van der Waals Epitaxial Ultrathin Two-Dimensional Nonlayered Semiconductor for Highly Efficient Flexible Optoelectronic Devices

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Supporting Information

ABSTRACT: Despite great progress in synthesis and application of graphene-like materials, it remains a considerable challenge to prepare two-dimensional (2D) nanostructures of nonlayered materials that may bring us surprising physical and chemical properties. Here, we propose a general strategy for the growth of 2D nonlayered materials by van der Waals epitaxy (vdWE) growth with two conditions: (1) the nonlayered materials satisfy 2D anisotropic growth and (2) the growth is implemented on the van der Waals substrates. Large-scale ultrathin 2D Pb₁₋ₓSnₓSe nanoplates (∼15−45 nm) have been produced on mica sheets by applying this strategy. Benefiting from the 2D geometry of Pb₁₋ₓSnₓSe nanoplates and the flexibility of mica sheet, flexible photodetectors that exhibit fast, reversible, and stable photoresponse and broad spectra detection ranging from UV to infrared light (375, 473, 632, 800, and 980 nm) are in situ fabricated based on Pb₁₋ₓSnₓSe nanoplates. We anticipate that more nonlayered materials will be developed into 2D nanostructures through vdWE, enabling the exploitation of novel electronic and optoelectronic devices.

KEYWORDS: 2D nanostructures, nonlayered materials, van der Waals epitaxy, flexible optoelectronic devices

Two dimensional (2D) materials such as graphene, BN, MoS₂, Bi₂Se₃, and In₂Se₃ have recently attracted considerable interest due to their fascinating properties such as high electron mobility, superconductivity, quantum Hall effects, and quantum anomalous Hall effect. Also, they show great potential in the applications of electronic and optoelectronic devices, including photodetectors, transistors, pressure sensors, spin-valleytronic devices, p–n diodes and light-emitting diodes. Furthermore, benefiting from their 2D geometry, planar materials exhibit high compatibility with traditional microfabrication techniques and flexible substrates, which makes them the ideal building blocks for the fabrication of wearable flexible electronic and optoelectronic devices. Importantly, due to strong in-plane covalent bonding in individual atomic layer and weak van der Waals interaction between two adjacent layers, it is easy to engineer 2D nanostructures of layered materials by chemical vapor phase deposition or mechanical exfoliation.

So far the preparation of 2D nanostructures is mainly restricted to the layered materials with planar crystal structure. However, many materials with important functions have nonlayered crystal structure such as SnTe, Pb₁₋ₓSnₓSe, and PnₓSnₓTe, a kind of topological crystalline insulators (TCIs) with narrow band gap and special applications in not only infrared detection but also spintronics devices. In contrast to layered materials, these materials normally have isotropic crystal structure and incline to stack into three-dimensional (3D) nanostructures due to the lack of driving force for the 2D anisotropic growth. Therefore, it is a big challenge to synthesize ultrathin 2D nanostructures of nonlayered materials, which impedes the exploration of their novel physical and chemical properties and their applications as nanoscale electronic and optoelectronic devices as being discussed in this work.

Here, by comparing the growth of Pb₁₋ₓSnₓSe nanoplates and SnTe nanopyramids in this work and Te nanoplates in our previous work, we have proposed a general strategy for the growth of 2D nanostructures of nonlayered materials by van der Waals epitaxy (vdWE) with two conditions: (1) the nonlayered materials satisfy 2D anisotropic growth and (2) the growth is implemented on the van der Waals (vdW) substrates. By utilizing this strategy, we have obtained large-scale 2D ultrathin Pb₁₋ₓSnₓSe nanoplates (∼15−45 nm) on layered mica sheets. Profiting from the insulativity and flexibility of mica sheets, flexible photodetectors based on Pb₁₋ₓSnₓSe nanoplates were in situ fabricated on mica sheets. The devices display broad spectra response ranging from UV to infrared light (375, 473, 632, 800, and 980 nm) and fast, stable, and reversible photoresponse even after being bent for 100 times with a bending radius of 4 mm, indicating that 2D Pb₁₋ₓSnₓSe nanoplates-based photodetectors on mica sheets have great application potential in flexible and wearable optoelectronic

