Sensitive Electronic-Skin Strain Sensor Array Based on the Patterned Two-Dimensional α-In$_2$Se$_3$

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ABSTRACT: Two-dimensional (2D) layered semiconductors have emerged as a highly attractive class of materials for flexible and wearable strain sensor-centric devices such as electronic-skin (e-skin). This is primarily due to their dimensionality, excellent mechanical flexibility and unique electronic properties. However, the lack of effective and low-cost methods for wafer-scale fabrication of these materials for strain sensor arrays limits their potential for such applications. Here, we report growth of large-scale 2D In$_2$Se$_3$ nanosheets by templated chemical vapor deposition (CVD) method, using In$_2$O$_3$ and Se powders as precursors. The strain sensors fabricated from the as-grown 2D In$_2$Se$_3$ films show two orders of magnitude higher sensitivity (gauge factor ~237 in ~0.39% to 0.39% uniaxial strain range along the device channel length) than what has been demonstrated from conventional metal- (gauge factor: ~1.5) and graphene-based strain sensors (gauge factor: ~2-4) in a similar uniaxial strain range. The integrated strain sensor array, fabricated from the template-grown 2D In$_2$Se$_3$ films, exhibits a high spatial resolution of ~500 μm in strain distribution. Our results demonstrate the applicability and highly attractive properties of 2D layered semiconductors in e-skins for robotics and human body motion monitoring.

INTRODUCTION

Electronic-skins or e-skins are bio-inspired devices, mimicking certain functionalities of human skin and have attracted considerable interest in the past decade. E-skins can be used in wearable health-monitoring devices and in autonomous artificial intelligence systems such as robots. Strain sensors are one of the key elements of e-skins. Indeed, a typical e-skin may require numerous strain sensors integrated onto a flexible substrate. Therefore, developing fabrication techniques for large-area strain sensor arrays is critical for the realization of e-skins. The integrated strain sensors should also have sufficient mechanical flexibility to allow for conformable architectures so that they could be used on arbitrarily curved and moving surfaces such as joints. This would require e-skins to have a high tactile sensitivity, capable of measuring conformable signal distribution with high spatial resolution.

Such a requirement demands materials with high mechanical compliance, good electrical performance and high processability (such as patterning) during device fabrication. Thus far, various nanomaterials such as carbon nanotubes, nanowires and graphene have been exploited to fabricate strain sensors to satisfy these requirements, mostly through composite materials. However, device reliability and batch to batch performance variability remain critical challenges for such devices when one-dimensional (1D) nanomaterials are used. Two-dimensional (2D) materials such as graphene and layered semiconductors do not have such limitations as their dimensionality is compatible with current thin film-based micro-fabrication techniques. Graphene strain sensors fabricated from large area films usually exhibit low sensitivity with small gauge factor (2-4). Two-dimensional layered semiconductors (e.g. MoS$_2$, In$_2$Se$_3$, GaSe and black phosphorus) have a sizeable bandgap and a large stretchability of ~5%-10%, making them attractive for highly sensitive strain sensors. To date, most of the developments have focused on electrical and optical properties, with only a few reports on the observation of their strain-induced changes in electrical properties and mechanical and piezoresistive properties of In$_2$Se$_3$. However, 2D MoS$_2$ or other transition metal dichalcogenides have never been realized for wearable strain sensors, primarily due to the lack of scale-patterned growth and effective device fabrication technique. Thus, it is of great interest to develop a scalable fabrication and integration strategy of 2D layered semiconductor-based strain sensors for wearable applications.

Indium selenide (In$_2$Se$_3$) is a III-ⅥI group layered chalcogenide compound with a direct bandgap of 1.36 eV and attracts strong interest for applications in photovoltaic and optoelectronics devices, phase change memory and ionic batteries. Figure 1a shows the structure of one of the major polymorphs of In$_2$Se$_3$, namely α-In$_2$Se$_3$. It is composed of vertically stacked Se-In-Se-In-Se quintuple layers, held together by weak van der Waals forces. Although 2D In$_2$Se$_3$ nanosheets and thin films have been successfully synthesized on mica by physical vapor transport (PVT) of direct In$_2$Se$_3$ powder evaporation, the mechanical and piezoresistive properties of this n-type semiconductor have not been investigated in detail.

