Monolayer MoSe$_2$ Grown by Chemical Vapor Deposition for Fast Photodetection

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**ABSTRACT** Monolayer molybdenum disulfide (MoS$_2$) has become a promising building block in optoelectronics for its high photosensitivity. However, sulfur vacancies and other defects significantly affect the electrical and optoelectronic properties of monolayer MoS$_2$ devices. Here, highly crystalline molybdenum diselenide (MoSe$_2$) monolayers have been successfully synthesized by the chemical vapor deposition (CVD) method. Low-temperature photoluminescence comparison for MoS$_2$ and MoSe$_2$ monolayers reveals that the MoSe$_2$ monolayer shows a much weaker bound exciton peak; hence, the phototransistor based on MoSe$_2$ presents a much faster response time (<25 ms) than the corresponding 30 s for the CVD MoS$_2$ monolayer at room temperature in ambient conditions. The images obtained from transmission electron microscopy indicate that the MoSe$_2$ exhibits fewer defects than MoS$_2$. This work provides the fundamental understanding for the differences in optoelectronic behaviors between MoSe$_2$ and MoS$_2$ and is useful for guiding future designs in 2D material-based optoelectronic devices.

**KEYWORDS:** transition metal dichalcogenides · photoresponse · MoSe$_2$ · MoS$_2$ · two-dimensional materials

Transition metal dichalcogenides (TMDs) with the formula MX$_2$, where M is a transition metal (Mo, W, and so on) and X is a chalcogen (S, Se, or Te), have attracted much attention due to their layer structure and semiconducting properties. These two-dimensional (2D) materials are in the form of X—M—X, where a plane of metal atoms is sandwiched between two planes of chalcogen atoms by covalent interaction, and different layers are held together by van der Waals interactions. These layer materials exhibit many distinctive characteristics such as outstanding flexibility, moderate carrier mobility, and layer-dependent electronic and optical properties. Thus, the TMD materials can serve as transparent and flexible field-effect transistors (FETs), photodetectors, photovoltaic cells, light-emitting diodes, and catalysts. In particular, TMD materials have been reported to absorb up to 5–10% of incident sunlight within a thickness less than 1 nm, which is about 1 order of magnitude higher absorption than GaAs and Si. The phototransistors based on monolayer MoS$_2$ show outstanding photoresponsivity even up to a few thousand A/W. Recently, a graphene/MoS$_2$ hybrid phototransistor was demonstrated to be able to provide a photogain of more than 10$^8$. However, the long response time of 4–30 s for monolayer MoS$_2$-based phototransistors, caused by persistent photocarriers generated from trapped defects or charged impurity states, limits their application for fast photon detection.
Recently, monolayer MoSe₂ has started to gain attention because it has many interesting electronic and optical properties similar to those of monolayer MoS₂, such as a direct band gap, strong photoluminescence (PL), and a large exciton binding energy. It is known that sulfur defects in the MoS₂ monolayer greatly affect the electronic transport and optical properties. Therefore, it would be meaningful to carefully compare the properties of monolayer MoS₂ and MoSe₂. One important question is whether the MoSe₂ monolayer grown by chemical vapor deposition (CVD) exhibits better optoelectronic characteristics. In this study, we synthesized monolayer MoSe₂ on sapphire by the gas phase reaction between MoO₃ and Se powders in a hot-wall tube furnace system, using a CVD method which has been reported elsewhere. X-ray photoemission spectroscopy (XPS) and transmission electron microscopy (TEM) measurements confirm that the MoSe₂ film is highly crystalline. By comparing the electrical devices fabricated with these two monolayers, we demonstrate that both MoS₂ and MoSe₂ monolayers exhibit a comparable mobility value for the electron transport. It is also noteworthy that electrical and ultraviolet photoemission spectroscopy (UPS) measurements demonstrate that MoS₂ is heavily n-doped but MoSe₂ is less n-doped. Low-temperature photoluminescence study reveals that the MoSe₂ monolayer has a much weaker bound exciton peak, indirectly suggesting that the MoSe₂ monolayer possesses fewer defects or impurities. Most interestingly, the CVD MoSe₂ monolayer exhibits a much faster response time (<25 ms) than MoS₂, making it superior for fast photodetection applications.

