000 h) ambient aging and compare atmospheric ambient pressure versus vacuum (~$1 \times 10^{-5}$Torr) environmental effects on the electrical properties of chemical vapor deposition (CVD) grown multilayer PdSe$_2$; furthermore, we investigate the potential to reverse aging effects through annealing in an inert environment. To rationalize the observed electrical property changes, first-principles density functional theory (DFT) calculations of adsorbed H$_2$O, O$_2$ and O on pristine and Se vacancies in single and multilayer PdSe$_2$ were performed.

RESULTS

To investigate the effects of short term ambient exposure on the electrical behavior of PdSe$_2$, a 6 layer PdSe$_2$ FET device was fabricated. Figure 1a shows an optical micrograph and Fig. 1b illustrates a schematic of all devices used in this study. As has been shown previously, PdSe$_2$ FETs annealed at 177 °C in inert gas for 12 min show a strong decrease in p-type conduction, increased n-type conduction, and a negative threshold voltage shift. To confirm this phenomena and investigate the stability of this treatment, Fig. 1c shows the transfer characteristics of a five-layer PdSe$_2$ device measured in air before a 177 °C anneal and the subsequent characteristics measured in air as a function of time after the anneal. We observe the reported strong n-type increase, p-type decrease, and negative threshold voltage shift; however, over a short ambient exposure time there is a strong reversal of these effects. The device shows an increase in the p-type conduction, a gradual decrease in the n-type conduction, and a strong positive threshold voltage shift toward the pre-anneal levels. It should be noted that there is an approximate 5-min delay between the anneal and the first air measurement reported; thus, there is likely some atmospheric exposure effects convoluted in the initial measurement.

To investigate the effect of ambient pressure on the electrical properties, Fig. 1d illustrates a series transfer characteristics of a 13-layer PdSe$_2$ device measured after the 177 °C anneal at various times during an ~22 h, ~$1 \times 10^{-5}$ Torr vacuum exposure. It should be noted there is a short period of time (~5 min) between the anneal and the vacuum pump down where the device was exposed to ambient air, first measurement is after 3 min in vacuum. Figure $1c, d$, both show the annealed samples have a dominant n-type conduction which we determine to be the pristine behavior of PdSe$_2$. During the vacuum exposure there is a small decrease in the p-type conduction, but at the longer exposure time, p-type conduction approaches the original value. Thus this short term effect (~20 min) could be due to trapped charge injection in the underlying SiO$_2$ layer caused during the repetitive forward sweep measurement from $-60V_{GS}$ to $+60V_{GS}$. The n-type conduction increases over the first 20 min and remains nearly constant over the next ~22 h. Overall, comparing Fig. 1c, d, dramatic degradation from pristine behavior is observed during atmospheric exposure, but arrested if device is held in vacuum indicating atmospheric adsorbents are the cause. Conversely, Bartolomeo et al. report strong pressure-dependent conduction in bulk-like exfoliated crystals where they observed reversible enhanced p-type conduction at atmospheric pressure and enhanced n-type conduction after an extended (10 h) high-vacuum exposure. Thus, our study which finds no significant pressure-dependent effects is a bit surprising since, as was recently demonstrated in WSe$_2$, thinner flakes are more susceptible to pressure effects than bulk-like flakes.

Subsequent to the initial short term exposure in Fig. 1, a seven-layer sample was fabricated, annealed, measured, and placed in ambient to be tested after 6, 60, 160, 430 and 840 h of ambient aging. At each aging time, the sample was measured in air, then in vacuum after a 72 h vacuum exposure. Figure 2a illustrates the n-type transfer characteristics measured in air immediately after the anneal, which we assume to be the pristine (time $t = 0$) characteristics. Figure 2a also shows the transfer characteristics of a 6 and 840 h aged sample measured in air and after the 72 h vacuum exposure. The first 6 h of ambient aging clearly suppresses the n-type conduction and significantly increases the p-type conduction. After the 72 h vacuum exposure, n-type conduction increases by a factor of ~4, while the change in p-type conduction is negligible. After 840 h of ambient aging, the device is purely p-type as all n-type conduction has been.

