Research Article

Confined van der Waals Epitaxial Growth of Two-Dimensional Large Single-Crystal In$_2$Se$_3$ for Flexible Broadband Photodetectors

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The controllable growth of two-dimensional (2D) semiconductors with large domain sizes and high quality is much needed in order to reduce the detrimental effect of grain boundaries on device performance but has proven to be challenging. Here, we analyze the precursor concentration on the substrate surface which significantly influences nucleation density in a vapor deposition growth process and design a confined micro-reactor to grow 2D In$_2$Se$_3$ with large domain sizes and high quality. The uniqueness of this confined micro-reactor is that its size is $\sim$10$^2$-10$^3$ times smaller than that of a conventional reactor. Such a remarkably small reactor causes a very low precursor concentration on the substrate surface, which reduces nucleation density and leads to the growth of 2D In$_2$Se$_3$ grains with sizes larger than 200 $\mu$m. Our experimental results show large domain sizes of the 2D In$_2$Se$_3$ with high crystallinity. The flexible broadband photodetectors based on the as-grown In$_2$Se$_3$ show rise and decay times of 140 ms and 25 ms, efficient response (5.6 A/W), excellent detectivity ($7\times10^{10}$ Jones), high external quantum efficiency (251%), good flexibility, and high stability. This study, in principle, provides an effective strategy for the controllable growth of high quality 2D materials with few grain boundaries.

1. Introduction

Two-dimensional (2D) materials have been considered promising candidates for miniaturized and high-performance electronic and optoelectronic devices due to their atomically flat and ultrathin nature and their lack of dangling bonds. Grain boundaries and defects in 2D materials can reduce charge transport, [1] mechanical, [2–4] and thermal properties [5]. Therefore, the controllable growth of 2D materials with large domain sizes and high quality with few grain boundaries and defects is important in order to achieve good device performance. To this end, different vapor deposition methods have been developed to grow 2D materials with large domain sizes, such as epitaxial growth on special substrates (e.g., sapphire [6] or mica [7, 8]), reducing nucleation density by locally feeding the precursors [9, 10], and passivating active sites during growth [11]. As summarized in Figure 1(a), the current domain sizes of semi-metallic graphene range from micrometers to meters [9, 12, 13], while semiconducting transition metal dichalcogenides (TMDCs) [14–16] and insulating hexagonal boron nitride (h-BN) have sizes up to hundreds of micrometers or larger [17–19]. Recently, another group of 2D materials with the structure A$_2$B$_3$, where A is a group III element and B is a group VI element, such as indium selenide (In$_2$Se$_3$, its structure is shown in Figure S1), has attracted increasing interest. First, In$_2$Se$_3$ has a direct bandgap of 1.36 eV [20], which is close to that of silicon (1.10 eV). Second, although some monolayer TMDCs like MoTe$_2$ also have a direct bandgap of 1.10 eV, they become indirect bandgap
materials as the number of layers increases [21], while In$_2$Se$_3$ is a direct bandgap material regardless of its thickness [22, 23]. Third, unlike black phosphorus which is also a direct bandgap 2D material, thin In$_2$Se$_3$ flakes are very stable in air, which is very important for practical applications. Recently, there has been pioneering work on the use of 2D In$_2$Se$_3$ in piezoelectronics [24, 25], optoelectronics [26], and photovoltaics [27]. We note that these reported 2D In$_2$Se$_3$ materials have small domain sizes (from a few to tens of micrometers, Figure S2b) [28–30]. Therefore, controllable growth of high quality 2D In$_2$Se$_3$ with large domains is of great importance to further use the growth reactor (Table S2). Based on formula (1), surface nucleation of the 2D materials (Figure S2b). By analyzing the influence the nucleation density, controlling the precursor formation a stagnant layer above the substrate. Due to the fact velocity gradually decreases to zero near the substrate surface, there is a velocity gradient of gas in a reactor, and the too to maintain a constant atmosphere [32]. As shown in Figure S2a, there is a velocity gradient of gas in a reactor, and the velocity gradually decreases to zero near the substrate surface, forming a stagnant layer above the substrate. Due to the fact that the precursor concentration on the substrate surface can influence the nucleation density, controlling the precursor concentration on the surface is important to control the nucleation of the 2D materials (Figure S2b). By analyzing the vapor phase deposition process, we have obtained the following formula for the precursor concentration on the surface: 

\[ C_s \sim \frac{1}{1 + k_s/\sqrt{d}} C_g \]  

(1)

where $C_g$ is the precursor concentration in the gas phase, $k_s$ is the surface reaction rate, and $d$ is the characteristic size of the growth reactor (Table S2). Based on formula (1), $C_s$ decreases as $d$ decreases, causing a lower concentration of precursor on the surface and consequently there is a lower nucleation density of 2D materials in a smaller growth reactor.

