High quality atomically thin PtSe$_2$ films grown by molecular beam epitaxy

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Abstract

Atomically thin PtSe$_2$ films have attracted extensive research interests for potential applications in high-speed electronics, spintronics and photodetectors. Obtaining high quality thin films with large size and controlled thickness is critical. Here we report the first successful epitaxial growth of high quality PtSe$_2$ films by molecular beam epitaxy. Atomically thin films from 1 ML to 22 ML have been grown and characterized by low-energy electron diffraction, Raman spectroscopy and x-ray photoemission spectroscopy. Moreover, a systematic thickness dependent study of the electronic structure is revealed by angle-resolved photoemission spectroscopy (ARPES), and helical spin texture is revealed by spin-ARPES. Our work provides new opportunities for growing large size single crystalline films to investigate the physical properties and potential applications of PtSe$_2$.

Introduction

Layered transition metal dichalcogenides (TMDCs) have attracted extensive interest for applications in electronics, optoelectronics and valleytronics due to the strong spin–orbit coupling, sizable band gap and tunability of the electronic structure by quantum confinement effect [1–4]. The past decade has witnessed significant efforts conducted on the atomically thin MoS$_2$ film [5–7]. However, its low mobility has limited applications, for instance, in high speed electronics [8, 9]. Finding thin films of other TMDC with better properties is highly desirable. Platinum diselenide (PtSe$_2$) has emerged of other TMDC with better properties is highly desirable. Platinum diselenide (PtSe$_2$) has emerged as an interesting compound that belongs to TMDC. As an interesting compound that belongs to TMDC. Although the bulk crystal is a semimetal [10, 11], monolayer (ML) PtSe$_2$ has been revealed to be a semiconductor with a band gap of $\approx$1.2 eV [12]. Importantly, the charge-carrier mobility of PtSe$_2$ has been predicted among the highest in TMDCs [9] and has been experimentally shown to be comparable to black phosphorene [13] yet with the advantage of much improved stability [14]. This makes PtSe$_2$ a promising candidate for high-speed electronics. Moreover, the hidden helical spin texture with spin-layer locking in monolayer PtSe$_2$ has been recently revealed [15], and such spin physics induced by a local Rashba effect has great potential for electric field tunable spintronic devices [16]. In addition, potential applications for photocatalytic activity [12, 17–19], photodetection [20, 21] and quick-response gas sensing [20, 22] has also been demonstrated. Therefore, PtSe$_2$ is an attractive candidate for a variety of applications. Obtaining high quality PtSe$_2$ films is a critical step toward this goal.

Monolayer PtSe$_2$ film has been first grown by direct selenization of Pt(1 1 1) substrate [12], which is convenient to yield large films up to millimeter size. However, the metallic Pt substrates hinders the electronics application and an insulating substrate is preferred. The direct selenization method results in a self-terminating monolayer thin film, while thicker films cannot be grown using this method. Although atomically thin PtSe$_2$ flakes with different thickness can be
mechanically exfoliated from the bulk crystals [14], the sample size is unsatisfactory and unscalable. Recently, the attempts of growing PtSe2 films by either chemical vapor deposition (CVD) [23, 24] or thermally assisted conversion (TAC) [20] have been reported, however, the polycrystalline nature and lack of atomic-level thickness control are yet to be improved. On the other hand, molecular beam epitaxy (MBE) can provide a better control in terms of growth dynamics and realization of large size, high quality single crystalline films on various substrates with controlled film thickness [25–29]. MBE has been playing as an important tool in the growth of layered materials and the fabrication of van der Waals heterostructures [30]. In the past years, MBE growth of atomically thin TMDC films has been accomplished on materials like MoSe2 [27, 28], NbSe2 [29] et al with atomic-level thickness control accuracy. However, the similar control of PtSe2 films with large-scale uniformity has not yet been realized.