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Fig. 1  a atomic force micrograph of 7 layer PdSe$_2$ device and b schematic of all devices used in this work. c transfer characteristics of an as-fabricated five-layer device and subsequent characteristics measured in air as a function of time after an inert, 177 °C – 12 min anneal. d transfer characteristics of a 13-layer PdSe$_2$ devices after the inert, 177 °C – 12 min anneal, measured during various times throughout a ~22 h, ~$1 \times 10^{-5}$ Torr vacuum exposure.
Fig. 2  a n-type transfer characteristics measured in air immediately after the anneal which we assume to be the pristine (time $t=0$) characteristics along with air and post 72 h vacuum exposure characteristics of same device after 6 and 840 h of ambient aging time. b, c plot the n- and p-type current at ±60 V gate voltage, respectively, versus time in air and after the 72 h vacuum exposure measurements.

suppressed in our gate voltage range. However, after the 72 h vacuum exposure some n-type conduction is recovered. Interestingly, the 840 h aging sample recovers more significantly than the 6 h aging sample (as evidenced by the significant threshold voltage shift) during the vacuum exposure. As will be discussed below, this suggests different aging by-products and in particular that the 6 h aging byproduct has a higher binding energy than the 840 h aging byproduct. Figure 2b, c are plots of the n- and p-type current at ±60 V gate bias versus atmospheric aging time, respectively, measured in air and after the 72 h vacuum exposure (See Fig. S2 for full transfer characteristics). We observe a very clear increase in the p-type conduction and decrease in the n-type conduction over this ambient aging time. Comparing the air and 72 h vacuum exposure measurements, we observe that the change in p-type conduction is negligible (decreases by an average factor of 1.3) and the n-type conduction increases more significantly. For instance, the n-type conduction over the first 160 h increases, on average, by a factor of ~5; at 430 and 840 h the device displays only p-type conduction in air; however, as shown in Fig. 2a, n-type conduction is recovered after vacuum exposure. Thus, the atmospheric aging appears to have a component that is partially reversible via room temperature vacuum exposure.

A complimentary six-layer PdSe$_2$ FET was fabricated and aged along with the sample described above, however this sample was re-annealed prior to each measurement. Figure 3a shows the transfer characteristics of this sample measured in air immediately after each anneal. (See Fig. S3 for transfer characteristics after a 72 h vacuum hold) Clearly the modest aging experienced up to 160 h is largely reversible by the anneal, however some residual degradation to the n-type conduction and enhancement in the p-type conduction remains. Beyond the 160 h measurement, both the n-type and p-type conduction decreases; thus another aging mechanism emerges between the 160 and 430 h aging, which is consistent with the dramatic change in the n-type conduction at 430 h in Fig. 2c. Recently, Bartolomeo et al. studied the hysteresis of multilayer PdSe$_2$ field effect transistors. They attributed the observed hysteresis to charge trapping at PdSe$_2$ defects and in the near interfacial SiO$_2$ gate region. We also performed hysteresis measurements for some of the aging conditions after the forward measurements made in Figs. 2a and 3 (see supplemental information Fig. S4 for the hysteresis curves). In general, our hysteresis data is similar to those presented in ref. 33.