Here, we demonstrate synthesis of 2D In$_2$Se$_3$ nanosheets and patterned In$_2$Se$_3$ thin-films by van der Waals epitaxial (vdW) chemical vapor deposition (CVD) method, using In$_2$O$_3$ and Se powder as the precursors. We fabricate strain sensors from the as-grown 2D In$_2$Se$_3$ films, which show ~2 orders of magnitude higher sensitivity (calculated gauge factor ~237 for ~0.39% to 0.39% uniaxial strain...
along the device channel length) than that of conventional metal strain sensors (gauge factor 1-5 for < 8% strain)\textsuperscript{28} and graphene strain sensors (gauge factor 2-4 for 0.93% strain)\textsuperscript{29} with good stability and repeatable performance. We also demonstrate large area integrated strain sensor arrays based on the patterned In\textsubscript{2}Se\textsubscript{3} thin films. The 0.5 mm × 1.9 mm individual sensors with 0.5 mm spacing exhibit high spatial strain resolution when used as a wearable device. Our results demonstrate a simple, universal growth and device integration approach towards 2D layered semiconductor-based strain sensors.

RESULT AND DISCUSSION

Our strategy for CVD synthesis of 2D In\textsubscript{2}Se\textsubscript{3} nanosheets is schematically illustrated in Figure 1b. The In\textsubscript{2}Se\textsubscript{3} nanosheets are epitaxially grown on mica substrates at 660 °C by CVD using powders of Selenium (Se) and Indium oxide (In\textsubscript{2}O\textsubscript{3}) as precursors and H\textsubscript{2}/Ar mixture as the carrier gas (see experimental section for details in supporting information). A reducing hydrogen atmosphere is essential for the 2D In\textsubscript{2}Se\textsubscript{3} growth, similar to the growth of Se-based TMD materials.\textsuperscript{29} Our CVD synthesis of 2D In\textsubscript{2}Se\textsubscript{3} is different from the methods in previous reports where In\textsubscript{2}Se\textsubscript{3} power was thermally evaporated to grow nanosheets at a higher temperature (850 °C)\textsuperscript{27}.

The as-synthesized 2D In\textsubscript{2}Se\textsubscript{3} nanosheets on transparent mica substrates are first identified by different optical contrast using optical microscopy. Figure 1c shows a typical optical image of discrete, triangular shaped In\textsubscript{2}Se\textsubscript{3} nanosheets on mica substrate with 100 μm lateral dimensions. The identical orientation observed here strongly indicates the nature of van der Waals epitaxy of In\textsubscript{2}Se\textsubscript{3} crystals on the mica substrate. The different optical contrasts for In\textsubscript{2}Se\textsubscript{3} crystals reflect different thickness. The thickness and morphology of the as synthesized atomically thin In\textsubscript{2}Se\textsubscript{3} nanosheets are measured by atomic force microscopy (AFM). Figure 1d-f show three typical AFM images of 2D In\textsubscript{2}Se\textsubscript{3} nanosheets with uniform thicknesses of 0.8, 1.9 and 3.1 nm, corresponding to mono-, bi- and trilayer, respectively. The 2D In\textsubscript{2}Se\textsubscript{3} nanosheets have flat surface, regular shape and sharp edges. The morphology of 2D In\textsubscript{2}Se\textsubscript{3} nanosheets on mica substrates is notably different from that of the irregular In\textsubscript{2}Se\textsubscript{3} nanocrystals that we synthesize on SiO\textsubscript{2} substrate (see Figure S1). We attribute this variation to surface electronic structure of these two substrates (see additional discussions in supporting information and Figure S1).

Figure 2. Characterization of as-grown 2D In\textsubscript{2}Se\textsubscript{3} nanosheets: (a) Raman spectrum. The excitation wavelength is 532 nm. (b) TEM selected area electron diffraction (SAED) pattern. Inset: a low magnification TEM image of a triangle-shaped In\textsubscript{2}Se\textsubscript{3} single crystal. (c) The corresponding HRTEM image. Inset: the associated reverse Fourier transform pattern. (d) EDX spectra.