In this work, we report the first epitaxial growth of high quality PtSe2 thin films on bilayer graphene/6H-SiC (0 0 0 1) substrate using MBE. We present a systematic study of the vibrational modes and core levels as a function of film thickness by Raman spectroscopy and x-ray photoemission spectroscopy (XPS). Moreover, the band structure measured from 1 ML to 22 ML PtSe2 thin films shows the shrinking of band gap as the film thickness increases. The helical spin texture with spin-layer locking in monolayer, bilayer and bulk PtSe2 was also investigated in detail. Such MBE growth method can be further extended to other insulating substrates.

Experimental section

Atomically thin PtSe2 films with varying thickness from 1 ML to 22 ML were grown on bilayer graphene/6H-SiC (0001) substrates using MBE in an ultrahigh vacuum system with a base pressure of 2 × 10⁻¹⁰ torr. The 6H-SiC (0001) substrate was degassed at 650 °C for 3 h in UHV chamber before the flash annealing process. After degas, the substrate was annealed from 650 to 1350 °C with a heating rate of 25 °C s⁻¹ and at 1350 °C for 30 s followed by a rapid quenching to 650 °C in 30 s. The uniform bilayer graphene was formed after 60 cycles of the flash annealing process, which was monitored by reflection high energy electron diffraction (RHEED) (figure 1(b)) and LEED (see figure S1 in the supplementary information (stacks.iop.org/TDM/4/045015/mmedia)). High-purity Pt (Alfa Aesar, 99.99%) and Se (Alfa Aesar, 99.999%) were evaporated using an e-beam evaporator and a Knudsen cell respectively, at a substrate temperature of 270 °C. An in situ annealing to 400 °C for 15 min could improve the crystalline quality. The growth rate was limited by the Pt flux (≈0.1 Å min⁻¹), and the flux ratio of RSe/RPt is kept at ~15/1 to ensure the selenium rich environment. The growth rate was determined to be 30 min per monolayer and the growth process was monitored in situ RHEED system. After growth, the samples were characterized by angle-resolved photoemission spectroscopy (ARPES) and low-energy electron diffraction (LEED). The surface morphology of the films was evaluated by atomic force microscopy (AFM). ARPES measurements were taken with a Scienta R8000 electron analyzer using UV lamp (21.2 eV) at the temperature of 80 K in a vacuum higher than 1 × 10⁻¹⁰ Torr. The ex situ XPS spectra of Pt 4f and Se 3d core-levels were recorded under ultra-high-vacuum conditions better than 1 × 10⁻⁸ mbar on a VG Scientific ESCAlab MkII system using Al Kα x-rays and an analyzer pass energy of 30 eV. Raman spectra were measured on a Horiba Raman system with an excitation wavelength of 633 nm and a 1800 lines/mm grating. Spin-ARPES measurements were performed at ESPRESSO endstation of Hiroshima Synchrotron Radiation Center under the temperature of 20 K, using photon energies of 21.2 eV (UV lamp) and 21 eV (Synchrotron radiation). The surface of PtSe2 films was covered by 20 nm thick amorphous selenium as a capping layer during the transfer and annealed to 220 °C to remove the Se capping layer before spin-ARPES measurements.

Results and discussion

PtSe2 crystallizes in stable 1T phase corresponding to the CdI2-type trigonal structure with P3 m1 space group (No. 162). The building block of PtSe2 contains one Pt atomic layer sandwiched between two Se layers, where Pt atoms are octahedrally coordinated by the Se atoms (figure 1(a)). Figures 1(b) and (c) show the RHEED patterns before and after growth of the PtSe2 film. RHEED pattern from the substrate are completely covered by sharp streaky stripes from the film within the first few minutes of growth. The surface morphology of the substrate is revealed by AFM image (figure 1(d)), with an average terrace of ≈300 nm and a step height of ≈0.75 nm (figure 1(f)) which is the typical height of triple SiC bilayer steps [31]. The surface morphology of the 0.8 ML PtSe2 film is shown in figure 1(e). With most of the areas covered by monolayer PtSe2, there is some small substrate surface exposed. The overall substrate steps are preserved after the growth. The line profile (figure 1(g)) across the step clearly shows the step height of 0.59 nm for 1 ML PtSe2 and 0.75 nm for the substrate. Due to the weak coupling between the graphene and sample, the PtSe2 films with varying thickness show negligible change in the in-plane lattice constant compared to the bulk crystal (see figure S2 in the supplementary information). The x-ray diffraction results are also shown in figure S3 in the supplementary information. Our MBE films with varied thickness provide a unique opportunity for a systematic study of the evolution of the structure vibration and electronic properties as a function of sample thickness.

