Band Gap-Tunable Molybdenum Sulfide Selenide Monolayer Alloy

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Transition metal dichalcogenide (TMD) monolayers have attracted much attention recently since they exhibit moderate carrier mobility values,[1-2] good bendability and direct band gaps,[3,4] which may allow them to serve for low-power electronics,[1-5,6] flexible[7] and optoelectronic devices.[8-10] In the application of optoelectronics such as photodetectors, photovoltaic cells and light-emitting diodes, the optical band gap of the semiconductor TMD may determine the efficiency and optical responsivity to different wavelengthes of light. Recently, the exfoliated TMD monolayers including MoS₂, MoSe₂, and WSe₂, which can absorb up to 5–10% incident sunlight in a thickness of less than 1 nm, have been shown to achieve 1 order of magnitude higher sunlight absorption than the most commonly used absorbers in solar cells GaAs and Si.[9] This strongly suggests that the TMD materials hold great promise for the device applications in nanoscale. To realize the high efficiency solar cells or other optoelectronic devices based on the TMD monolayers, it is crucially important to develop a strategy to tune the optical band gap of the TMD monolayers. Strain engineering has been proposed to modify the optical band gap of the monolayer TMDs,[11-15] Moreover, the stacking of various TMD monolayers has also been proposed as an approach to modulate their band gaps.[10] The band gap engineering of TMD has become an important topic. In early studies the TMD solid solutions both in the metal (e.g., Mo₆W₁₋ₓS₂) and chalcogen (e.g., MoS₂Seₓ(1-x)) sublattice forms have been realized by the direct vapor transport growth, where the stoichiometric amounts of desired powder elements were introduced into a quartz ampoule for crystal growth.[17,18] Meanwhile, the growth of MoS₂, WSe₂ and WS₂ monolayers has been reported recently by using sulfurization or selenization of transition metal oxides with chemical vapor deposition (CVD) techniques.[19-21] The density-functional theory (DFT) calculations show that the single layers of mixed TMDs, such as MoS₂Seₓ(1-x) are thermodynamically stable at room temperature,[22] so that such materials can be manufactured using chemical-vapor deposition technique. It is therefore useful to know whether it is possible to realize the synthesis of MoS₂Seₓ(1-x) monolayers which exhibit intriguing electronic properties and tunable optical band gaps. Very recently, the transition-metal dichalcogenide monolayer alloys (MoₓWₚS₂) have been obtained by mechanical cleaving from their bulk crystals[23] where the band gap emission ranges from 1.82 eV to 1.99 eV. Note that the mechanical cleavage is valuable for fundamental research; however, a simple and scalable method to obtain TMD monolayers with controllable optical energy gaps is still urgently needed.

In this contribution, we report that the MoS₂ monolayer flakes prepared by CVD can be selenized in the presence of selenium vapors to form MoS₂Seₓ monolayers. The optical band gap of the obtained MoS₂Seₓ, ranging from 1.86 eV to 1.57 eV, is easily controllable by the selenization temperature. It is key demonstration for controlling electronic and optoelectronic structures of TMD monolayers using a simple method, where approach is straightforward and applicable to the band gap engineering for other TMD monolayers.

The CVD-grown MoS₂ monolayers were synthesized based on our previous reports.[19] In brief, the triangular MoS₂ flakes are formed by the vapor phase reaction of MoO₃ with S powders, where the MoS₂ monolayers with a lateral size up to tens micron can be obtained and which growth method has been adopted by many other groups.[24,25] To modulate the electronic structures and optical band gaps of the MoS₂ monolayer, we perform the selenization in a hot-wall furnace at various temperatures. The scheme in Figure 1a illustrates the experimental set-up for the selenization process, where the inlet gas (a mixture of Ar and H₂) carries the vaporized...
selenium to the heated MoS₂ flakes. It is noted that hydrogen gas is necessary in the process to avoid the oxidation of MoS₂ by residual oxygen or unavoidable oxygen leaking from the environment to the chamber. Figures 1b and 1c show the optical micrographs for the as-synthesized MoS₂ and selenized MoS₂ (at 800 °C) on sapphire substrates, respectively. We note that there is no obvious change in size and shape of the MoS₂ flakes after selenization. Figures 1d and 1e display the atomic force microscopy (AFM) images for the MoS₂ flakes before and after selenization (800 °C). Note that the change in thickness after selenization is within the measurement errors.

