In this work, we present a comprehensive theoretical and experimental study of quantum confinement in layered platinum diselenide (PtSe$_2$) films as a function of film thickness. Our electrical measurements, in combination with density functional theory calculations, show distinct layer-dependent semimetal-to-semiconductor evolution in PtSe$_2$ films, and highlight the importance of including van der Waals interactions, Green’s function calibration, and screened Coulomb interactions in the determination of the thickness-dependent PtSe$_2$ energy gap. Large-area PtSe$_2$ films of varying thickness (2.5–6.5 nm) were formed at 400 °C by thermally assisted conversion of ultra-thin platinum films on Si/SiO$_2$ substrates. The PtSe$_2$ films exhibit $p$-type semiconducting behavior with hole mobility values up to 13 cm$^2$/Vs. Metal-oxide-semiconductor field-effect transistors have been fabricated using the grown PtSe$_2$ films and a gate field-controlled switching performance with an $I_{ON}/I_{OFF}$ ratio of $>$230 has been measured at room temperature for a 2.5–3 nm PtSe$_2$ film, while the ratio drops to $<2$ for 5–6.5 nm-thick PtSe$_2$ films, consistent with a semiconducting-to-semimetallic transition with increasing PtSe$_2$ film thickness. These experimental observations indicate that the low-temperature growth of semimetallic or semiconducting PtSe$_2$ could be integrated into the back-end-of-line of a silicon complementary metal-oxide-semiconductor process.

In 2015, Wang et al.\textsuperscript{8} reported that the surface of a Pt(111) crystal can be selenized to form ML PtSe$_2$ at 270 °C. This method is convenient to yield large-area films up to millimeter size and allows the band structure of ML PtSe$_2$ to be studied. However, the metallic Pt substrate hinders electronic applications where an insulating substrate is generally needed. Although atomically thin PtSe$_2$ flakes with different thickness can be mechanically exfoliated from the bulk crystals\textsuperscript{13,14} and are very well suited for fundamental studies, this approach is not scalable. Recently, the growth of PtSe$_2$ films on sapphire substrates by chemical vapor deposition (CVD) at 900 °C\textsuperscript{15} and PtSe$_2$ synthesis through direct reaction of metal platinum foil and selenium powder under high pressure and high temperature (600–800 °C)\textsuperscript{16} have been reported. PtSe$_2$ films grown on sapphire substrate by CVD at 500 °C was recently reported indicating how the doping type of the films can be modified by the stoichiometry of the PtSe$_2$ films by a rapid or slow cool down process, which modifies the Se precursor supply.\textsuperscript{17} In ref.\textsuperscript{18} 1 ML to 22 ML PtSe$_2$ films have been grown on bilayer graphene/6H-SiC (0001) substrates by molecular beam epitaxy, which in principle could be extended to grow large size films on dielectric substrates.

In this study, the electronic structure and carrier transport properties of PtSe$_2$ films with different thicknesses are investigated theoretically and experimentally. First-principles calculations considering vdw interactions for pristine PtSe$_2$ films are performed. Calibration of Green’s function with screened Coulomb interaction (GW) is utilized to predict the quantitative values of the
bandgap energy. The bandgap opening in few-layer PtSe₂, reported in other works, is shown to depend strongly on the simulation framework, with a progressive increase in the PtSe₂ energy gap when considering density function theory (DFT), to DFT with the addition of vdW interactions, and finally to DFT with vdW interactions and screened Coulomb interaction. The Bohr radius provides an estimation of when the quantum effects modify the band structure. The Bohr radius of 10 nm is calculated for bulk PtSe₂ with electron-effective mass of 0.22×m₀ and bulk PtSe₂ dielectric constant of 40.24 Within this simulation framework, we investigate the impact of Pt vacancies on the PtSe₂ band structure and the density of states (DoS). For ML and bilayer structures, our atomic-scale simulations reveal that Pt vacancies lead to the creation of localized energy states in the bandgap and a shift in the Fermi level towards the PtSe₂ valence band.