Based on the above analyses and previous works [33, 34], we designed a confined micro-reactor to greatly reduce the size of the growth space so as to grow 2D In$_2$Se$_3$ with large domain sizes. Specifically, the micro-reactor is composed of two slices of freshly cleaved mica, stacked face to face. The space (∼20-50 μm) is reduced. Second, the mica, used as a substrate for van der Waals epitaxial growth, benefits the growth of 2D In$_2$Se$_3$ with large domain sizes and thin thickness, because the atomically smooth surface and lack of dangling bonds greatly reduce strain from lattice mismatch between the mica and In$_2$Se$_3$. As a result, in the confined micro-reactor, high-quality In$_2$Se$_3$ with domain sizes larger than 200 μm has been grown on the mica. Moreover, direct growth on flexible mica facilitates the fabrication of flexible photodetectors which have a response time of 140 ms for rise and 25 ms for decay, high responsivity (5.6 A/W), high detection (7×10$^{10}$ Jones), and large external quantum efficiency (EQE, 251%). After bending 1000 times, the photodetector showed a steady photocurrent with an 80% retention, indicating good flexibility.

2. Results

As shown in Figure 1(b), the confined micro-reactor is composed of two slices of freshly cleaved mica, stacked face to face. The space (∼20-50 μm) is reduced. Second, the mica, used as a substrate for van der Waals epitaxial growth, benefits the growth of 2D In$_2$Se$_3$ with large domain sizes and thin thickness, because the atomically smooth surface and lack of dangling bonds greatly reduce strain from lattice mismatch between the mica and In$_2$Se$_3$. As a result, in the confined micro-reactor, high-quality In$_2$Se$_3$ with domain sizes larger than 200 μm has been grown on the mica. Moreover, direct growth on flexible mica facilitates the fabrication of flexible photodetectors which have a response time of 140 ms for rise and 25 ms for decay, high responsivity (5.6 A/W), high detection (7×10$^{10}$ Jones), and large external quantum efficiency (EQE, 251%). After bending 1000 times, the photodetector showed a steady photocurrent with an 80% retention, indicating good flexibility.

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the sample transition, which equals 2 for indirect bandgap materials and 0.5 for direct bandgap materials. \( E_g \) was calculated to be 1.48 eV for \( n = 0.5 \) (Figure 2(f)), which is close to the value reported in previous work (1.36 eV) [20]. In total, all these spectroscopy results indicate that the synthesized materials are uniform In\(_2\)Se\(_3\) with good stoichiometry and optical quality.

We also investigated the structure and crystal quality of the material using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD pattern of the In\(_2\)Se\(_3\) grown on the mica substrate in the confined reactor was compared with the patterns of bulk In\(_2\)Se\(_3\) and mica, and it was found that, except for the peaks from the mica substrate, all peaks originated from In\(_2\)Se\(_3\) (Figure S6). Additionally, the In\(_2\)Se\(_3\) has a high crystallinity because the peaks are very sharp. The TEM samples were prepared using a modified transfer method assisted by polydimethylsiloxane (PDMS) and polymethyl methacrylate (PMMA, see details in the Supporting Information). After repeated trial and error, we developed this method to transfer 2D In\(_2\)Se\(_3\) onto arbitrary substrates such as plastics, SiO\(_2\)/Si, a copper grid, and indium tin oxide (ITO) glass (Figures S7a-d). Raman spectra show that the transferred samples have very similar spectra to the as-grown ones (Figures S7e-i), indicating that negligible damage was done to the samples during transfer. Figure 3(a) shows a high-angle annular dark-field scanning TEM (HAADF-STEM) image of a triangular 2D In\(_2\)Se\(_3\) flake. The corresponding energy dispersive X-ray spectroscopy (EDS) elemental maps show the uniform distributions of In and Se atoms in the In\(_2\)Se\(_3\) (Figures 3(b) and 3(c)). Additionally, quantitative analysis of the EDS results (Figure 3(d)) shows an In:Se atomic ratio of 2:3, in good agreement with the XPS results. Figure 3(e) is an optical image of a In\(_2\)Se\(_3\) flake transferred onto a TEM copper grid. The high-resolution TEM (HRTEM) image confirms that it has high quality, and the lattice spacing of 0.35 nm corresponds to the In\(_2\)Se\(_3\) (100) lattice planes (Figure 3(f)) [40]. Selected area electron diffraction (SAED, Figures 3(g)–3(l)) patterns were recorded from six positions in this flake (marked 1–6 in Figure 3(e)) far away from each other. It can be seen that all the patterns...
have hexagonal symmetry with the same crystallographic orientation, confirming that it is a single crystal domain. All these results confirm that the 2D In$_2$Se$_3$ grown in the confined micro-reactor is high quality and highly crystalline.