The MBE grown PtSe2 films are characterized by Raman spectroscopy and XPS. Figure 2(a) shows the Raman spectra of PtSe2 films with varying thicknesses. The high quality films result in much sharper
spectra than exfoliated flakes [14] and three peaks are clearly identified as $E_g$, $A_{1g}$ and LO. In all PtSe$_2$ films, two prominent peaks at $\sim$180 cm$^{-1}$ and $\sim$208.5 cm$^{-1}$, correspond to the $E_g$ and $A_{1g}$ Raman active modes respectively [20, 24]. The spectral intensity is normalized by $E_g$ peak. The $E_g$ mode corresponds to an intra-layer in-plane vibration of Se atoms moving in opposite directions and the $A_{1g}$ mode involves the out-of-plane vibration of Se atoms moving away from each other. The $E_g$ mode shows a clear red shift with increasing film thickness (figure 2(b)), while the $A_{1g}$ mode is pinned at 208.5 cm$^{-1}$ at the first few layers thin film. A red shift of $A_{1g}$ peak is also observed in thicker (22 ML) PtSe$_2$ film, which is less significant compared with $E_g$ mode. The red shift of $E_g$ and $A_{1g}$ peaks still exist in bulk PtSe$_2$ single crystal (see figure S4 in supplementary information). This anomalous behavior may be attributed to stacking-induced structural
changes and long-range Coulombic interlayer interactions \cite{24, 32}. Moreover, the peak intensity of the $A_{1g}$ mode relative to that of the $E_g$ mode increases from 1 ML to 22 ML (figure 2(c)), consistent with the enhanced van der Waals interactions in thicker films \cite{32}. The peak at $\sim$240 cm$^{-1}$ is attributed to a longitudinal optical (LO) mode, which is a combination of the out-of-plane ($A_{2u}$) and in-plane ($E_u$) vibrations of platinum and selenium atoms respectively, with a similar origin to those observed in HfS$_2$, ZrS$_2$ and CdI$_2$ \cite{33, 34}. The zoom-in spectra in figure 2(d) show the LO mode in 1 ML PtSe$_2$ film that splits into two peaks at $\sim$236 cm$^{-1}$ and $\sim$239 cm$^{-1}$. With increasing thickness, such two peaks merge into one broader

![Figure 3](image1.png)

**Figure 3.** Electronic structure evolution with thickness in PtSe$_2$. (a)–(e) LEED pattern of 1, 2, 3, 7 and 22 ML PtSe$_2$ thin films. (f)–(j) ARPES spectra of 1, 2, 3, 7 and 22 ML PtSe$_2$ thin films along the $\Gamma$–$K$ direction taken at 21.2 eV.

![Figure 4](image2.png)

**Figure 4.** Spin texture of PtSe$_2$ 1 ML, 2 ML films and bulk single crystal. (a) and (b) Spin-resolved energy distribution curves (EDCs) for the 1 ML PtSe$_2$ in-plane tangential direction at emission angles of $-4^\circ$ and $4^\circ$, respectively. (c) and (d) Spin-resolved EDCs for bilayer PtSe$_2$ in-plane tangential direction at emission angles of $-4^\circ$ and $4^\circ$, respectively. (e) Spin-resolved EDCs for the bulk PtSe$_2$ in-plane tangential direction at emission angles of $-4^\circ$. (f) ARPES data of 2 ML PtSe$_2$ film measured at different emission angles.
hump. Figures 2(e) and (f) shows the XPS spectra of Pt and Se. The shift in the core level suggests a change in the chemical environment in monolayer PtSe$_2$ film. Since the oxygen peak remains unchanged in these films (see figure S5 in the supplementary information), which suggests the air-stability of PtSe$_2$ film, the energy shift in Pt and Se corelevels could be explained by the valence band alignment at the contact of graphene and PtSe$_2$ thin film. As few-layer PtSe$_2$ is a semiconductor, at the interface of PtSe$_2$ and graphene, the valence band alignment would modulate the energy position of band structure slightly. In monolayer PtSe$_2$ film, the band bending at the contact with graphene is shown as n-type Schottky contact with 240 meV energy shift, while the Schottky barrier height is much lower in thicker films, consistent with recent first-principles calculations [35].