To reveal the optical properties of the selenized MoS₂ flakes, we perform the photoluminescence measurements using microscopy- focused light (spot size: 0.7 µm). Figure 2a shows the optical micrographs of a triangular MoS₂, where the circles indicated with the colors from purple to black represent the measurement sites from the corner though the center to the edge. Figure 2b is the photoluminescence spectra collected for the samples before and after selenization at different temperatures. The photoluminescence peak position (~668 nm) for the pristine MoS₂ does not vary with the measurement sites from the corner to the edge. The emission peak wavelength 667 nm for the MoS₂ selenized at 600 °C is still pretty similar to that of the pristine MoS₂ samples. The peak wavelength for the sample selenized at 700 °C is at 726 nm and the wavelength continues to increase to 768 nm and 790 nm for the samples selenized at 800 °C and

Figure 1. (a) Schematic illustration of the experimental set-up for the selenization process, where the inlet gas (a mixture of Ar and H₂) carries the vaporized selenium to the heated MoS₂ flakes. And optical micrographs for the (b) as-synthesized MoS₂ and (c) selenized MoS₂ (at 800 °C) on sapphire substrates. AFM images for the MoS₂ flake (d) before and (e) after selenization (at 800 °C)
900 °C respectively. The emission wavelength 790 nm for the MoS₂ selenized at 900 °C is very close to the reported values from 792 nm[26] to 800 nm[27] for exfoliated monolayer MoSe₂. Our experimental results suggest that the temperature is a dominant parameter to control the optical properties of the obtained MoSₓSeᵧ materials. The calculations by Hannu-Pekka Komsa et al.[28] predict that the mixture of MoS₂ and MoSe₂ should be energetically favored over the segregated phases even at 300 K due to the fact that the entropic contributions promote the mixing.[22] However, our reaction process involves the Mo-S bond breaking, where enough thermal energy should be provided to overcome the reaction barrier and then enable the replacement of S with Se.

It is also informative to examine the homogeneity of the selenization of MoS₂. Taking the 900 °C selenization as an example, the photoluminescence spectra in Figure 2b show that the emission wavelength at the corner site is 10 nm longer than that obtained at the center site of the sample. The longer emission wavelength at the corner site indicates that the selenization is preferable at the location with more edges or defects. The center part is relatively inert to the selenization. Based on Figure 2b, the largest band gap energy difference across the 900 °C selenized sample is estimated to be at most 17 meV (e.g. The gap energy difference between the center and the corner sites). These results in Figure 2 suggest that thermodynamic parameter (temperature) is dominating the structures and optical properties of selenized samples.

Figure 3 shows the Raman spectra for the MoS₂ flakes before and after selenization at different temperatures. It is clearly seen that the characteristic peaks of MoS₂ including E₁ₛ² at 385.6 cm⁻¹ and A₁₉ at 405.8 cm⁻¹[19] are observed for both the pristine and 600 °C treated samples, indicating that the selenization at 600 °C does not obviously change the structure of MoS₂. The MoS₂ flakes after selenization at 700 °C exhibit several unidentified peaks at 225.1 and 267.1 cm⁻¹, which are likely attributed to the vibration from the partially selenized Mo-S structures and worth further investigations in the future. When the selenization temperature is increased to 800 °C, the observed Raman features, at
A pristine MoS\(_2\) sample is also shown in Figure 4 for comparison. The observed trend strongly agrees the conversion of Mo-S bonding structures. Most importantly, the conversion is governed by the selenization temperature, indicating that the process is thermodynamically controlled.