To explore these effects experimentally, we have synthesized large-area PtSe₂ films by thermally assisted conversion (TAC) of pre-deposited Pt layers at 400 °C on Si/SiO₂ substrates. Hall measurements of the PtSe₂ films reveal p-type majority carriers for all TAC-grown PtSe₂ films with mobilities in the range of 5–13 cm²/V·s. Back-gated PtSe₂ metal-oxide-semiconductor field-effect transistors (MOSFETs) demonstrate p-channel behavior, consistent with the experimental van der Pauw Hall measurements of the large-scale films. The Hall analysis and the back-gated PtSe₂ MOSFET characteristics are both consistent with the theoretical calculations, showing p-type PtSe₂ films and a transition from semimetallic behavior for films from 5 to 6.5 nm to a semiconducting behavior for a film thickness of 2.5 to 3 nm.

RESULTS

First-principles ab initio calculations

Bulk PtSe₂ is a semimetal with trigonal symmetry, where Pt atoms are coordinated by six neighboring Se atoms. In ultra-thin PtSe₂ films, PtSe₂ bandgaps open up. The effects of quantum confinement (QC) determine the value of the confinement-induced bandgap in the PtSe₂ thin films. Ab initio techniques are applied to study PtSe₂ thin films. Standard theoretical methods for calculating band structure based on DFT are well known to under-estimate the predicted bandgaps primarily due to approximations for the electronic exchange and correlation energies. vdW interlayer interaction in layered materials such as PtSe₂ improves the structural and electronic properties description obtained by DFT calculations. Hence, we have incorporated vdW interaction in our calculations by adding a nonlocal vdW term to local and semi-local exchange correlation functionals. In addition, to provide further improved quantitative description of the bandgap energies, GW (G: Green’s function and W: screened Coulomb interaction) calibration in combination with a many-body perturbation theory is also implemented. Green’s function theory provides quasi-particle energies using the electron self-energy operator containing the effects of exchange and correlations with other quasi-particles.

Figure 1a illustrates the band structure of a ML PtSe₂ film. The ML PtSe₂ has an indirect bandgap of 1.2 eV when GW correction is not accounted for. The band structure of bulk PtSe₂ is shown in Supplementary Fig. 1, which exhibits the semimetallic characteristic and is in good agreement with literature, where both electron and hole pockets coexist on the Fermi surface. With the increase of number of PtSe₂ layers, the energy level of valence band maximum (VBM) exceeds that of conduction band minimum (CBM), leading to overlap of bands and hence semiconductor-to-semimetal evolution. In the GW calculations, the method in ref. has been used enabling improved convergence in the bandgap energies with a reduced set of empty states. Due to the computational demands of GW calculations, this approach was applied to films between 0.5 and 2 nm thickness and used to extrapolate the effect of QC for thicker films as shown in Fig. 1b. A decrease in bandgap energy by increasing the number of layers has been shown to be due to interlayer coupling and screening effects, which change the electronic wave function hybridization in the valleys of both the valence and conduction bands. As can be seen in Fig. 1b, bandgap values calculated using DFT, DFT + vdW, and GW calibration are 1.2 (0.15) eV, 1.2 (0.51) eV, and 2.43 (1.5) eV for ML (bilayer) PtSe₂ film, respectively. In other words, comparable bandgaps to conventional semiconductors are expected in thin PtSe₂ films; for example, bilayer and trilayer PtSe₂ films have bandgaps comparable with GaAs and Ge, respectively. Our predicted bandgap values are benchmarked against other values from literature in Fig. 1b.

The role of vacancies is also investigated from first-principles using fully relativistic electronic structure calculations based on DFT implemented in OpenMX and QuantumATK. The electronic energy within the framework of Kohn–Sham DFT is calculated using pseudo-atomic localized basis functions. The localized basis functions allow the consideration of larger supercell dimensions and hence lower vacancy density. The effect of SOC must be considered in PtSe₂ films due to its strong effect in the 5d orbitals of the transition metal atoms. Grimme’s dispersion correction for the vdW interaction is also incorporated in our calculations. Periodic boundary conditions are applied to create simulation supercells and the cell dimension along the film growth axis is chosen to be >2 nm to avoid any interaction between the periodic images of the neighboring slabs. The geometries are fully relaxed until the force acting on each atom is <0.01 eV/Å. The structure consists of a single defect in 6×6×1 supercell corresponding to defect density of 2.3×10¹³ cm⁻². The periodic images of the point defects are more than 2 nm apart from each other, where defect–defect interaction is negligible. In the calculation of point defects, instead of removing the atom from the lattice, it is replaced by an “empty” atom. Empty atoms are basis functions in the vacancy center with zero pseudopotential cores and zero number of electrons. These basis set orbitals can be populated to host a finite electron density in a region where there are no real atoms. The lattice parameters of the relaxed pristine PtSe₂ film after geometry optimization are shown in Supplementary Fig. 2. After the geometry optimization of the structure with the Pt vacancy, the position of the point-defect neighbor atoms is modified in comparison with their position in the pristine structure as shown in this figure. The Se atoms at the top layer next to the Pt vacancy move outward, while the Se atoms at the bottom layer move downward. This movement of the Se atoms results in a slight shrinkage of Pt-Se bond lengths (Dₚ₋ₛₑ) near the vacancy from 2.54 to 2.51 Å and an increase in the diagonal separation between the Se-Se atoms from 2×Dₚ₋ₛₑ = 5.08 to 5.45 Å, as indicated in the Supplementary Fig. 2, and are consistent with the previously reported results (ref. and ref. 45 therein; ref. 31 and ref. 42 therein).

