Mixed-dimensional (0D, 1D, and 3D) heterostructures based on 2D layered materials have been proven as a promising candidate for future nanoelectronics and optoelectronics applications. In this work, it is demonstrated that 1D atomic chain based Se nanoplates (NPs) can be epitaxially grown on monolayer ReS$_2$ by a chemical transport reaction, thereby creating an interesting mixed-dimensional Se/ReS$_2$ heterostructure. A unique epitaxial relationship is observed with the (110) planes of the Se NPs parallel to the corresponding ReS$_2$ (010) planes. Experimental and theoretical studies reveal that the Se NPs could conjugate with underlying monolayer ReS$_2$ via strong chemical hybridization at heterointerface, which is expected to originate from the intrinsic defects of ReS$_2$. Remarkably, photodetectors based on Se/ReS$_2$ heterostructures exhibit ultrahigh detectivity of up to $8 \times 10^{12}$ Jones, and also show a fast response time of less than 10 ms. These results illustrate the great advantage of directly integrated 1D Se based nanostructure on planar semiconducting ReS$_2$ films for optoelectronic applications. It opens up a feasible way to obtain mixed-dimensional heterostructures with atomic interfacial contact by epitaxial growth.

1. Introduction

Recently, 2D + nD ($n = 0, 1, \text{and} 3$) mixed-dimensional heterostructures have been intensively investigated for their potential applications in modern nanoelectronics and optoelectronics.$^{[1-9]}$ Most of these heterostructures are formed by a top-down approach with a polymethyl methacrylate (PMMA)-assisted transfer process,$^{[10,11]}$ which makes it possible to integrate a variety of materials with different functionalities. However, the manual transfer technique provides too much indeterminacy to control the stacking orientation and contact quality between materials. On the other hand, the bottom-up approach, that is, direct epitaxial growth by a chemical vapor deposition (CVD) process, provides a powerful approach to fabricate heterostructures with particular stacking modes. A variety of hybrid structures have already been constructed using this strategy, including MoS$_2$/WS$_2$, MoSe$_2$/graphene, MoS$_2$/SnS$_2$, and CdS/MoS$_2$.$^{[8,12-14]}$ However, it remains a challenge to control the interfacial quality, since the dissimilar materials in such heterostructure are stacked together by van der Waals (vdW) interaction without covalent bonding. The vdW gap could still significantly deteriorate the charge transfer efficiency and affect the physical properties of the heterostructure.$^{[15-18]}$

Most of the components in the reported mixed-dimensional heterostructures are layered materials with the same planar crystal structures. However, 1D van der Waals elemental materials Se and Te could also exhibit interesting physical properties such as high photoconductivity, high piezoelectricity, thermoelectricity, and nonlinear optical responses.$^{[19-24]}$ In trigonal Se, the Se atoms are covalently bonded along the c axis into a spiral chain, and these isolated chains could be stacked radially by weak van der Waals interactions to form a hexagonal structure. The direct growth of such 1D van der Waals materials on 2D layers is unexplored and these heterostructures could also be of great interest for applications. However, lattice mismatch creates huge challenges to directly integrate 1D Se/Te into other planar 2D materials. Different from commonly studied group II–IV transition metal dichalcogenides (TMDs) with triangular prismatic crystal structures (such as MoS$_2$ and WSe$_2$), the ReS$_2$ lattice is highly asymmetric due to Peierls distortion. The unique 1T’ structure introduces many distinct binding sites for atom absorption on the ReS$_2$ surface, resulting in the spontaneous growth in vertical mode.$^{[25-27]}$ Inspired by this fact, we postulate that these sites with high chemical activity could facilitate the subsequent heterogeneous growth by covalent bonding. Thus, we could design and prepare ReS$_2$-based intimate heterostructures with ideal interfacial quality.
In this work, we demonstrate that 1D van der Waals Se formed as nanoplates (NPs) can directly grow on monolayer ReS2, thereby creating an interesting mixed-dimensional Se/ReS2 heterostructure. This heterogeneous growth exhibits an epitaxial relationship with the (110) planes of the Se lattice parallel to the (010) planes of ReS2. Detailed atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) characteristics reveal an atomically close contact between Se and ReS2 with covalent bonding, which is further confirmed by density functional theory (DFT) calculations. Photodetectors based on the Se/ReS2 heterostructure present ultrahigh detectivity of $8 \times 10^{12}$ Jones and a fast response time of less than 10 ms, significantly superior to the performance of photodetectors based on other analogue hybrid structures. This work provides us a new angle to design and prepare mixed-dimensional heterostructures based on 2D materials, and it also opens up a useful platform of novel nanomaterials systems for nanoscale electronics and optoelectronics applications.