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Figure 1. Schematic illustrations, SEM, and AFM characterizations of van der Waals epitaxial ultrathin 2D Pb$_{1-x}$Sn$_x$Se nanoplates. Pb$_{1-x}$Sn$_x$Se with cubic crystal structure (a) can be tailored into ultrathin 2D nanostructures (b) by vdWE at certain growth temperature under which Pb$_{1-x}$Sn$_x$Se is of 2D anisotropic growth. (c) OM image of Pb$_{1-x}$Sn$_x$Se nanoplates with source temperature 600 °C and substrate temperature 460 °C, inset is the photograph of a flexible mica sheet. (d) Magnified SEM images of triangle and square Pb$_{1-x}$Sn$_x$Se nanoplates with source temperature 550 °C and substrate temperature 410 °C. (e) Magnified SEM images of triangle and square Pb$_{1-x}$Sn$_x$Se nanoplates with source temperature 600 °C and substrate temperature 460 °C. The growth time for the products shown in panels c, d, and e is 1 min. (f,g) The growth time increases to 5 and 30 min respectively keeping source temperature 600 °C and substrate temperature 460 °C. (h) AFM image of a Pb$_{1-x}$Sn$_x$Se nanoplate with substrate temperature 410 °C, showing thickness of 81 nm. (i) AFM image of a Pb$_{1-x}$Sn$_x$Se nanoplate with substrate temperature 460 °C, showing thickness of 81 nm. (j) Histogram of Pb$_{1-x}$Sn$_x$Se nanoplates thickness with substrate temperature 410 °C, smooth curve is the Gaussian fit of the thickness distribution.
The mechanism of temperature-modulated domain size and thickness of Pb$_{1-x}$Sn$_x$Se nanoplates is analyzed in the Supporting Information.

In order to investigate the crystal structure, we have performed transmission electron microscopy (TEM) on Pb$_{1-x}$Sn$_x$Se nanoplates. Both the triangle and square nanoplates exhibit smooth surface as displayed by the low-resolution TEM images in Figure 2a,d respectively. High-resolution TEM (HRTEM) images (Figure 2b,e) demonstrate both triangle and square Pb$_{1-x}$Sn$_x$Se nanoplates are well-refined single crystalline. Here the HRTEM images in Figure 2b,e were obtained from the regions labeled by yellow squares in Figure 2a,d respectively. Each of the in situ selected area electron diffractions (SAED) (insets of Figure 2b and e) exhibits a single set of perfect cubic pattern which is in agreement with the cubic symmetry of Pb$_{1-x}$Sn$_x$Se. Therefore, the top and bottom surfaces of the triangle nanoplate can be assigned to (002) and (002) facets that belong to topologically protected surfaces.

One possible explanation is that Pb$_{1-x}$Sn$_x$Se first crystallizes toward [110] direction and forms a rectangle Pb$_{1-x}$Sn$_x$Se nanoribbon (Supporting Information Figure S3a). Then Pb$_{1-x}$Sn$_x$Se nanoribbon grows up along lateral [110] and [110] directions with final exposed equivalent {200} crystal facet.

Figure 2. TEM and Raman characterizations of Pb$_{1-x}$Sn$_x$Se nanoplates. (a,d) Low-resolution TEM images of triangle and square Pb$_{1-x}$Sn$_x$Se nanoplates respectively, yellow square denotes regions where HRTEM images were taken. (b,e) HRTEM images of triangle and square Pb$_{1-x}$Sn$_x$Se nanoplates respectively with corresponding SAED as the insets. (c) TEM-EDX mapping of triangle Pb$_{1-x}$Sn$_x$Se nanoplate from (a). (f) Raman spectra of Pb$_{1-x}$Sn$_x$Se nanoplate with peak of 112 cm$^{-1}$.