Using supercells in studying the effects of vacancies is inevitable in first-principles calculations. However, as the size of the supercell increases, the corresponding first Brillouin zone (BZ) shrinks and as a result bands of the supercell are extremely “folded” into the first BZ. Therefore, it is challenging to analyze the effects of vacancies and impurities perturbation and to directly compare the folded bands with the reference band structure of a primitive cell or with the experimental results obtained by angle-resolved photoemission spectroscopy (ARPES) measurements. A procedure to unfold the primitive cell Bloch character hidden in the supercell eigenstates is known as “unfolding.” By applying the unfolding procedure, the band structure of a supercell will be mapped to the band structure of a reference primitive cell.

Utilizing linear combination of atomic orbital basis sets in the presence of a perturbation, such as vacancy, allows mapping of the symmetry breakers, which perturb the band structure.
The unfolded band structures of the ML and bilayer PtSe₂ films with a Pt vacancy are shown as contour plots in Fig. 2. The primitive cell band structure of pristine PtSe₂ is shown by black solid lines, which are in excellent agreement with band structures experimentally obtained by angle-resolved photoemission spectroscopy (ARPES) measurements for monolayer and bilayer PtSe₂. Total density of states (DoS) of each film is shown using black solid lines, which are in excellent agreement with band structures experimentally obtained by angle-resolved photoemission spectroscopy (ARPES) measurements for monolayer and bilayer PtSe₂. Total density of states (DoS) of each film is shown in the right panel. The localized states corresponding to the Pt vacancy are located close to the edge of the valence band within the bandgap as can be seen, the Fermi level is shifted towards the valence band edge in the case of Pt vacancy, indicating that the Pt vacancy results in a p-type characteristic of the PtSe₂ films. Another important outcome of this study is that on the contrary to most of the other ultra-thin TMDs, indirect-to-direct transition of bandgap is not observed in ML PtSe₂ film (ref. 34 and references therein).

Experimental results

In this study, PtSe₂ thin films are synthesized by TAC of pre-deposited Pt layers on Si/SiO₂ substrates. A growth temperature of 400 °C was used, and growth was achieved directly on the Si/SiO₂ substrate (see the Methods section for more details). In order to investigate the influence of QC effects in PtSe₂ films with different thicknesses are prepared. Cross-sectional transmission electron microscope (XTEM) images of the as-grown films with 0.7 and 1 nm Pt nominal thickness as the staring material are shown in Fig. 3, illustrating the layered structure and polycrystalline nature of the PtSe₂ films after conversion. The PtSe₂ film thicknesses are 2.5–3 and 5–6.5 nm for the two Pt starting films after the TAC process. XTEM images of the transferred films are shown in Supplementary Fig. 5, demonstrating successful film transfer. Raman spectra of the PtSe₂ films grown from various Pt thicknesses, that is, 0.7, 1, and 1.5 nm, are shown in Supplementary Fig. 6.
layers, respectively. Films are all planar and layered along the 2.5 nm thickness range of converted PtSe2 from HR-XTEM. The few-layer structure and the approximate thickness of the films are synthesized from 0.7 to 1 nm Pt starting nominal thickness are intervals are shown in Supplementary Table 1, confirming results of the two different batches made with 3-month occasions over the course of 3 months. The Hall-effect measurements are performed in a van der Pauw configuration with a LakeShore Model 8404 AC/DC (alternate current/direct current) Hall-effect measurement system. See the Methods section for more details. The room temperature Hall-extracted properties of the PtSe2 films are summarized in Table 1. A typical two-point I-V characteristic is shown in Supplementary Fig. 7. The sample has an almost square area of 1 cm². To ensure reproducibility, 5–6.5 nm PtSe2 samples were made on different occasions over the course of 3 months. The Hall-effect measurement results of the two different batches made with 3-month intervals are shown in Supplementary Table 1, confirming the reproducibility of the process. Very consistent Hall data are obtained growing the PtSe2 films on different substrates, for example, sapphire, results of which are shown in Supplementary Table 2.