2. Results and Discussion

Figure 1a shows a schematic illustration of the epitaxially grown Se/ReS2 heterostructures, which are prepared by a two-step vapor deposition process as illustrated in Figure S1 (Supporting Information). In the first stage, ReS2 monolayers are synthesized on a freshly cleaved fluorophlogopite mica substrate by CVD in a tube furnace, where ReO3 powders react with sulfur vapor at a high temperature of 600 °C for 10 min. The subsequent Se/ReS2 heterogeneous growth was conducted using vacuum vapor deposition at 275 °C. The mica substrate coated with ReS2 monolayers is placed at the end of a quartz ampoule with Se powder in the center, and it is then placed in a furnace and vacuum pumped until the pressure is less than 10⁻⁴ Torr. After 30 min of reaction, trigonal Se NPs are observed on the monolayer ReS2 surface (Figure 1b).

The Se/ReS2 heterostructures were characterized by scanning electron microscopy (SEM) as shown in Figure 1c and Figure S2 (Supporting Information). Most of the Se NPs exhibit triangular or hexagonal shapes with lateral lengths ranging from 100 to 800 nm, significantly superior to the performance of photodetectors based on other analogue hybrid structures. This work provides us a new angle to design and prepare mixed-dimensional heterostructures based on 2D materials, and it also opens up a useful platform of novel nanomaterials systems for nanoscale electronics and optoelectronics applications.
noted that these triangular-shaped ReS$_2$ monolayers are expected to grow with the Re chains’ [010] direction parallel with the edge (Figure 2d), which is confirmed by high-resolution transmission electron microscopy (HRTEM) discussed later. Thus, it would be straightforward to determine the crystalline direction of the Se NPs by comparing them to the edge of the ReS$_2$ flakes (Figure 2b,e). The statistics chart reveals that the Se NPs have a tendency to grow with the triangle sides parallel to the [010] direction of ReS$_2$ (Figure 1e,f).

We transferred these Se/ReS$_2$ heterostructures onto Cu grids and performed transmission electron microscopy (TEM) to further identify the morphology and epitaxy relationship of the heterostructures. Triangular or hexagonal Se NPs can be clearly seen as shown in Figure 3a,b. High-angle annular dark field scanning-transmission electron microscope (STEM) (HAADF-STEM) was performed on a pure ReS$_2$ monolayer area (Figure 3c). Distinct Re–Re DS-chains could be observed, and the fringe space of [010] lattice planes was measured to be 3.4 Å, well in agreement with the optimized ReS$_2$ lattice constant. The STEM image obtained of Se NPs reveals a perfect hexagonal crystal structure, which indicates that the Se NPs are grown with the [001] axis vertically aligned with underlying ReS$_2$ (Figure 3d). To further identify the exact epitaxy relationship, selected area electron diffraction (SAED) patterns were also extracted (Figure 3e). Two sets of sixfold symmetric diffraction spots could be clearly identified, where the brighter and outer set corresponds to the Se NPs while the weaker one belongs to the monolayer ReS$_2$. By comparing the SAED pattern with the morphology, we can conclude that the Se NPs are epitaxially grown with the (110) plane parallel to the (010) plane of ReS$_2$ (Figure 3f).

The quality of interface contact is another important issue that must be addressed. It is necessary to determine the contact mode of Se/ReS$_2$ heterostructure, since high-quality contact would better facilitate charge transfer and separation at interface.\textsuperscript{[29,30]} As shown in Figure 4a, the Se NPs were scratched away using AFM, and the contact quality could be directly evaluated by the ratio of lift-off area to the underlying ReS$_2$. Figure 4b,c shows typical SEM images of the Se/ReS$_2$ heterostructure before and after the Se NPs are scratched away. We can see that the underlying ReS$_2$ was completely lifted off, exposing the bare mica substrate with the triangular shape. The corresponding AFM height profile was presented in Figure 4d. The pit depth is about 1.0 nm, almost the same as the thickness of monolayer ReS$_2$, and no ReS$_2$ residues could be detected in the exposed area. The EDX elemental maps of the scratched Se NPs are presented in Figure S6 (Supporting Information), where Re and S could be distinctly detected on the bottom of Se NPs. The results indicate that the monolayer ReS$_2$ is conjoined tightly with above Se NPs by the whole contact area with high interface quality.