Generally, compared to monolayer semiconductors, few-layer ones with direct and appropriate bandgaps are promising candidates for photodetectors due to their enhanced light absorption, lower energy loss during photo-electron conversion, and better carrier transfer between source and drain [41]. TMDCs like MoS$_2$ cannot satisfy all the requirements at the same time because it has an indirect-to-direct bandgap transition when the number of layers decreases from a few layers to a monolayer, so that few-layer MoS$_2$ has a low photo-electron conversion efficiency and monolayer MoS$_2$ has weak light absorption.[39, 42] Hence, for MoS$_2$ and many other TMDCs, a sacrifice of properties is unavoidable to get a balance between light absorption and photo-electron conversion efficiency [43]. Fortunately, In$_2$Se$_3$ is a direct bandgap material regardless of its thickness and shows clear advantages in optoelectronics [22, 23]. Therefore, we fabricated two terminal devices on a flexible mica substrate using 2D In$_2$Se$_3$ with large domain sizes and high quality as the channel material and studied their photoresponse behavior (Figures 4(a) and 4(b)). Several key parameters including dark current ($I_{dark}$), rise time ($t_r$), decay time ($t_d$), responsivity ($R$), detectivity ($D^*$), and EQE were systematically investigated under 660 nm incident light. Figure 4(c) shows that the photocurrent ($I_{ph}$ defined as $I_{ph} = I_{light} - I_{dark}$) increases with the incident light power, and the largest on/off ratio reaches 460. Unlike other narrow bandgap semiconductors, In$_2$Se$_3$ shows a large photo-induced on-off ratio, due to its appropriate bandgap and high quality, i.e., lack of defects. In order to investigate the response speed and stability of the photodetector, time-resolved photoresponse measurements were performed by turning on/off the incident light with a chopper, while a high-speed oscilloscope was used to monitor the device current. As shown in Figure 4(d), the In$_2$Se$_3$ photodetector remains stable under several on/off light switching events (660 nm incident light at $V_{dd} = 1$ V) with a nearly constant “on-state” current of ~25 nA (Figure 4(d)), with $t_r$ and $t_d$ calculated to 140 ms and 25 ms, respectively (Figures 4(e) and 4(f)). We note that the response time is much slower than commercial Si based photodetectors (~5.9 µs). Further engineering and optimization of the quality of materials and interface cleanliness of devices should improve the response time. Note that, after bending 1000 times, the current remains steady with a retention of >80% (with an “on-state” current of ~20 nA, Figure 4(d)). We also shined 850 and 940 nm incident light on the device and it showed good stability (Figures S8a and S8b). It is well known that
most semiconductors are sensitive to visible light, but few show an appropriate responsivity and response speed to NIR light. These results suggest that the In$_2$Se$_3$ is a promising candidate for high-performance photodetectors in the UV-Vis-NIR region. Meanwhile, when we changed the power of the incident 660 nm light ($P_{in}$), different $I_{ph}$ values were obtained (Figure S9). The relationship between $I_{ph}$ and $P_{in}$ is fitted by $I_{ph} = aP^n$. In our experiments, the parameters $a$ and $n$ were calculated to be 0.89 and 0.68, respectively (Figure 4(g)). Moreover, as shown in Figure 4(h), we obtained
a remarkable responsivity of 5.6 A/W (under $P = 10.2 \, \mu W \, \text{cm}^{-2}$, $V_{ds} = 1 \, \text{V}$), which was calculated from the following formula:

$$R = \frac{I_{\text{ph}}}{P_{\text{in}} S}$$  (3)

where $R$ is the responsivity and $S$ is the effective area of the photodetector. This responsivity is $10^3$ times higher than the reported value of multilayer MoS$_2$-based phototransistors (around $7.5 \times 10^{-3}$ A/W), presumably because few-layer MoS$_2$ has an indirect bandgap [37]. In addition, based on the following formula,
where \( D^* \) is detectivity and \( e \) is the charge of an electron, we calculated the detectivity and found an identical trend with responsivity. Impressively, its maximum \( D^* \) reaches \( 7 \times 10^{10} \) Jones (under \( P = 10.2 \mu \text{W cm}^{-2}, V_{ds} = 1 \text{ V} \)) as shown in Figure 4(h), and this value is three orders of magnitude higher than that of MoSe\(_2\) photodetectors [37]. This detectivity is superior to the vast majority of reported 2D material-based phototransistors. Finally, we calculated EQE based on the different light photoresponses (Figure S10), using the following:

\[
\text{EQE} = \frac{Rhc}{\lambda e} \quad (5)
\]

where \( h \) is Planck’s constant, \( c \) the velocity of light, and \( \lambda \) the wavelength of the incident light. The EQE of the In\(_2\)Se\(_3\) photodetector (\( V_{ds} = 1 \text{ V} \)) was calculated to be 1135% at 365 nm, 495% at 445 nm, 127% at 520 nm, 154% at 590 nm, 251% at 660 nm, and 18% at 850 nm. These results suggest that few-layer In\(_2\)Se\(_3\) grown on mica, as a direct bandgap semiconductor, is suitable for use in flexible broadband photodetectors.

A comparison of the performance of photodetectors using our 2D In\(_2\)Se\(_3\) and other 2D materials is shown in Table 1. Overall, the combination of high responsivity, high detectivity, and flexibility makes In\(_2\)Se\(_3\) a promising material for flexible broadband photodetectors. We believe that the large size, high quality, and thin thickness of the In\(_2\)Se\(_3\) can prolong the photo-excited carrier lifetime and result in a high photoresponsivity. In addition, the use of a mica substrate which has an atomically flat surface may reduce trap states at the interface between the In\(_2\)Se\(_3\) and the mica substrate, leading to long photo-excited carrier lifetime. As shown from the formula \( R \propto I_{ph} \propto \Delta \sigma = q(\mu_h + \mu_p)(\Delta p) \exp(-t/\tau) \), it is clear that a longer photo-excited carrier lifetime (\( \tau \)) leads to improved photoconductivity (\( \sigma \)), a larger photocurrent, and better responsivity.

### 3. Discussion

In summary, we designed a confined micro-reactor that greatly reduces the size of the growth space and thus the nucleation density of 2D materials. As a result, we achieved the growth of 2D In\(_2\)Se\(_3\) with large domain sizes and high quality. Because of the large domain size, high quality, and layer-independent direct bandgap, we have been able to fabricate In\(_2\)Se\(_3\)-based flexible photodetectors, which have a fast response speed, and high responsivity, detectivity, and EQE. The strategy used here could potentially shed light on the growth of other 2D materials, facilitating their application in a wide-range of devices.

### 4. Materials and Methods

**Materials and Chemicals.** In\(_2\)Se\(_3\) powder (99.99%, Alfa Aesar, USA), fluorophlogopite mica ([KMg\(_6\)(AlSi\(_3\)O\(_{10}\))F\(_2\)], Tiancheng Fluorphlogopite Mica Co., Ltd., China), polydimethylsiloxane (PDMS) tape (200 μm thickness, Hangzhou Bao Er De New Materials Technology Co., Ltd., China), polymethyl methacrylate (PMMA, 950 K, ALLRESIST, AR-P 672.045, Germany), acetone, and ethanol (AR, Shanghai Macklin Biochemical Co., Ltd., China) were used as received.

**Vapor Phase Growth of 2D In\(_2\)Se\(_3\).** In our experiments, growth was conducted in a homemade atmospheric pressure vapor deposition furnace equipped with a 1-inch diameter quartz tube (TF55035C-1, Lindberg/Blue M). The quartz boat containing In\(_2\)Se\(_3\) powder was put at the center of the furnace, and two slices of freshly cleaved mica were placed downstream (8-10 cm), stacked face-to-face, and served as a confined micro-reactor for 2D In\(_2\)Se\(_3\) growth. The furnace was heated to the growth temperature of 850 °C, which was determined by the thermo-gravimetric analysis (Figure S3), with a ramp rate of 30 °C min\(^{-1}\), and kept there for 5-30 min for the growth. Ar was introduced during the ramping and growth periods at a flow rate of 50-100 standard cubic centimeters per minute (sccm, with a purity of 99.99%). After growth, the furnace was cooled to room temperature under 50 sccm Ar. In the controlled growth experiments, 2D In\(_2\)Se\(_3\) was grown on a freshly cleaved mica substrate placed in the same location but without the other mica sheet.