The few-layer structure and the approximate thickness of the PtSe2 films, examined by high-resolution XTEM (HR-XTEM), are presented in Fig. 4a. As can be seen, the PtSe2 thin films synthesized from 0.7 to 1 nm Pt starting nominal thickness are 2.5–3 and 5–6.5 nm thick, corresponding to 5–6 and 10–12 atomic layers, respectively. Films are all planar and layered along the XTEM lamella and are polycrystalline, with several nanometer-sized crystalline domains. Hall-effect measurements on all PtSe2 films indicate p-type dominant carrier type, consistent with our atomic-scale simulation including the effects of Pt vacancies in the films (see Fig. 2). The presence of grain boundaries and vacancies is not unexpected given the polycrystalline nature of the films. It is important to note that adsorbates could also be contributing to the p-type behavior observed in the PtSe2 films; hence, an investigation of how the ambient and pressure influence the electrical properties of the PtSe2 films would be valuable in terms of providing a more complete understanding of the factors, which impact the carrier type and carrier density in PtSe2 films. This is the area of an on-going study. The Hall measurements in Table 1 indicate an increase in sheet carrier concentration, and a corresponding decrease in sheet resistivity, as the PtSe2 thickness increases. This is consistent with a semiconductor-to-semimetal evolution in ultra-thin PtSe2 films calculated with our atomic-scale simulations (Fig. 1). As presented in Table 1, the Hall hole mobility values are in the range of 5 to 13 cm²/V·s.

To further explore the electrical properties of the PtSe2 films, back-gated FETs were fabricated by patterning Ni/Au metal stack as the source and drain metal contacts to the PtSe2 films on ~85 nm SiO2 on p++-Si (Si/SiO2), followed by defining channel regions of different lengths and widths through etching (see Methods section for details). The p++-Si is used as a shared “metal” back-gate electrode. A polymer-support film transfer
process was carried out to allow transfer of the PtSe2 films from their original synthesized Si/SiO2 substrates onto an unprocessed Si/SiO2 for the fabrication of back-gate FETs (see Methods section for details). The motivation for the PtSe2 film transfer is evident from Fig. 4a, indicating potential diffusion of Pt into the underlying SiO2 during the film synthesis,35 shown by the red arrows. A range of samples were diced from the same growth run based on a channel thickness of 5 nm (left) before and (right) after transfer. Red arrows point to the dark regions under the PtSe2 film inside the oxide. Scale bar is 10 nm. b Room temperature transfer characteristic of a back-gated field-effect transistor (FET) device with a channel thickness of 2.5–3 nm PtSe2, a channel length of 15 µm, and channel width of 45 µm at VDS = 1 V. P-type characteristic and high ON/OFF ratio of 230 has been measured. Field-effect mobility is µFE = 0.3 cm2/V·s. c Room temperature output characteristic of the same device as in b illustrating linear and symmetric variation of the channel current with the drain voltage. d Transfer characteristic of a device with channel length of 15 µm and channel width of 45 µm, and PtSe2 channel thickness of >5 nm at VDS = 50 mV, showing very small current modulation. E_A,ON and E_A,OFF in b and d are the activation energies at “ON” and “OFF” states, respectively. b and d demonstrate the layer-dependent quantum confinement (QC)-induced bandgap opening reflected in the electrical characteristics of the PtSe2 FETs.
reduced voltage drop across the channel. To investigate this point, we calculated the channel resistance \( R_{ch} = \frac{V_{DS}}{I_{DS}} \approx 10^5 \Omega \), where \( R_{ch} \) is the channel resistivity (see Table 1). Considering the total resistance \( R_{tot} = \frac{V_{DS}}{I_{DS}} \approx 3.4 \times 10^6 \Omega \), we obtain a large contact resistance of \( R_c = \frac{R_{tot} - R_{ch}}{2} \approx 1.65 \times 10^6 \Omega \) compared to the channel resistance; hence, the actual voltage drop across the channel would be \( V_{ch} \approx 0.03 \text{V} \). Using \( V_{ch} \) instead of \( V_{DS} \) in the \( g_m \) equation, we obtain \( \mu_{FE} \approx 10 \text{cm}^2/\text{V} \cdot \text{s} \), which is close to the value obtained from Hall analysis and comparable to reported mobility for CVD-grown films. It is important to note that the corrected \( \mu_{FE} \) value of \( \approx 10 \text{cm}^2/\text{V} \cdot \text{s} \) is only an indicative value at the given \( V_{DS} \) since the channel and contact resistances are expected to vary with the gate field. The polycrystalline nature of our synthesized PtSe₂ films could be another origin of the relatively low mobility compared to previously reported values of 7–210 cm²/V·s obtained from mechanically exfoliated PtSe₂ flakes. However, considering the benefits of our growth process, namely, the low synthesis temperature, scalability and ease of controlling layer thickness, and the back-gated MOSFET characteristics in Fig. 4b and c, this is quite promising for a p-channel material formed at 400 °C. Contact engineering could further improve the device performance by structuring PtSe₂ films, benefiting from thick “bulk” semimetallic regions as source and drain contacts, and thin semiconducting channel connecting source and drain regions. Due to the linear behavior of the output characteristic of the FETs (Fig. 4c), the possibility of a Schottky barrier-limited field-effect mobility is discarded. This linear behavior could also be attributed to the small band offset at the source and drain contacts with respect to the edge of the valence band of the channel region in the case of Pt vacancies (see Fig. 2). Many reports in literature have indicated an ambipolar behavior in the transfer characteristic for TMD-based MOSFETs. Our devices do not indicate an ambipolar response, and are consistent with a tunnel junction for holes and a Schottky barrier for electrons at the PtSe₂/Ni interface.