X-ray photoelectron spectroscopy (XPS) spectra were taken on a pristine PdSe$_2$ sample, samples that were aged in atmosphere for ~120 and ~1000 h, and for reference a PdSe$_2$ sample that was exposed to a 15 s inductively coupled oxygen plasma exposure. Figure 4 illustrates the 3d spin orbit split 5/2 and 3/2 peaks for 3a, Pd and 3b, Se. Kibis et al. recently studied the thermal and plasma oxidation of Pd metal and showed that metallic Pd has 3d 5/2 peak at 335.2 eV, and the typical PdO (Pd$^{+4}$) peak is at 337 eV. Furthermore, the metastable PdO$_2$ (Pd$^{+4}$) exhibit a 3d 5/2 at 338.2 eV. The pristine PdSe$_2$ (Pd$^{+4}$) peak position of the Pd 3d 5/2 is at 337.4 eV. This is a lower binding energy relative to PdO$_2$, consistent with Se having a lower electronegativity than O and thus forming a less ionic bond. To confirm the position of the PdO$_2$ peak, we exposed a PdSe$_2$ sample to oxygen plasma under similar conditions that were found to oxidize a single layer of WSe$_2$. The ~120 h aged sample has a small Se–O shoulder emerge at ~59 eV and all Pd and Se peaks are shifted ~0.2 eV to lower energy compared to the pristine sample. This peak shift is consistent with a Fermi energy shift to toward the valence band and thus consistent with the observed increase of p-type conduction. At ~1000 h, the S–O peak is still evident, however even more pronounced is the emergence of the PdO$_2$ peaks at ~338 (5/2) and 343.4 eV (3/2). The Pd and Se peaks are shifted ~0.4 eV to lower energy relative to the pristine sample, which is again consistent with electrical results which show increased p-type behavior at longer ambient aging times. Consistent with Kibis et al, the plasma oxidized PdO$_2$ 3d peaks are ~0.2 eV lower energy compared to the long term ambient aged PdO$_2$ 3d peak. Kibis et al found the PdO$_2$ oxide from both oxidation methods had low thermal stability over ~127 °C, so to support the claim that PdO$_2$ is forming as PdSe$_2$ samples age in ambient, the ~1000 h aged sample was treated with a 177 °C – 12 min anneal in situ and measured again. Figure 4 shows that after the anneal, oxide peaks
DISCUSSION

To understand the observed change in the PdSe$_2$ electrical properties in response to the annealing process during the atmospheric aging and vacuum exposures, we carried out DFT calculations for the binding energies of adsorbed H$_2$O and O$_2$ on pristine single layer PdSe$_2$ as well as several physi- and chemisorbed species at Se vacancy sites for both single and six-layer PdSe$_2$. The computed binding energies and charge transfers (from the PdSe$_2$ to the adsorbents) are summarized in Table 1. Figure 5 compares the associated band structure calculations for the various defect complexes in six-layer PdSe$_2$. Similar calculations for one-layer PdSe$_2$ can be found in supplemental information Fig. S5. Note that the band gap reduction from one-layer (1.36 eV) to six layers (0.27 eV) is slightly overestimated relative to experimentally determined optical band gaps.$^{15}$

Interestingly, while the O$_2$ and H$_2$O physisorbed binding energies and electron transfers per adsorbed molecule from the surface are appreciable, as shown in Fig. 1d, the electrical characteristics of the annealed device is relatively stable after the short air exposure and subsequent 22-h vacuum exposure. The change in PdSe$_2$ electrical properties during ambient air exposure demonstrated in Fig. 1c is thus not attributed to O$_2$ or H$_2$O physisorption, which presumably has no energy barrier and would saturate very rapidly upon exposure to ambient. Furthermore, due to the low physisorption binding energies the electrical behavior would be reversible on a much faster time scale than the experimental room temperature vacuum measurements (see residence time plots for O$_2$ and H$_2$O physisorption in supplemental information Fig. S6). Physisorption of H$_2$O to Se vacancies has a higher binding energy, however, Fig. 5d shows that for the six-layer PdSe$_2$, only one of the Se donor levels is degenerate with the conduction band, and thus only a modest Fermi energy shift is expected from this defect complex. Furthermore, this binding energy is also low and thus H$_2$O would be rapidly desorbed in vacuum, so the relative stability in a room temperature vacuum exposure suggests that this defect complex is not responsible for the observed ambient exposure aging (see H$_2$O-Se vacancy residence time plot in supplemental information Fig. S6). To estimate the activation energies associated with the observed electrical changes, we correlate the short ambient aging time constant to a simple activated chemisorption process. The estimated time ($\tau_R$) associated with for the n-type conduction to reduce to 1/e (36%) is $\sim$10 min and thus the activation energy can be estimated by $\tau_R = \tau_0 \exp\left(\frac{E_a}{kT}\right)$; where $\tau_0$ is the vibration frequency of the physisorbed species ($\sim 10^{13}$/s), $E_a$ is activation energy, $k$ is Boltzmann’s constant, and $T$ is temperature. From this expression, an activation energy of $\sim 0.94$ eV can be estimated. Furthermore, one can estimate the binding energy of this chemisorbed state by comparing the change in n-type current

Fig. 3 Transfer characteristics of a six-layer PdSe$_2$ FET measured immediately in air after a 177 °C – 12 min anneal at each of the specified total ambient aging times.