Figure 3. Comparison of growth on mica and Si at various temperatures. (a,b) SEM images of Pb$_{1-x}$Sn$_x$Se micronanostructures on mica. (c,d) SEM images of Pb$_{1-x}$Sn$_x$Se micronanostructures on Si. (a,c) The source and substrate temperatures are set to be 550 and 410 °C respectively. (b,d) The source and substrate temperatures are set to be 600 and 460 °C respectively. The growth duration of all experiments are set to be 1 min. (e,f) Schematic illustrations of Pb$_{1-x}$Sn$_x$Se micronanostructures growth process on the surface of mica and Si, respectively.
surfaces (Supporting Information Figure S3b). In most cases, epitaxial growth occurred at the two equivalent lateral surfaces of Pb$_{1-x}$Sn$_x$Se nanoribbon which are (1$\overline{1}$0) and (110) surfaces. Thus, we can see in Figure 1c most nanoplates are square. The lack of bottom corner in square nanoplate (Figure 2d) could be ascribed to an incomplete growth of Pb$_{1-x}$Sn$_x$Se nanoribbon along (110) or (1$\overline{1}$0) direction. This phenomenon can also be observed in some SEM images (Figure 1d,e). As a result, what causes the 2D anisotropic growth of Pb$_{1-x}$Sn$_x$Se nanoplates is that {110} equivalent surfaces have higher growth activation in comparison with other facets. TEM-EDX elemental mapping shows Pb, Sn, and Se distribute evenly in the entire nanoplate without detectable phase separation (Figure 2c). Quantitative analysis of TEM-EDX indicates the elemental ratio of Pb, Sn, and Se is $\sim$0.21:0.79:1.00. Raman spectra (Figure 2f) of a Pb$_{1-x}$Sn$_x$Se nanoplate displays an obvious peak at 112 cm$^{-1}$ that originates from longitudinal optical (LO) phonon mode.31 Above results confirm Pb$_{1-x}$Sn$_x$Se nanoplates obtained in our work are of high quality.

We now discuss the mediation of substrate surface electronic properties on the vapor deposition of Pb$_{1-x}$Sn$_x$Se nanoplates. Nonlayered materials normally have three-dimensional (3D) bonded crystal structures and lack an intrinsic driving force for 2D anisotropic growth. Consequently, 3D nanoarchitectures are often obtained in CVD growth process.22 However, for some nonlayered materials, their anisotropic growth of 2D structure can be activated by modulating growth parameters such as temperature, pressure, and flow rate. As demonstrated in this work, Pb$_{1-x}$Sn$_x$Se is of 2D anisotropic growth due to the high growth activation of {110} surfaces. Thus, after nucleation, Pb$_{1-x}$Sn$_x$Se grows along chemical inert surface of mica sheets without restriction of large lattice mismatch,32,33 also known as van der Waals epitaxial growth. Figure 3a,b exhibits the SEM images of 2D Pb$_{1-x}$Sn$_x$Se nanoplates obtained on mica. The source temperatures are set to 550 and 600°C, respectively, and the substrate temperatures are set to 410 and 460°C, respectively. The advantages of vdWE lie in the following aspects: (1) overlayer is perfectly relaxed without excessive strain in the heterointerface; (2) strict requirement of lattice matching is circumvented (Figure 3e), enabling the growth of defect-free overlayer with different crystalline symmetry to that of substrate and (3) chemically inert mica surface facilitates the migration of adatoms, promoting the lateral growth of 2D Pb$_{1-x}$Sn$_x$Se nanoplates. This growth mode reminds us of the deposition of thin film by Volmer–Weber mode in which the interaction between adatoms and substrate is much weaker than