The Se/ReS$_2$ heterostructure is characterized by Raman spectroscopy with a 532 nm laser at room temperature (Figure 4e,f). The peak located at $\approx$233 cm$^{-1}$ can be distinctly detected, which belongs to the E$^2$ mode of trigonal Se.\textsuperscript{[20,31]} All peaks related to ReS$_2$ exhibit a clear blue shift, with a maximum difference of up to 3.3 cm$^{-1}$ for the III peak of ReS$_2$ (238 cm$^{-1}$). In order to evaluate the influence of the hetero-interface on the Raman shift in ReS$_2$, we have constructed a Se NB-ReS$_2$ heterostructure by PMMA-assisted transfer technique (Figure S7, Supporting Information), where the Se NBS and underlying ReS$_2$ are expected to contact with each other by van der Waals interaction without chemical hybridization. Remarkably, in such kind of hybrid structure, the Raman peaks belonging to ReS$_2$ do not show any change compared with pure ReS$_2$.
The reduction of electron density in ReS$_2$ would result in the efficient charge transfer at the chemically hybridized Se NPs, further confirming the existence of the Se-Re covalent bonds and interface acts as a fast transmission path for charge transfer. \cite{7} Porting Information). Remarkably, the binding energy of Se 3d levels in band alignment, \cite{32,33} and the Se-Re covalent bond at the interface. In the Se NP-ReS$_2$ heterostructure, electrons in monolayer ReS$_2$, indicating that the shift of Raman peaks in ReS$_2$ is mainly determined by the chemically hybridized Se NPs at the interface. In the Se NP-ReS$_2$ heterostructure, electrons in ReS$_2$ tend to transfer from Se due to the difference of Fermi levels in band alignment,\cite{32,33} and the Se-Re covalent bond at interface acts as a fast transmission path for charge transfer.\cite{7} The reduction of electron density in ReS$_2$ would result in the weakening of the electron-phonon coupling effect and explains the observed Raman peak shift.\cite{34} XPS was also performed to evaluate the doping effect of Se NPs on monolayer ReS$_2$, we fabricated field effect transistors through a standard electron beam lithography (EBL) process (Figure S11, Supporting Information). Compared with pure monolayer ReS$_2$ devices, the hybrid devices exhibit a smaller on/off ratio ($\approx$10$^4$), and the on-state current is reduced by one order of magnitude at the same source current (Figure S12, Supporting Information). The field-effect mobility ($\mu$) can be extracted from the transfer curves using $\mu = L_{in}/W \times (1/C_{bg}) \times d/dV_{bg}$, where $L_{in}$ and $W$ represent the channel length and width, respectively, and $C_{bg}$ is the capacitance of SiO$_2$. The value is expected to be 22 cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K for a monolayer ReS$_2$ device. After Se epitaxy growth, the mobility is reduced significantly to 0.17 cm$^2$ V$^{-1}$ s$^{-1}$ mainly due to the reduction of the drain current induced by the p-type Se NPs. In order to better understand the change in transport behavior, we have used DFT calculations to obtain the electronic band structure of the Se/ReS$_2$ hybrid system. As shown in Figure 5f,g after Se growth, some deep-impurity levels are introduced around the Fermi level, which would lead to the accumulation of electrons at negative back gate voltages and a high level of off-state current.\cite{41} On the other hand, the p-type Se NPs could also act as electron acceptors and reduce the carrier density in underlying ReS$_2$. Thus, the on-state current could be greatly suppressed, resulting in the low on-off ratio observed in the Se/ReS$_2$ hybrid devices.\cite{42}