Fig. 4 3d spin orbit split 5/2 and 3/2 peaks for a Pd and b Se for: a pristine PdSe$_2$ sample; a PdSe$_2$ sample exposed to a 15 s remoted O$_2$ plasma; PdSe$_2$ samples aged in atmosphere for 120, and 1000 h; and the 1000 h aged sample after a 177 °C – 12 min anneal in situ.
after the 72 h vacuum exposure by simple first order desorption kinetics:
\[ \frac{dC}{dt} = \frac{1}{\tau_{\text{des}}} C_0 \exp\left(\frac{t}{\tau_{\text{des}}}\right) \]
where \( C \) is concentration, \( t \) is time, \( \tau_{\text{des}} \) is the desorption residence time, and \( C_0 \) is the concentration at \( t = 0 \). The estimated binding energy associated with the room temperature change in n-type conduction is 1.07 eV.
 Comparing these values to the calculated DFT results suggests that the electrical property changes in response to ambient air exposure can be attributed to an activated chemisorption of \( \text{O}_2 \) at Se vacancies. While not specifically calculated, one cannot rule out that some of the chemisorbed \( \text{O}_2 \) molecules result from the oxygen evolution reaction from adsorbed \( \text{H}_2\text{O} \) catalyzed at the Pd sites associated with the selenium vacancy. As demonstrated in Table 1 and Fig. 5c, molecular \( \text{O}_2 \) can chemisorb to unsaturated Pd atoms since the \( \text{O} = \text{O} \) double bond can transit to a single bond. While the \( \text{O}_2 \) molecular chemisorption leaves a defect level near the conduction band edge in single layer \( \text{PdSe}_2 \) (See Fig. S3), both Se vacancy levels are degenerate with the conduction band in the 6 layer material. DFT calculations of the barrier energy associated with the activated chemisorption of physisorbed \( \text{O}_2 \) to chemisorbed \( \text{O}_2 \) at the \( \text{V}_{\text{Se}} \) was determined to be about 0.85 eV, which is in good agreement with the estimated value from the time constant of 0.94 eV. The calculated binding energy for the 6 layer chemisorbed \( \text{O}_2 \) molecule at the Se vacancy is 1.61 eV for the most stable adsorption configuration. The observed room temperature vacuum recovery, however, suggests a slightly lower binding energy of \( \sim 1.07 \text{ eV} \); DFT calculations of chemisorbed \( \text{O}_2 \) molecule rotated 90° yields a slightly lower binding energy of 1.30 eV. This suggests that the computed binding energy of chemisorbed \( \text{O}_2 \) molecule at the \( \text{V}_{\text{Se}} \) can vary from 1.30 to 1.61 eV depending on the initial orientation of \( \text{O}_2 \) molecule. In the lower energy case, the reversibility of this short term ambient aging when annealed at 177 °C for 12 min is expected (see 177 °C residence times for 1.1, 1.3, and 1.61 eV in supplemental information Fig. S6) and is experimentally observed in Fig. 3.

The long term aging associated with >160 h ambient exposure is attributed to a dissociative adsorption/reaction of the \( \text{O}_2 \) molecules to atomic \( \text{O} \) and subsequent \( \text{PdO}_2 \) formation, as evidenced by the emergence of \( \text{PdO}_2 \) in the XPS spectra of a ~1000 h aged sample at ~338 eV.\(^{34,35}\) \( \text{PdO}_2 \) formed by plasma oxidation of Pd was found to have low thermal stability >127 °C,\(^{34}\) and thus should sublime during the 177 °C anneal resulting in damaged surface layer(s) and reduced electron mobility, as seen in the post anneal 430 and 840 h transfer characteristics in Fig. 3. To test this, the ~1000 h aged sample was annealed in situ at