To reveal the evolution of the electronic structure as a function of film thickness, we show in figure 3 LEED and ARPES data taken from 1 ML film to 22 ML PtSe$_2$ films. Figures 2(a)–(e) show LEED patterns with different film thickness. In 1 ML film (figure 3(a)), both the signals from the PtSe$_2$ film (indicated by white arrows) and the substrate (grey arrow) are observed. PtSe$_2$ grows mainly along the orientation of the graphene substrate with a small distribution of azimuthal angles due to the weak coupling between PtSe$_2$ and graphene, showing an arc-like feature in the LEED signal. As the growth proceeds (figures 3(b)–(e)), the substrate is completely covered by PtSe$_2$, and the LEED pattern from graphene disappears. ARPES dispersions measured along the Γ-K high symmetry direction are shown in figures 3(f)–(j). Our data of 1 ML PtSe$_2$ film (figure 3(f)) match well with previous results on 1 ML PtSe$_2$ film grown by direct seleniumization method [12], showing a semiconductor with the top of the valence bands at $-1.2$ eV. For films thicker than 1 ML, an additional band with an M-shape (indicated by gray arrow in figure 3(g)) emerges. This band moves toward the Fermi energy, indicating a reduction of the band gap as predicted [36]. The M-shape valence band eventually develops into a three dimensional Dirac cone in the bulk topological Dirac semimetal [10, 11]. By increasing the film thickness to 22 ML, the ARPES data show effectively the same electronic band structure as the bulk Dirac semimetal except a 350 meV energy shift (see figure S6 in the supplementary information). The ARPES experiments thus provide a direct evidence for the tunable bandgap with varying film thickness.

We further perform spin-ARPES measurements to reveal the spin texture of PtSe$_2$ films. Figure 4(a)–(d) shows spin-ARPES measurements along the Γ-K and Γ′-K′ high symmetry directions of both 1 ML and 2 ML films. Large spin contrast is observed along the tangential direction ($\theta$) at emission angles of $-4\degree$ and $4\degree$, respectively (dashed line in figure 4(f)). The radial (r) and out-of-plane (z) directions show negligible spin contrast (see figure S7 in the supplementary information). This is consistent with the helical spin texture as previously reported in 1 ML PtSe$_2$ films on Pt(111) substrate [15], confirming that it is an intrinsic effect of the PtSe$_2$ film rather than the influence from Pt substrate. Similar helical spin texture is also observed in centrosymmetric bulk PtSe$_2$ crystals (figure 4(e)), supporting the spin-layer locking mechanism induced by local Rashba effect [16]. Such helical spin texture induced by local Rashba effect makes it potentially useful for electric field tunable spintronics.

**Conclusion**

To summarize, we have successfully achieved epitaxial growth of high quality PtSe$_2$ thin films with controlled thickness using MBE. The samples are characterized by AFM, Raman, XPS, LEED and the electronic structure is revealed by APRES. ARPES measurements reveal a distinct tunable bandgap in atomically thin films. The MBE growth can also be extended to insulating substrates. Combined with its unique high charge-carrier mobility and air stability, PtSe$_2$ is a promising candidate for applications in new-generation electronic devices. Our work reveals the interesting physics in thin PtSe$_2$ films and the MBE growth can in principle be extended to grow large size single crystalline films on a variety of substrates.

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**Competing financial interests**

The authors declare no competing financial interests.

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