**Transfer of As-Grown 2D In\(_2\)Se\(_3\) onto a TEM Grid.** The TEM samples were prepared by transferring 2D In\(_2\)Se\(_3\) using a PMMA and PDMS assisted transfer method [44]. First, PMMA solution was spin-coated onto the mica substrate with the grown In\(_2\)Se\(_3\) (3000 rpm for 1 min). Second, the substrate was heated in air at 170 °C for 5 min to form a PMMA film which served as a supporting layer and protected the In\(_2\)Se\(_3\) in the following steps. Third, the PDMS tape was placed on the PMMA and the substrate was heated at 180 °C.
for 5 min to make a strong bond between the PDMS and PMMA. Fourth, the PDMS/PMMA/In$_2$Se$_3$ was peeled off the mica substrate. Due to the hydrophobicity of PMMA and hydrophilicity of the mica, some water was introduced at the PMMA/mica interface to assist the separation of PMMA/In$_2$Se$_3$ and the mica substrate during the peeling-off. Fifth, the PDMS/PMMA/In$_2$Se$_3$ was attached to target substrates, followed by removing the PDMS tape. Finally, the PMMA was removed by hot acetone and the transferred In$_2$Se$_3$ sample was dried naturally in an ambient environment for further characterization.

Characterization of 2D In$_2$Se$_3$. The side view of the space between the two mica sheets was checked by SEM (Hitachi SU8010, Japan). Optical images of the In$_2$Se$_3$ crystal were taken using an optical microscope (Carl Zeiss Microscopy, Germany). The thickness of the In$_2$Se$_3$ was determined by AFM (tapping mode, Bruker Dimension Icon, Germany). Raman spectroscopy was performed under a 532 nm laser excitation (Horiba LabRAB HR800, Japan). The laser spot was 1 mm and the laser power on the sample surface was less than ~100 μW. Structural and chemical analyses of the samples were performed by XRD (Cu Kα radiation, λ = 0.15418 nm, Bruker D8 Advance, Germany), XPS (Thermo Scientific K-Alpha XPS, using Al (Kα) radiation as a probe, USA), and TEM (FEI Tecnai F30, 300 kV acceleration voltage, USA) with an attached EDS unit. UV-Vis-NIR absorption spectra were performed by XRD (Cu Kα radiation, λ = 0.15418 nm, Bruker D8 Advance, Germany), XPS (Thermo Scientific K-Alpha XPS, using Al (Kα) radiation as a probe, USA), and TEM (FEI Tecnai F30, 300 kV acceleration voltage, USA) with an attached EDS unit. UV-Vis-NIR absorption spectra were conducted to study the continuous In$_2$Se$_3$ films (Perkin-Elmer Lambda 950 spectrophotometer, USA).

Device Fabrication and Measurements. The as-grown In$_2$Se$_3$ sample was aligned with a shadow mask and titanium/gold (Ti/Au, 5 nm/50 nm) electrodes were then made by electron beam evaporation. Electrical measurements were conducted under a microprobe station and semiconductor property analyzer (Keithley 4200 SCS, USA) under ambient environment at room temperature. LEDs with different wavelengths ranging from 365 nm to 940 nm were used as incident light during photodetection measurements (CEL-LED535, LED Multiband and High-power Supply, China).

Conflicts of Interest

The authors declare no conflicts of interest.

Authors’ Contributions

Lei Tang and Changjiu Teng contributed equally to this work.

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Supplementary Materials

Figure S1. Crystal structure of layered In$_2$Se$_3$ with each layer composed of Se-In-Se-In-Se atomic sheets. Figure S2. Schematics showing viscous laminar flow in the vapor deposition process and related physical parameters. Figure S3. Thermo-gravimetric analysis of the In$_2$Se$_3$ source in an Ar atmosphere, and the temperature window for the growth of 2D In$_2$Se$_3$ in this work is shown by the green region. Figure S4. AFM images of the as-grown 2D In$_2$Se$_3$ on mica by confined growth. Figure S5. Survey XPS spectrum of as-grown 2D In$_2$Se$_3$ on mica. Figure S6. XRD patterns of 2D In$_2$Se$_3$ grown on mica (red) with reference patterns from a blank mica substrate (blue), bulk In$_2$Se$_3$ (green), and a simulated diffractogram (black). Figure S7. PDMS assisted transfer of 2D In$_2$Se$_3$ from a mica substrate onto different substrates. Figure S8. Time-resolved photoresponse of the 2D In$_2$Se$_3$ photodetector under 850 nm and 940 nm light. Figure S9. I–V curves of the 2D In$_2$Se$_3$ photodetector under 660 nm incident light with different power values. Figure S10. I–V curves of the 2D In$_2$Se$_3$ photodetector under different incident light wavelengths. (Supplementary Materials)

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