Electrical behavior of the PtSe₂ FETs was also characterized at different temperatures. The variation of the drain current activation energy with back-gate voltage is shown in Supplementary Fig. 9. For the transferred PtSe₂ film, in Supplementary Fig. 9a, the activation energy changes from 190 meV in the OFF state, which is close to the extrapolated PtSe₂ bandgap, to around 50 meV in the ON state. In the case of the non-transferred PtSe₂ films (see Supplementary Fig. 9b), the extracted \( E_A \) is in the range of 140–160 meV and does not change by the back-gate voltage. This result, in conjunction with the TEM analysis in Fig. 4a, indicates an interaction of the Pt with the SiO₂ substrate during growth, which prevents back-gate modulation of the current. The effect is removed after PtSe₂ film transfer, where back-gate modulation of the drain current and variation in the associated activation are evident. In the case of the PtSe₂ films with a thickness >5 nm, shown in Supplementary Fig. 9c, the extracted \( E_A \) is around ~50 meV and demonstrates no variation with back-gate voltage consistent with our atomic-scale simulations (see Fig. 1), suggesting very small bandgap for a >5 nm PtSe₂ films. These results demonstrate that bulk PtSe₂ exhibits metallic-like properties, in clear contrast to the semiconducting few-layer PtSe₂.

As shown in Supplementary Fig. 10, for the transferred film with 2.5–3 nm PtSe₂ channel thickness, the \( I_{on}/I_{off} \) of a typical device \((W/L = 40 \mu \text{m} \times 20 \mu \text{m}, L = 15 \mu \text{m})\) increases with reducing temperature. From Supplementary Fig. 10, it is evident that the temperature dependence of the drain current activation energy is primarily driven by the 200 meV activation energy of the OFF state current, which results in the increase of \( I_{on}/I_{off} \) from ~80 (at 30 °C) to ~4.5 × 10² (at −50 °C). From a technology point of view, room temperature characteristics of FET devices is of most importance; nonetheless, by extrapolating the temperature-dependent data of Supplementary Fig. 10, the \( I_{on}/I_{off} \) could increase to >1.5 × 10³ at 20 K, which would be comparable with the previously reported ratio on an exfoliated PtSe₂ flake at cryogenic temperatures.