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**Table 1.** Calculated binding energies and charge transfers for various species to pristine \( \text{PdSe}_2 \) and selenium vacancies (\( \text{V}_{\text{Se}} \)) in \( \text{PdSe}_2 \).

| Species          | \( \text{H}_2\text{O} \) binding (eV) | \( \text{H}_2\text{O} \) charge (e\(^{-}\)) | \( \text{O}_2 \) binding (eV) | \( \text{O}_2 \) charge (e\(^{-}\)) | \( \text{O} \) binding (eV) | \( \text{O} \) charge (e\(^{-}\)) |
|------------------|-------------------------|---------------------------------|------------------------|---------------------------------|------------------------|---------------------------------|
| \( 1 \text{L} \) | 0.13                    | 0.15                            | 0.10                   | 0.06                            | 2.10                   | 0.87                            |
| \( 1 \text{L} \ \text{V}_{\text{Se}} \) | 0.48                    | 0.51                            | 1.61                   | 1.09                            | 2.10                   | 0.87                            |
| \( 6 \text{L} \ \text{V}_{\text{Se}} \) | 0.64                    | 0.46                            | 1.30 \*1.61            | 1.11                            | 1.99                   | 0.75                            |

\*rotated 90° relative to 1.61 eV orientation
is arrested when the device is placed in vacuum, con
the pristine n-type behaving device exhibits a decrease in n-type
inert atmosphere anneal. Longer term aging (>430 h) yields a
vacuum exposure and is fully recoverable via a low temperature
the Fermi energy towards the valence band coinciding with the
defect complex eliminates the selenium vacancy gap states near
energy consistent with the experimentally estimated values; the
purely p-type air measurement recovers only some residual n-
change in the threshold voltage of the long term aged sample
Aesar) was placed in the heating center of the furnace and 1.5 g Se powder
method in a one inch tube furnace. The growth was carried out at
Growth
is lower than the chemisorbed O2 as evidenced by the signi
the main text are forward sweeps where Vg starts at the most negative
value and sweeps toward the most positive value and the curves were
were collected in 20–30 s (or an average of 4–6 V/s). To study the effect of low
temperature annealing, anneals were performed in a nitrogen glove box
for 12 min at 177 °C. Samples were typically measured in air, then after
–20 min and subsequent 72 h, −1 × 10−6 Torr vacuum exposure, and then
again in air. XPS measurements were performed in a Thermo Electron
ESCALAB Xi system with an energy resolution of 0.1 eV. The spot size of the
x-ray was approximately 650 × 650 μm and thus the XPS signal is an
average of many individual PdSe2 grains (and background SiO2). See
supplemental information Fig. S1 for optical image of a typical CVD growth
of the PdSe2.

Density functional theory calculations
Plane-wave density functional theory (DFT) package VASP was used for
first-principles calculations with the projector-augmented-wave (PAW)
pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) exchange-
correlation functional. In addition, we adopted the van der Waals (vdW)
density functional method optPBE-vdW to describe the vdW interactions.
To model the PdSe2 surface, single-layer and six-layer PdSe2 structures
were built by a periodic slab geometry, where a vacuum separation of
about 21 Å in the out-of-plane direction was used to avoid spurious
interactions with periodic images. The cutoff energy was set at 400 eV, and
a 12 × 12 × 1 k-point sampling was used. All atoms were relaxed until the
residual forces were below 0.02 eV/Å, and in-plane lattice constants were
also optimized using the method of calculating the total volume (i.e., ISIF = 4 in
VASP). Then 4 × 4 × 1 supercell structures of single-layer and six-layer
PdSe2 were constructed with a single Se vacancy introduced on the surface
to study the adsorption of O2, O, and H2O, where the k-point sampling was
reduced to 2×2×1. All the atoms were relaxed until the residual forces
below 0.02 eV/Å.

DATA AVAILABILITY
The datasets generated during and/or analyzed during the current study are available
from the corresponding author on reasonable request.

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