We have systematically investigated the optoelectronic properties of Se/ReS$_2$ based photodetectors. A device schematic is illustrated in Figure 6a. Figure 6b shows typical output characteristics ($I_{ds} - V_d$) of hybrid devices under different laser illumination conditions ($\lambda = 322, 370, 417, 532$, and $633$ nm), where the incident power was fixed at 0.24 mW cm$^{-2}$. The photocurrent rises gradually with the decrease of laser wavelength,
which can be attributed to the increasing photogenerated electron-hole pairs by higher photon energies.\(^4\) As an important figure-of-merit for photodetector, the dark current of Se/ReS\(_2\) hybrid device was measured to be less than 10 pA at \(V_\text{g} = -30\) V (Figure 6c), much lower than that in monolayer ReS\(_2\) devices (\(\approx 5\) nA). Two important parameters for photodetectors, photoresponsivity \((R_\lambda)\) and detectivity \((D^*)\), are defined as

\[
R_\lambda = \frac{I_\text{ph}}{P} \quad (1)
\]

\[
D^* = \frac{RS^{1/2}}{(2qI_d)^{1/2}} \quad (2)
\]

where \(I_\text{ph}\), \(I_\text{d}\), \(P\), and \(S\) represent the photocurrent, dark current, incident power, and effective illuminated area, respectively.

The maximum \(R_\lambda\) was estimated to be 36 A W\(^{-1}\) with a 0.03 mW cm\(^{-2}\) incident power density \((V_\text{ds} = 3\) V and \(V_\text{g} = 0\) V). This value is comparable with previously reported photodetectors based on mixed-dimensional heterostructures such as CdS-MoS\(_2\) and WS\(_2\)/CH\(_3\)NH\(_2\)PbI\(_3\).\(^{[5,8,42-45]}\) Under illumination, most of the photoexcited electrons in ReS\(_2\) are trapped in the conduction band due to a high energy barrier (Figure S13, Supporting Information), which is introduced by the difference in conduction levels. At the same time, photogenerated electrons in Se NPs could quickly transfer to underlying ReS\(_2\), whereas holes are confined in the Se NPs. Both the interstructure absorption in ReS\(_2\) and carrier transfer from Se could contribute to the channel current under illumination, leading to the enhancement of responsivity in the Se-ReS\(_2\).
Figure 6. Optoelectronic properties of the Se/ReS\(_2\) heterostructure phototransistor. a) Schematic diagram of a back-gated Se/ReS\(_2\) photodetector. b) Output curves of the device under different illumination wavelengths. Inset shows an optical microscope image of the device, scale bar is 5 µm. c) Transfer curves of the device measured under 370 nm illumination at different power densities at \(V_\text{g} = 0\) V. d) Typical rise or decay characteristics of the photocurrent with the laser illumination switched on or off under illumination with different laser power. e) A separated response and reset cycle of the device.

heterostructure. Owing to the suppressed dark current and increased responsivity, detectivity \(D^*\) of the hybrid devices could reach up to \(8 \times 10^{12}\) Jones under the same measurement condition, which is almost 3 orders of magnitude larger than that of the monolayer ReS\(_2\) device, and is even superior to that of commercial Si based devices.\(^{[46]}\) Both the \(R_0\) and \(D^*\) decrease linearly with the incident power, indicating the photoresponse of the hybrid device is mainly determined by the photocarriers.\(^{[5]}\) A comparison of the critical parameters between Se/ReS\(_2\) hybrid photodetectors and other analogue hybrid photodetectors is given in the Table 1.

Fast response speed is another key factor for high-performance photodetectors, which determines the capability of devices to follow a fast-switching optical signal. Figure 6e shows the comparison of one ON/OFF switching cycle of a Se-ReS\(_2\) device under different incident power densities. The drain current quickly increases up to saturation once the laser is turned on, and it quickly recovers back to original level as the laser is turned off. Both the rise and decay times are less than 10 ms, which is the limit of our measurement set-up (Figure 6f). In contrast, the response speed of ReS\(_2\) photodetectors is much slower, up to 5 s. The optoelectronic performance of the devices based on the Se nanobelt-ReS\(_2\) heterostructure was also investigated for comparison. Remarkably, the photoresponse and response speed do not show much difference if no chemical bonding exists at the Se-ReS\(_2\) interface (Figure S14, Supporting Information). These results indicate that the sensitive photoresponse of Se-ReS\(_2\) heterostructure is determined by the chemical hybridization at the material interface.