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Figure 4. Flexible optoelectronic devices based on Pb$_{1-x}$Sn$_x$Se nanoplates on mica sheets. (a) Photograph of 2D Pb$_{1-x}$Sn$_x$Se nanoplates-based device; inset is the OM image of electrodes pattern. (b) $I$–$V$ curves in the dark and in the presence of 375, 473, and 632 nm laser of a single Pb$_{1-x}$Sn$_x$Se nanoplate photodetector; inset is the SEM image of the device. (c) Time-dependent photoresponse of Pb$_{1-x}$Sn$_x$Se nanoplate device at various light intensity with voltage bias of 2 V and laser wavelength of 473 nm. (d) A separated response and reset cycle; inset is the power dependence of photocurrent at 473 nm and 2 V bias. (e,f) Time-dependent photoresponse of Pb$_{1-x}$Sn$_x$Se nanoplate device at 375 and 632 nm, respectively. (g) $I$–$V$ curves in the dark and in the presence of 800 nm laser of another Pb$_{1-x}$Sn$_x$Se nanoplate photodetector, inset is the SEM image of the device. Time-dependent photoresponse of Pb$_{1-x}$Sn$_x$Se nanoplate device with laser wavelength of 800 nm (h) and 980 nm (i). The light power of 800 and 980 nm lasers is set to be 540 mW and 3.06 mW, respectively. The corresponding voltage bias is 2 and 1.5 V, respectively.
that between adjacent adatoms. Irregular Pb$_{1-x}$Sn$_x$Se microcrystals with high density are observed on mica surface at higher growth temperature of 510 °C and source temperature of 650 °C (Supporting Information Figure S4a), which would be resulted from (1) overmuch supply of vapor source at high source temperature and (2) over high migration rate of adatoms at high substrate temperature, both of which cause the fast growth of Pb$_{1-x}$Sn$_x$Se microcrystals along multiple crystal directions and the stacks of products on mica surface. However, 2D Pb$_{1-x}$Sn$_x$Se nanoplates cannot be acquired on the surfaces of 3D bonded Si substrate even if we exerted the same growth conditions as that on mica as shown in Figure 3c,d. Although Pb$_{1-x}$Sn$_x$Se nanoplates are observed on Si substrate at substrate temperature of 410 °C and source temperature of 550 °C (Figure 3c), their structures are vertical instead of planar, making them incompatible with traditional microfabrication technologies. The apparent morphological differences between the products on mica and that on Si originate from the variation of substrate electronic structure. Because of its 3D bonded crystal structure, Si surface accommodates large numbers of unsaturated dangling bonds. Therefore, large lattice mismatch between Si(100) surface and Pb$_{1-x}$Sn$_x$Se (~10.4%) impedes the direct epitaxial growth of Pb$_{1-x}$Sn$_x$Se nanoplates along the substrate surface. Also, strong interaction between substrate and adatoms, caused by dangling bonds on the surface of 3D bonded Si, increases the migration energy barriers of adatoms. The nearly vertical geometry of Pb$_{1-x}$Sn$_x$Se nanoplates dramatically reduces interface area and thus easily relieves strain energy via lateral relaxation. As for the products at higher growth temperature on Si (substrate temperature 460 °C and source temperature 600 °C), they are cubic or irregular microcrystals (Figure 3d). The vertical size of cubic microcrystals is much larger than that of Pb$_{1-x}$Sn$_x$Se nanoplates on mica. Migration barrier energy $E_0$ of adatoms on Si surface is much bigger than that on mica because of the stronger interaction between adatoms and Si substrate. Considering the migration coefficient $D$ is related to migration barrier energy by

$$D \propto e^{-E_0/kT}$$  \hspace{1cm} (1)

where $k$ is the Boltzmann constant and $T$ is the substrate temperature. Consequently, migration coefficient on Si surface ($D_s$) is far lower than that ($D_{mica}$) on mica with the same growth temperature and time. Thus, we can see the stack of cubic Pb$_{1-x}$Sn$_x$Se microcrystals on Si surface but planar Pb$_{1-x}$Sn$_x$Se nanostructure on mica surface. Some Pb$_{1-x}$Sn$_x$Se microcrystals with vertical orientation are also obtained (Figure 3d), which can be explained by the fact that vertical architecture favors strain relaxation due to its small interface area (Figure 3f).

Therefore, by carefully analyzing the vdWE growth of Pb$_{1-x}$Sn$_x$Se nanoplates in this work and Te nanoplates in our previous work,$^2$ we can conclude two conditions for the growth of 2D nonlayered materials by vdWE: (1) the nonlayered materials satisfy 2D anisotropic growth and (2) the growth is implemented on the vdWE substrates. This can be further confirmed by the growth of SnTe nanostructures (Supporting Information Figure S5). Although SnTe displays perfect vdWE growth that regular nanopyrramids array is formed on mica sheets at growth temperature of 510 °C and source temperature of 650 °C, SnTe nanostructures are not planar architecture owing to the 3D isotropic growth.