The crystal structure of the as-grown In\textsubscript{2}Se\textsubscript{3} is characterized by Raman spectroscopy. Note that we observe Raman spectrum only from thicker In\textsubscript{2}Se\textsubscript{3} nanosheets (> 5 nm) as thinner layers are easily damaged, even under low power (~ 1 mW) laser illumination.\textsuperscript{30} Figure 2a shows a typical Raman spectrum of the as-grown In\textsubscript{2}Se\textsubscript{3} nanosheets. The three Raman peaks at ~108, ~180 and ~203 cm\textsuperscript{-1} observed here are attributed to A\textsubscript{1g}, (LO+TO), A\textsubscript{1g} (TO) and A\textsubscript{1g} (LO) phonon mode in α-In\textsubscript{2}Se\textsubscript{3}, respectively.\textsuperscript{31,32} These Raman features unequivocally identify the as-grown In\textsubscript{2}Se\textsubscript{3} nanosheets to be the α polymorph. X-ray photoelectron spectroscopy (XPS) is next used to determine the elemental composition and bonding types of the as-grown nanosheets (Figure S2). The full scale XPS spectrum (Figure S2a) confirms that all spectral features are originated from a pure phase In\textsubscript{2}Se\textsubscript{3}. The In 3d\textsubscript{5} and Se 3d\textsubscript{5} doublets can be well-approximated by a combination of individual components that confirm the chemical bonds of In-Se in the In\textsubscript{2}Se\textsubscript{3} films. The stoichiometric ratio of In and Se estimated by XPS analysis is 2:3. The microstructure and chemical composition of the 2D In\textsubscript{2}Se\textsubscript{3} nanosheets are further characterized by transmission electron microscopy (TEM), selective area electron diffraction (SAED) and energy dispersive spectroscopy (EDX). Figure 2b inset shows a typical low magnification TEM image of a In\textsubscript{2}Se\textsubscript{3} nanosheet. The SAED pattern (Figure 2b) shows a 6-fold symmetry, indicating an orientation along the <00\textsubscript{1}> zone axis and a good crystalline

![Figure 1. Synthesis of 2D In\textsubscript{2}Se\textsubscript{3}: (a) Crystal structure of α-In\textsubscript{2}Se\textsubscript{3}. (b) Schematic illustration of the CVD growth process of 2D In\textsubscript{2}Se\textsubscript{3} on to mica substrates. (c) Optical microscope image of as-grown triangular In\textsubscript{2}Se\textsubscript{3} nanosheets on mica substrate. (d)-(f) AFM image and corresponding height profile of In\textsubscript{2}Se\textsubscript{3} nanosheets with ~1-3 nm thickness.](image-url)
quality. A typical high-resolution TEM (HRTEM) image shown in Figure 2c confirms an ideal hexagonal lattice structure with a lattice spacing of 0.35 nm, corresponding to the lattice constant of \( (100) \) lattice plane of \( \alpha-In_{2}Se_{3} \). The stoichiometric ratios of In and Se is estimated to be 2:3 by EDX analysis (Figure 2d) and is consistent with the XPS measurements. These measurements confirm successful synthesis of single-crystalline \( \alpha-In_{2}Se_{3} \) nanosheets.

Direct growth of patterned crystals is an important step towards large scale fabrication and efficient integration of as-grown 2D \( In_{2}Se_{3} \) for practical applications in electronics and optoelectronics. We achieve this by selectively modifying the surface of the mica substrates. Figure 3a shows a schematic illustration of the patterned growth process. The mica substrates are patterned by area-selective oxygen plasma etching using 100 nm thermally evaporated Cu as the mask. In addition to the change in surface properties, the rms surface roughness of the mica substrate is increased from ~0.17 nm to 0.57 nm due to oxygen plasma treatment; Figure S4. The 2D \( In_{2}Se_{3} \) films nucleate and epitaxially grow on the untreated region of the substrate rather than on the oxygen plasma treated area. Using this approach, thin film \( In_{2}Se_{3} \) crystals with various patterns including microscale strip array, rectangular array and circle array can be achieved on the surface modified mica substrates (Figure 3b-d). These patterned \( In_{2}Se_{3} \) films have a larger thickness (7.5–15 nm) due to longer growth time to achieve continuous \( In_{2}Se_{3} \) films. A representative AFM image (Figure 3b inset) confirms this, showing ~8.2 nm thickness of a patterned \( In_{2}Se_{3} \) thin-film.