**DISCUSSION**

Considering the potential technology implications of this work, TAC of Pt to PtSe₂ is a scalable process that can be achieved at 400 °C. Figure 5 shows the results presented in this work compared to alternative approaches to form PtSe₂, which have been reported in the literature. The figure plots the maximum temperature of the process against the area of the PtSe₂ samples formed. The plot highlights that the TAC process can form PtSe₂ below the BEOL thermal budget limit for silicon CMOS (at around 450 °C), and importantly, this growth is achieved on amorphous SiO₂. This opens up the possibility that these films could be integrated into the BEOL of a silicon CMOS process, to provide semiconducting or semimetallic layers above conventional integrated circuits. For the samples presented in this work, it was necessary to transfer the PtSe₂ films, with evidence that Pt was interacting with the SiO₂ near-surface region during PtSe₂ formation. This motivates the need to study in detail the potential interaction of the Pt with the SiO₂, as well as exploring insulating diffusion barriers, which could circumvent the need for PtSe₂ film transfer. This is an area of ongoing research.

In conclusion, this work presents a theoretical and experimental study of QC effects in layered PtSe₂ films as a function of film thickness. PtSe₂ films with layer numbers increasing from 1 to 4 were studied by ab initio simulations with fully relaxed structures. VdW interactions and GW calibration have shown significant modification in the bandgap energy of the films, predicting QC-induced bandgaps comparable with conventional semiconductors for ML (2.43 eV) and bilayer (1.50 eV) PtSe₂ consistent with film thickness less than the calculated Bohr radius. The influence of Pt vacancies on the PtSe₂ band structure considering SOC has been investigated, indicating that a Pt vacancy acts as an acceptor, moving the Fermi level towards the PtSe₂ valence band edge. Large-area PtSe₂ films with different thicknesses were synthesized by a TAC process at 400 °C on Si/SiO₂ substrates. The PtSe₂ films exhibit a p-type nature with mobility values in the range of...
Back-gated FET devices with different channel dimensions were fabricated using CMOS standard photolithography and etching showing room temperature $I_{on}/I_{off}$ of excess 230 for a 2.5–3 nm PtSe$_2$ film, which drops to about 1.4 for 5–6.5 nm PtSe$_2$ channel, consistent with the ab initio simulations of a semimetal-to-semiconductor transition due to QC effects in thin films.

Our theoretical and experimental results demonstrate the potential for large area growth of polycrystalline PtSe$_2$ thin films for applications in the next generation of nanoelectronic devices. The ability to form layered PtSe$_2$ at 400 °C on an amorphous SiO$_2$ substrate, with hole mobilities exceeding 10 cm$^2$/Vs, opens up potential applications in areas such as flexible electronics and integrating new functions into the BEOL of existing semiconductor technologies.

**METHODS**

Details of DFT and GW calculations

PtSe$_2$ electronic structures are calculated using DFT as implemented in OpenMX, QuantumATK and Quantum Espresso. OpenMX and Quantum Espresso calculate the electronic energy within the framework of Kohn–Sham DFT using pseudo-atomic localized basis and plane wave basis functions, respectively. The plane wave calculations are performed with an energy cutoff of 180 Rydberg and $16 \times 16 \times 1$ $k$-point Monkhorst–Pack grid. Norm-conserving pseudopotentials and generalized gradient approximation (GGA) for the exchange correlation potential are considered. Numerical atomic orbital basis sets of $s^3p^3d^2$ are used for both Pt and Se atoms in OpenMX. Green’s function theory provides quasi-particle energies using the electron self-energy operator containing the effects of exchange and correlations with other quasi-particles. The Yambo program is used in this work to perform the GW calibration to quasi-particle energies within first-order perturbation theory starting from the Kohn–Sham eigenstates. The effective Coulomb interaction is set to zero in real space within the vacuum region such that quasi-particles do not interact with their periodic images. As a result, the periodicity of the structure is reduced using a cutoff for the Coulomb interaction in the direction transverse to the PtSe$_2$ film. In the GW calculations, the method in ref. has been used enabling improved convergence in the bandgap energies with a reduced set of empty states as well as requiring the GW correction to be applied for individual $k$-points of interest. A 16 $\times$ 1 $\times$ 1 $k$-point Monkhorst–Pack grid in the irreducible BZ is used with all $G$-vectors included in the GW calculations.

**Materials synthesis**

PtSe$_2$ thin films were synthesized using a TAC process similar to that previously described for MoSe$_2$ and WS$_2$. PtSe$_2$ was synthesized by sputtering onto Si/SiO$_2$ substrates using a Gatan precision etching and coating system. The Pt samples were selenized in a quartz tube furnace with two independently controlled heating zones. Pt samples were loaded in the primary heating zone to evacuate the system and keep it under vacuum, and the pressure during selenization was typically $\sim$0.7 Torr. A dwell time of 2 h was used to ensure complete selenization.