RESULTS AND DISCUSSION

Synthesis of the MoSe₂ Monolayer. The experimental setup for growing monolayer MoSe₂ using MoO₃ and Se powder precursors in a hot-wall CVD system is schematically illustrated in Figure 1a. Hydrogen was introduced as a reducing agent during the growth process. The morphology of the MoSe₂ grown on sapphire substrates varies with the distance of the substrate from the MoO₃ source, as shown in Figures 1b,c. The optical micrograph (OM) in Figure 1b shows that
the sparsely distributed triangular crystals (lateral size ∼5 μm) are found in most areas of the substrate located furthest from the MoO3 source. When the substrate is close to the MoO3 source, the nucleation density becomes much higher such that these small domains easily merge to form a continuous film, as shown in the atomic force microscopy (AFM) image in Figure 1c. Moreover, the cross-sectional height profile in Figure 1d shows that the thickness of the MoSe2 film is ∼0.7 nm, corresponding to a monolayer and consistent with published monolayer thickness.6,37 Figure 1e shows the OM of the MoSe2 monolayer. In addition to the MoSe2 monolayer, we occasionally observe the growth of second-layer MoSe2 on top of some monolayer flakes, as shown in Supporting Information Figure S1. The occasionally found MoSe2 second layers are normally in the areas with high substrate roughness or with some particles, likely due to the rough surfaces or particles that are able to assist the nucleation of the second layer.

**Structural Characterization of MoSe2.** The layer dependence of Raman features has been reported for TMDs such as MoS2, MoSe2, and WS2.7,16,38,40 In Figure 2a, the synthesized monolayer MoSe2 exhibits two characteristic peaks located at 241.2 and 286.7 cm⁻¹, associated with the out-of-plane A1g mode and in-plane E2g1 mode, respectively.6,35 Furthermore, the Raman peak at ∼353 cm⁻¹, which has been demonstrated to relate to the interlayer interaction, is not observed in our monolayer MoSe2.38 This suggests that the CVD synthesized MoSe2 is indeed one monolayer. Figure 2b displays the PL spectrum for monolayer MoSe2. Only a strong peak located at 793 nm is observed, attributed to the direct band gap emission from A excitons.6,35,37 It is noted that the indirect gap emission is absent in the monolayer, and the strong A exciton emission from the monolayer is in good agreement with a recent report.38,41 In addition, the XPS spectra for the CVD synthesized monolayer MoSe2 in Figure 2c,d confirm the stoichiometry of MoSe2. The peaks at 228.8 and 232 eV are attributed to the doublet Mo 3d5/2 and Mo 3d3/2 binding energies, respectively, for Mo4+.42,43 The peaks corresponding to the Se 3d5/2 and Se 3d3/2 orbitals of

Figure 2. (a) Raman spectrum for the monolayer MoSe2, obtained in a confocal Raman spectrometer excited by a 473 nm laser. (b) Photoluminescence spectra for the CVD monolayer MoSe2, obtained in a microscopic PL system (excitation wavelength 532 nm). (c,d) XPS spectra of the monolayer MoSe2 film, where the (c) Mo 3d and (d) Se 3d binding energies are identified. (e) High-resolution TEM image of monolayer MoSe2, with an inset showing its Fourier transform pattern. (f) Enlarged TEM image, where the Mo and Se atoms are identified. The inset is a simulated HRTEM image of monolayer MoSe2.
Divalent selenide ions (Se\(^{2-}\)) are observed at 54.4 and 55.2 eV.\(^{42,43}\) Aberration-corrected high-resolution TEM (HRTEM) images demonstrate a high crystallinity of monolayer MoSe\(_2\), in which the Se and Mo atomic columns can be directly identified (Figure 2e,f). The remarkable contrast difference between Se and Mo is in good agreement with the simulated HRTEM image for monolayer MoSe\(_2\) (Figure 2f). The lattice constant of the 2D hexagonal lattice is measured directly from the image and the corresponding Fourier transform and determined to be \(a = 0.323\) nm, consistent with that of bulk MoSe\(_2\).