![Figure 3](image)

To reveal the electronic properties of as-grown \( In_{2}Se_{3} \), field effect transistors (FETs) are fabricated with a back-gated configuration; Figure S3. All measurements are performed under ambient environment. The 2D \( In_{2}Se_{3} \) FETs exhibit a typical n-type semiconductor behavior as the current increases with the applied gate voltage sweeping from negative to positive values (the transfer curves shown in Figure S3a). The field effect mobility of the 2D \( In_{2}Se_{3} \) FETs is calculated to be \( 1.1 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1} \) in ambient environment. This is similar to other 2D III-VI layered semiconductors (e.g. GaSe, GaS and InSe) observed in similar device configurations. The current ON/OFF ratio is \( \sim 10^{3} \) as shown in the logarithmic transfer curve in Figure S3a. The transfer curves also show an obvious hysteresis phenomenon. This is attributed to the surface charges trapped between \( In_{2}Se_{3} \) and SiO\(_2\) substrate.

Piezoresistive effect is the change in resistivity of a material under mechanical deformation and forms the foundation of the majority of the strain sensors. To investigate the piezoresistive effect of our 2D \( In_{2}Se_{3} \) films, we fabricate strain sensors on flexible polyethylene terephthalate (PET) substrates. The \( In_{2}Se_{3} \) thin films are transferred onto PET by Poly(methylmethacrylate) (PMMA)-assisted transfer method, similar to what is used for the transfer of other layered crystals. After the transfer, the PMMA is dissolved in acetone, leaving \( In_{2}Se_{3} \) crystals on PET. Au electrodes for the devices are next fabricated by thermal evaporation. Conductive copper (100 µm) wires are then bonded onto the Au electrodes. We use polydimethyldisiloxane (PDMS) to protect the devices. A typical optical image of a strain sensor (Figure 4a) shows that the device is mechanically robust and bendable. The inset in Figure 4a shows an optical microscope image of a sensor. The channel length and width are 0.5 mm and 1.9 mm, respectively. By radially bending outward (inward), we subject the sensor under uniaxial tensile (compressive) stress along the device channel length. This applied uniaxial tensile strain is determined by the relation \( \varepsilon = \tau/2R \), where \( R - \tau/2 \) is the radius of the curvature during bending tests (0.75 cm for compressive stress, 0.75 cm for tensile stress and \( \tau = 160 \text{ µm} \) is the thickness of the PET substrate (Figure 5)). The current-voltage (I-V) characteristics of the individual strain sensor are measured in sync with the bending of the flexible PET substrate under different tensile and compressive modes (Figure 4b). The current increases and decreases symmetrically under the operation of uniaxial tensile and compressive strains. To evaluate the performance of the strain sensors, the normalized change in current is calculated using the equation: \( \Delta I = (I - I_{0})/I_{0} \), where \( I \) and \( I_{0} \) are the currents under stress/strain (bent) and no strain (relaxed), respectively. The normalized increase in current is 120.6% at 0.39% uniaxial tensile strain. This is further increased to 184.5% at 1.06% uniaxial tensile strain; Gauge factor (a characteristic parameter representing sensitivity of strain sensors) can be derived from the relation \( \Delta I/I_{0} \). The calculated gauge factor for our strain sensor is 237 in the region I and 92 in region II (Figure 4c), indicating high sensitivity. This gauge factor is comparable to that of state-of-the-art silicon strain sensors (200), and much higher than those of conventional metal foil (1-5) and graphene (2-4) strain sensors. To evaluate the mechanical stability of the strain sensor, we apply multiple bending cycles (120 cycles) under 0.39% uniaxial tensile strain along the device channel. The normalized change in current is shown in Figure 4d. A stable response across the bending cycles is observed, indicating mechanical robustness and good stability for our strain sensors. The high performance of the \( In_{2}Se_{3} \) strain sensors could be exploited as flexible devices for real-time human motion monitoring and robotic applications. We therefore fabricate a sensor array to demonstrate the applicability of our 2D \( In_{2}Se_{3} \) in e-skin devices.
The location of each device on the finger joint is determined by its coordinate number as shown in the model shown in Figure 5c. Each device responds to the stimuli applied over a small area of ~0.95 mm². The e-skin displays sensitive response to the strain varieties at different area over the curved surface of the finger joint during its movement (Figure 5c). Indeed, the five devices along the middle of the array (marked by A, B, C, D and E in Figure 5c) confirm this spatial sensing. The spatial sensing ($\Delta I/I_0 \sim 18\%$ for A, $\sim 82\%$ for B, $\sim 122\%$ for C, $\sim 79\%$ for D and $\sim 23\%$ for E) is achieved at a small spacing of 0.5 mm along this line (Figure 5d and Figure S6). Note that devices A and E experience the least bending while C experiences the most. Thus, they represent the minimum and maximum $\Delta I/I_0$, respectively. The data from the bending measurements is collected by monitoring the change in current on a reconstructed contour map; Figure 5e. Our strain sensor array exhibits excellent spatial strain resolution, indicating their promising applications as high-performance e-skin in wearable intelligent devices.