As mentioned before, the distorted 1T' structure of ReS\(_2\) introduces many intrinsic defects, resulting in significant carrier scattering and slow photocarrier response. In this way, the recombination process of photogenerated electron-hole pairs could be inhibited, resulting in slow response speed.\(^{[5,27]}\) In Se-ReS\(_2\) heterostructures, the chemically bonded Se atoms could passivate the defects, and the chemical hybridization at the interface can provide a fast transmission path for photocarrier separation and transfer between Se and ReS\(_2\).\(^{[7]}\) Besides,
the Se nanocrystals could also act as a recombination center for these photogenerated electron-hole pairs, resulting in reduced composite time once the light is turned off.[8]

3. Conclusion

In conclusion, a new mixed-dimensional heterostructure based on nonlayered Se NPs atop ReS$_2$ monolayers was achieved using a two-step vapor deposition method. The Se NPs are covalently bonded with the ReS$_2$ monolayer, exhibiting an epitaxy relationship with the Se (110) plane parallel to the corresponding ReS$_2$ (010) plane, which was confirmed by XPS, Raman, TEM, and DFT calculations. Owing to the chemical hybridization at the interface, the hybrid Se-ReS$_2$ photodetectors exhibit a fast response time of less than 10 ms, and detection sensitivity enhanced by almost three orders of magnitude up to $10^{12}$ Jones compared with the monolayer ReS$_2$ counterpart devices. Overall, our results demonstrated a promising optoelectronic device built on a Se-ReS$_2$ mixed-dimensional heterostructure, enabling superior device performance beyond traditional TMD-based photodetectors.

4. Experimental Section

Growth of ReS$_2$ Monolayer: Monolayer ReS$_2$ was grown by a CVD method in a two-zone furnace. Sulfur powder was placed in the low-temperature zone, which was heated to 200 °C at a ramping rate of 5 °C min$^{-1}$ and maintained for 10 min. 20 mg ReO$_3$ powder (Alfa Aesar, purity: 99.99%) was placed in a ceramic boat in the high-temperature zone with freshly cleaved fluorophlogopite mica above it. The high-temperature zone was heated to 600 °C with a 15 °C min$^{-1}$ ramping rate and maintained for 10 min. Argon with 40 sccm was used as the carrier gas to convey vapor species downstream to the mica substrate.

Raman and STEM Measurements: The synthesized samples were characterized using a HORIBA LabRAM HR800 Raman spectrometer. The system is equipped with a 532 nm wavelength He-Ne excitation laser. Before measurement, the system was calibrated with the Raman peak of Si at 521 cm$^{-1}$. HAADF-STEM was performed with an FEI Talos F200X with an acceleration voltage of 200 kV.

Device Fabrication and Characterization: The samples were transferred onto 90 nm SiO$_2$/Si substrates using PMMA-assisted method. EBL was used to pattern electrodes, followed by electron beam evaporation of 30 nm Ti and 100 nm Au as metal contacts. The channel length $L_p$ was designed to be 5 μm while the channel width $W_{ch}$ is 8 μm. The device was measured with a probe station connected to a semiconductor characterization system (4200SCS, Keithley) at room temperature. For photodetection, a laser source (Perot Benchtop) calibrated by a characterization system (4200SCS, Keithley) at room temperature. The system is equipped with a 533 nm wavelength He-Ne excitation laser. Before measurement, the system was calibrated with the Raman peak of Si at 521 cm$^{-1}$. HAADF-STEM was performed with an FEI Talos F200X with an acceleration voltage of 200 kV.

DFT Calculation: DFT calculations were performed with projector augmented-wave pseudopotentials using the Vienna Ab initio Simulation Package. For all DFT calculations, the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional was used. Van der Waals interactions were included using density functional methods optB88. In ionic relaxation calculations, the plane-wave kinetic energy cutoff was 650 eV. The Brillouin zone was sampled with a Gamma centered mesh of dimensions $8 \times 8 \times 1$ for ReS$_2$, and $4 \times 4 \times 1$ for structures with S and Se atom absorbed. The convergence criteria for electronic self-consistent loop were set to $1 \times 10^{-6}$ eV. The optimization persisted until the maximum Hellmann–Feynman force was below 0.01 eV Å$^{-1}$ for all atoms. 16 Å vacuum is used to eliminate interactions between periodic adjacent cells.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Note: The format of Figure 6 and typos in Table 1 were corrected on November 28, 2018 after initial online publication.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

CVD, epitaxial growth, mixed-dimensional heterostructure, photodetectors, ReS$_2$ monolayers, Se nanoplates

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