**Electric Double-Layer Transistors.** The electrical characteristics of the electric double-layer transistors (EDLTs) were measured directly for the monolayer MoSe\(_2\) films on sapphire substrates. The detailed description of EDLT fabrication was reported in previous studies\(^3,5\) and is illustrated in Figure S2. The output characteristics for the MoSe\(_2\) devices are also shown in Figure S2. Figure 3a shows the OM top view image of the MoSe\(_2\) EDLT, where the channel width and length are 90 and 1000 \(\mu\)m, respectively. Figure 3c displays the p- and n-channel drain current as a function of the reference voltage \(V_R\) for monolayer MoSe\(_2\) EDLT at the applied drain voltage \(V_D = -0.1\) and 0.1 V, respectively. Note that \(V_R\) is the measured voltage between the electrolyte and MoSe\(_2\), that is, the voltage for the electric double layer on MoSe\(_2\) surfaces. Since the gate voltage applied on the top Pt metal is partially consumed by the electric double layer on the gate electrode, \(V_R\) is used instead for the gate dependence measurements. Although some reports have claimed that MoSe\(_2\) is an n-type semiconductor,\(^{44}\) we clearly observe an ambipolar transport behavior instead since the electric double layer exhibits a higher gating efficiency. Figure 3c shows that the threshold voltage for the n-channel is 0.64 V in the forward scan, smaller than the 1.46 V value for the p-channel, indicating that the MoSe\(_2\) is an n-type preferred ambipolar semiconductor. However, a unipolar n-type electrical characteristic is presented for MoS\(_2\) using the same EDLT technology as shown in Figure 3b. Furthermore, we did not observe any hole transport current in the same negative gate voltage range (–1.6 to 0 V) for MoS\(_2\). The field-effect mobility was calculated using the standard formula in the linear region, \(\mu = (L/W)C_i \times (\Delta V_D/\Delta V_R)\), where \(\mu\) is the field-effect mobility, \(W\) is the channel width, \(V_D\) is the drain voltage, \(C_i\) is the measured specific capacitance of the ion gel, \(L\) is the channel length, and \(I_D\) is the drain current. The highest carrier mobility obtained for the MoSe\(_2\) monolayer is 23 cm\(^2\)/Vs for electron transport and 15 cm\(^2\)/Vs for hole transport. For the MoS\(_2\) monolayer, the electron mobility is around 17 cm\(^2\)/Vs. As shown in the insets of Figure 3.
Figure 3b–d, the current ON–OFF ratio is as high as $10^4$–$10^5$ for both MoSe$_2$ and MoS$_2$. The comparative EDLT measurement results for both MoSe$_2$ and MoS$_2$ are listed in Table 1. In brief, MoSe$_2$ exhibits a similar electron mobility value and ON–OFF current ratio compared with MoS$_2$, which also makes it a promising candidate for FET applications.

Ultraviolet Photoemission Spectroscopy. UPS is used to explore the energy level alignment with respect to the Fermi energy ($E_F$). The MoS$_2$ and MoSe$_2$ monolayers are separately transferred onto Si substrates coated with 60 nm thermally evaporated Au. The Au layer serves as a reference for $E_F$, assigned to 0 eV. As shown in Figure 4a, the valence band ($E_V$) for MoS$_2$ and MoSe$_2$ on Au/Si substrates is, respectively, located at 1.75 and 1.20 eV below $E_F$ by linearly extrapolating the leading edge of the spectrum to the baseline. In addition, the work function ($\Phi$) can be calculated using $\Phi = h\nu - E_{onset}$, where $h\nu$ is the incident photon energy (40.8 eV) and $E_{onset}$ is the onset level related to the secondary electrons, as shown in Figure 4b. Hence, the $\Phi$ for MoS$_2$ and MoSe$_2$ on Au/Si substrates is 4.20 and 4.27 eV, respectively. Note that the work function value obtained for monolayer MoS$_2$ is consistent with several other reports. In addition, the optical band gaps of the CVD monolayer MoS$_2$ and MoSe$_2$ are determined to be $\sim$1.83 and $\sim$1.51 eV, respectively, from the absorption spectra (Figure S3). Thus, the energy band diagrams of CVD monolayer MoS$_2$ and MoSe$_2$ relative to the Fermi level $E_F$ of gold films are illustrated in Figure 4c,d. The energy separation $\Delta E$ between the conduction band of MoS$_2$ and the $E_F$ of Au is $\sim$0.08 eV, indicating that CVD monolayer MoS$_2$ is heavily n-doped, consistent with unipolar n-type electrical transport behavior. On the other hand, the energy separation $\Delta E$ between the conduction band of MoSe$_2$ and the $E_F$ of Au is $\sim$0.31 eV, indicating that the CVD monolayer MoSe$_2$ is slightly n-doped, consistent with the n-type preferred ambipolar electrical transport behavior.

Optical Properties. To examine the gate-dependent photoresponse characteristics, the MoS$_2$ and the MoSe$_2$ films are transferred onto 300 nm SiO$_2$/Si substrates, and the phototransistors are patterned using standard photolithography. Figure S4 shows the optical image of the interdigitated electrodes used, where the contact metal layers, 10 nm Ti and 80 nm Au, are deposited by thermal evaporation. The 532 and