To satisfy with the requirements of wearable intelligent systems and wearable/healthcare applications, the strain sensors must be integrated on to a flexible platform. The integrated 2D In$_2$Se$_3$ strain sensor array is fabricated from the patterning 2D In$_2$Se$_3$ thin film using a simple and low-cost mask process. The schematic of this process is presented in Figure 5a. A typical e-skin sensor array we fabricate contains $5 \times 5$ devices on PET and is protected by PDMS (Figure 5b); To test the functionality of the array on to conformal surfaces, the $5 \times 5$ strain sensor array chip is attached to the back of a mid-finger joint (Figure 5c). The location of each device on the finger joint is determined by its coordinate number as shown in the model shown in Figure 5c. Each device responds to the stimuli applied over a small area of ~0.95 mm². The e-skin displays sensitive response to the strain varieties at different area over the curved surface of the finger joint during its movement (Figure 5c). Indeed, the five devices along the middle of the array (marked by A, B, C, D and E in Figure 5c) confirm this spatial sensing. The spatial sensing ($\Delta I/I_0 \sim 18\%$ for A, $\sim 82\%$ for B, $\sim 122\%$ for C, $\sim 79\%$ for D and $\sim 23\%$ for E) is achieved at a small spacing of 0.5 mm along this line (Figure 5d and Figure S6). Note that devices A and E experience the least bending while C experiences the most. Thus, they represent the minimum and maximum $\Delta I/I_0$, respectively. The data from the bending measurements is collected by monitoring the change in current on a reconstructed contour map; Figure 5e. Our strain sensor array exhibits excellent spatial strain resolution, indicating their promising applications as high-performance e-skin in wearable intelligent devices.

To evaluate the potential for 2D In$_2$Se$_3$ strain sensor for human-motion detection, the strain sensor is attached on to elbow and wrist joints as a wearable electronic device; Figure 4e-f. For each bending-stretching motion of the elbow and wrist, the strain sensor shows a rapid, stable and repeatable response. The results are attributed to the change in resistance in In$_2$Se$_3$ under a relaxed and uniaxial tensile stress along the channel length. We note that the strain sensor easily picks up slight wrist motions with $\Delta I/I_0 \geq 90\%$. Thus these devices are attractive candidates to wearable and human-machine interface applications.

**CONCLUSIONS**

In conclusion, we have demonstrated a highly sensitive, conformal e-skin fabricated using a 2D In$_2$Se$_3$ strain sensor array. Continuous and patterned 2D In$_2$Se$_3$ films are synthesized by a van der Waals epitaxy CVD method. We measure two orders of magnitude higher gauge factor in 2D In$_2$Se$_3$ compared to those of metal and graphene. The flexible and wearable strain sensors show an excellent sensitivity, good stability and repeatable behavior in response to wrist and elbow joint movements. Further, e-skin based on the sensor arrays fabricated from patterned
2D In$_2$Se$_3$ exhibit high spatial resolution on conformal surfaces, underscoring its potential in high sensitivity strain sensing in wearable applications.

ASSOCIATED CONTENT

Supporting information: Experimental section, synthesis of In$_2$Se$_3$ on SiO$_2$ substrate, XPS characterization of as-grown In$_2$Se$_3$, electronic properties of the In$_2$Se$_3$ FETs, AFM topographic images of mica, schematic of the two-point bending test and calculation of strain and I-V curves measured from the corresponding E device in Figure 5c. The supporting information is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions
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Notes
The authors declare no competing financial interest.

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