Benefiting from the flexibility of mica sheets and 2D geometry of Pb$_{1-x}$Sn$_x$Se nanoplates, flexible photodetectors based on Pb$_{1-x}$Sn$_x$Se nanoplates were in situ fabricated on mica sheets by traditional device fabrication techniques as shown in the Supporting Information. Figure 4a is the photograph of flexible photodetector of which the inset signifies the optical microscopy (OM) image of electrodes array. Figure 4b exposes the electrical transport characteristic of single triangle Pb$_{0.21}$Sn$_{0.79}$Se nanoplate-based flexible photodetector on mica sheet. (a) Photograph of instrument used for bending. Time trace of photoresponse before (b) and after (c) bending the device for 100 times.

$\text{Figure 5. Durability measurements of Pb}_{1-x}\text{Sn}_x\text{Se nanoplates-based flexible photodetector on mica sheet. (a) Photograph of instrument used for bending. Time trace of photoresponse before (b) and after (c) bending the device for 100 times.}$

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We further carried out photoresponse experiments of Pb$_{2-x}$Sn$_x$Se nanoplate on near-infrared light (800 and 980 nm). As shown in Figure 4g–i, the device shows reversible and fast response on both 800 and 980 nm infrared light. The light power of 800 and 980 nm near-infrared light is set to 540 and 3.06 mW, respectively. Theoretically, photoresponse range of Pb$_{2-x}$Sn$_x$Se nanoplate can extend to mid-infrared light (<3 μm) due to its narrow bandgap (~0.43 eV). Limited by experimental conditions, we have not executed the corresponding experiments. However, we have investigated the absorption of Pb$_1$Sn$_x$Se nanoparticles array on mica sheet which displays a wide absorption spectra from 250 nm to 2.5 μm (Supporting Information Figure S7), indicating the application potential of Pb$_{1-x}$Sn$_x$Se nanoparticles as mid-infrared detector.

In order to assess the durability of the Pb$_{1-x}$Sn$_x$Se nanoplates-based flexible optoelectronic devices, the device was bent for 100 times with a bending radius of 4 mm as shown in Figure S. Decrease of both dark current and photocurrent are caused by contact barrier due to the relaxation of the electrode contacts (Figure S3c). By improving the device fabrication techniques, the contact stability would be enhanced. Although the photocurrent decreases after bending, the current of device increases sharply once the light is on, suggesting the high durability and sensitivity of the Pb$_{1-x}$Sn$_x$Se nanoplates-based flexible photodetector.

In summary, we have conducted the growth of large-scale ultrathin 2D Pb$_{1-x}$Sn$_x$Se nanoplates with a thickness of ~15–45 nm through vdWE techniques on mica sheets. Together with our previous work about vdWE growth of 2D Te nanoplates, we conclude that vdWE can be universally used to synthesize 2D nanostructures of nonlayered materials on condition that they have the property of 2D anisotropic growth. Developing 2D nanostructures of nonlayered materials will enrich the family of 2D materials and introduce novel electronic and optoelectronic device applications. As demonstrated in this work, 2D Pb$_{1-x}$Sn$_x$Se nanoplates-based flexible photodetectors display fast, reversible, and stable photoresponse with wide spectral range response from UV to infrared light. Further, owing to the similarity of surface chemical properties between mica and other layered materials, it is strongly expected to obtain vertical heterostructures of nonlayered/layered semiconductors by using vdWE such as Pb$_{1-x}$Sn$_x$Se nanoplates/few-layers BN that are promising materials in the fabrication of high-performance electronic and optoelectronic devices.

**ASSOCIATED CONTENT**

**Supporting Information**
Experimental section, SEM, TEM, and AFM images, statistic of Pb$_{1-x}$Sn$_x$Se nanoplates domain size, and photoresponse of square Pb$_{1-x}$Sn$_x$Se nanoplate. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

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