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650 nm CW lasers are used as the light sources to study the MoS2 and MoSe2 phototransistors. Figure 5a presents the typical transport curves of the two phototransistors in the dark and under illumination. In the dark, the n-channel subthreshold voltage $V_{th}$ of the MoSe2 and MoS2 is $\sim 7$ V and $\sim 46$ V, respectively, corroborating that the MoS2 on SiO2 is much more heavily n-doped. The mobilities of MoSe2 and MoS2 transistors are $\sim 0.012$ cm$^2$/Vs at $V_g = 60$ V ($V_g - V_{th} = 53$ V) and $\sim 0.021$ cm$^2$/Vs at $V_g = 17$ V ($V_g - V_{th} = 53$ V), respectively. Compared with the devices on sapphire, the mobilities of the devices on SiO2 are about 3 orders of magnitude lower, which may be caused by several factors including the possible degradation by transfer processes, the scattering effect from charge impurities added during the transfer process, and damage caused by patterning. Under illumination at a power density of $\sim 0.31$ and 0.59 W/cm$^2$, the OFF state currents of both devices increase by $\sim 3$ orders of magnitude. The photogain ($G$), given by $G = h\nu I_{ph}/(\eta e P_0)$, is an index to quantify the conversion efficiency of incident photons to photogenerated carriers, where $I_{ph}$ is the net photocurrent, $P_0$ is the absorbed laser power, $h$ is Planck’s constant, $e$ is the charge of an electron, and $\nu$ is the frequency of incident light. Assuming $\eta = 100\%$, the photogain of the MoS2 phototransistors is $\sim 0.2$, much higher than $\sim 5 \times 10^{-4}$ of the MoSe2 phototransistor in the OFF state. The MoSe2 band diagrams in Figure 4c,d indicate that the electron Schottky barrier of MoSe2 is higher, resulting in the smaller photogain of MoSe2 on SiO2. This also accounts for the lower OFF state dark current for MoSe2 ($\sim 10^{-12}$ A vs $\sim 10^{-10}$ A for MoS2).

Figure 5c,d shows the time-resolved photocurrent for monolayer MoSe2 and MoS2 films, respectively, under ON/OFF light illumination at $V_{ds} = 1$ V in ambient environment. A fast rise and decay response time shorter than $\sim 25$ ms for MoSe2 is observed. However, the photocurrent of the MoS2 phototransistors takes more than 30 s to saturate and decay. The persistent photocurrent is normally attributed to defect or charge impurity states inside the band gap. Figure 5e,f shows the PL spectra of the monolayer MoSe2 and MoS2 at room and low temperatures. We observe only
one peak at room temperature, ∼1.55 eV for the MoSe₂ and ∼1.88 eV for the MoS₂, corresponding to the direct band-to-band A excitonic transition. The peak intensity for monolayer MoSe₂ at room temperature is stronger than that of monolayer MoS₂, and the full width at half-maximum of ∼42 meV for monolayer MoSe₂ is smaller than the ∼51 meV value of monolayer MoS₂. When the temperature decreases to 12 K, an additional sub-band-gap emission at the low energy side between 1.4 and 1.9 eV appears for the monolayer CVD MoS₂, which could be attributed to the defect or charge impurity states. Due to the additional binding to defects or charge impurities, the energy of the bound exciton peak is lower than that of the free exciton peak. The large width of the bound exciton peak indicates the presence of different kinds of defects or charge impurity sites since different binding energies are needed. In contrast, no sub-band-gap emission is observed at the low-energy side for the CVD MoSe₂ monolayer, implying better crystalline quality and fewer defects or charge impurity states, thus resulting in higher band-to-band free exciton recombination rates. Some reports have pointed out that the persistent photoconductance arises from the defects or charge impurities inside the band gap. Hence, the extra photogenerated carriers in the MoS₂ arising from the defects or charge impurity states could be responsible for its slow light response time. Figure S5 shows the HRTEM image for the CVD MoS₂ monolayers with abundantly disordered atom arrangement highlighted by dashed circles, which is in clear contrast to the HRTEM for CVD MoSe₂ in Figure 2e,f.

Moreover, the CVD MoS₂ shows significantly lower stability in ambient environment, where its PL intensity normally decays in 2 or 3 days. We notice that the shelf-lifetime can be increased to more than 1 week if the sample is stored in a drybox, indicating that the moisture may react or catalyze the formation of defects in MoSe₂. By contrast, PL measurements suggest that the CVD MoSe₂ monolayer exhibits a much longer shelf-lifetime, typically more than 4 weeks, in the same ambient storage condition. These observations are also in line with a relatively larger amount of defects in MoS₂ revealed by TEM.

**CONCLUSIONS**

In conclusion, we have synthesized crystalline monolayer MoSe₂ by the gas phase selenization of MoO₃ in a hot-wall CVD chamber. From the analyses of EDLT and UPS measurements, the MoSe₂ exhibits a slight n-type preferred ambipolar behavior, while the MoS₂ shows heavily n-doped electrical characteristics. In addition, the defect-less crystalline structure for the MoSe₂ is identified through the low-temperature PL, whereas relatively abundant defects occur in MoS₂. This study shows that CVD synthesized monolayer MoSe₂ has great potential in flexible transparent optoelectronic applications.
REFERENCES AND NOTES