Hall-effect measurements

The Hall-effect measurements were performed in a van der Pauw configuration with a LakeShore Model 8404 AC/DC Hall-effect measurement system. The system can provide DC or AC magnetic fields over a variable range up to $\pm$1.7 T (DC) or a fixed range up to $\pm$1.2 T root mean square at a frequency of 0.1 or 0.05 Hz. The measurements in this work were performed at room temperature. The main parameters directly applied, measured, and extracted with the Hall-effect measurement system are the measured Hall voltage, $V_{H}$ = $R_{H}$ $I_{H}$, where $R_{H}$ is the extracted sheet Hall coefficient and $I_{H}$ is the applied excitation current, $B$ is the applied DC or AC magnetic field, $R_{H}$ is the extracted sheet Hall coefficient, $I_{H}$ is the extracted sheet carrier concentration (where the carrier concentration (n) is given by $n = \phi / q$, $\phi$ is the applied Hall factor (equal to unity for this work), $\mu$ is the extracted Hall mobility, $\rho$ is the measured sheet resistivity by four-point measurement, where $\rho = (\pi F_{AB} (R_n + R_B)/(2\ln(2)))$, with the resistivity given by $\rho = t \rho$, and $R_n$ and $R_B$ are the measured four-point orthogonal resistances, and $F_{AB}$ is the solution to the van der Pauw equation and is proportional to the ratio of the perpendicular four-point orthogonal resistances between the equivalent geometrical contacts (i.e., $R_n$ and $R_B$). $F_{AB}$ is between 0 and 1.0 depending on the accuracy of the solution to the van der Pauw equation (all results reported here are between 0.99 and 1.0).

Transmission electron microscopy

XTEM was prepared using a Dual Beam Focused Ion Beam (FIB) FEI Helios NanoLab 600i. A 50 nm carbon layer, which was followed by a 300 nm platinum layer, were deposited within the Dual Beam FIB by electron beam-induced deposition and 2 µm-thick carbon layer with ion beam-induced deposition. These three layers were grown for protection before the milling process. The lamella was prepared and thinned down to less than 200 nm thickness. The thinning at 30 kV was finished by polishing at 5 kV to reduce the ion beam-induced damage to a <2 nm thin layer on both sides. TEM analysis was performed using a JEOL JEM-2100 at 200 kV in bright field mode.

**Back-gated device fabrication and electrical characterization**

Back-gate field-effect transistors were fabricated by patterning source and drain metal contacts using standard photolithography followed by e-beam evaporation of Ni (20 nm)/Au (200 nm) and lift-off process. The PtSe$_2$ film was then patterned using a photore sist mask and an SF$_6$-based inductively coupled plasma etch to form the channel, as shown in the inset of Fig. 4b. Electrical transport properties of the back-gated devices were measured with a semiconductor device parameter analyzer (Agilent B1500a) and using Cascade semi-automated probe station at room and different temperatures.

**Film transfer process**

The synthesized as-grown PtSe$_2$ thin films were transferred onto unprocessed Si/SiO$_2$ substrates using a typical polymer-support transfer technique. Poly(methyl methacrylate) (PMMA, MicroChem) was spin coated onto the as-grown PtSe$_2$. The SiO$_2$ layer under the PtSe$_2$ was removed by a wet-etching process using 2 M sodium hydroxide at room temperature. After cleaning in de-ionized water, the PtSe$_2$ with PMMA layers were transferred onto the substrates. The PMMA was removed by immersion in acetone at room temperature for 20 min.

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**AUTHOR CONTRIBUTIONS**

L.A. conducted the theoretical calculations and atomic-scale simulations. N.M., C.O.C. and C.P.C. synthesized PtSe$_2$ films and performed spectroscopic characterization. F.G. conceived and designed the experiments and the mask layout, performed Hall-effect measurements, film transfer and device fabrication, and electrical characterization. S. M., K.F.B., and J.L. helped with device characterization. G.M. performed TEM. R.S., T.S.-L., R.D., E.C. and R.E.N. performed other sample characterizations. F.G. and L.A. wrote the manuscript. P.K.H. and G.S.D. helped with the planning of the experiments and the interpretation of the results, and supervised the project. All authors discussed the results and reviewed the manuscript.

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