To understand the differences between the MoS\(_2\) flakes selenized at various temperatures, X-ray photoemission spectroscopy (XPS) was adopted to characterize the chemical bonding structures. Figure 5 displays the detailed XPS scans for the Mo, S and Se binding energies for the as-grown MoS\(_2\) and those after selenization, where the magnitude of each profile was normalized for easier comparison. The as-grown MoS\(_2\) exhibits two characteristic peaks at 232.5 and 229.3 eV, attributed to the Mo 3d\(_{5/2}\) and Mo 3d\(_{3/2}\) binding energies for Mo\(^{4+}\).[29] The peaks, corresponding to the S 2p\(_{3/2}\) and S 2p\(_{1/2}\) orbital of divalent sulfide ions (S\(^{2-}\)) are observed at 163.3 and 162.1 eV.[30] A doublet peak (232.4 cm\(^{-1}\), 235.6 cm\(^{-1}\)) attributed to the MoO\(_3\) is also observed. When the sample is selenized at 600 °C, a weak doublet (55.3 cm\(^{-1}\), 54.5 cm\(^{-1}\)) assigned to Se 3d\(_{5/2}\) and Se 3d\(_{3/2}\) binding energy appears in addition to the above mentioned XPS peaks for as-grown MoS\(_2\) flakes. With the increasing selenization temperature, the doublets peaks (Se 3d\(_{5/2}\), Se 3d\(_{3/2}\)) and (Se 3p\(_{3/2}\), Se 3p\(_{5/2}\)) become more prominent. Meanwhile, the S 2p\(_{3/2}\) and S 2p\(_{1/2}\) binding energies become less pronounced. For the sample selenized at 900 °C, only a Mo doublet and two Se doublets are observed, confirming the selenization of MoS\(_2\).

The selenization process takes effect at the temperature higher than 600 °C and the evolution of the optical band gap suggests the gradual conversion of MoS\(_2\) to MoS\(_x\)Se\(_y\) and then MoSe\(_2\) with the increasing temperature. Figure 5 also reveals that some Mo-O bonds exhibit in the as-grown and 600 °C selenized MoS\(_2\) and the oxygen-species are not detectable after selenization with a higher temperature, which is likely due to that the hydrogen gas takes the effect. To get an idea of the temperature effect, we estimate the percentage of selenization, a ratio between Mo-Se and (Mo-Se+Mo-S), using the obtained XPS spectra. The Mo-Se percentage for the as-grown MoS\(_2\) and those selenized at 600 °C, 700 °C, 800 °C and 900 °C is 0%, 14.5%, 73.8%, 95% and 100% respectively. The observed trend strongly agrees the conversion of Mo-Se bonds. Most importantly, the conversion is governed by the selenization temperature, indicating that the process is thermodynamically controlled.

In summary, we report that the CVD-grown MoS\(_2\) monolayer flakes can be selenized in the presence of selenium vapors. The optical band gap, ranging from 1.86 eV (667 nm) to 1.57 eV (790 nm), is controllable by the selenization temperature. XPS analysis suggests the gradual conversion of MoS\(_2\) to MoS\(_x\)Se\(_y\) and then MoSe\(_2\) with the increasing selenization temperature. This approach, replacing one chalcogen with selenium, demonstrates the potential for MoS\(_2\) monolayer flakes to be selenized in a controllable manner with potential applications in device fabrication.
by another in a gas phase, is promising in modulating the optical and electronic properties of other TMD monolayers.

**Experimental Section**

*Synthesis of Monolayer MoS$_2$:* Triangular MoS$_2$ single crystals were synthesized by the modified processes of our previous work.[19] In brief, c-plane sapphire (0001) substrates [Tera Xtal Technology Corp.] were first cleaned in a piranha solution [H$_2$SO$_4$/H$_2$O$_2$ (70:30)] at 100 $^\circ$C for 1 h. Substrates were placed in the center of a 4 inch tubular furnace on a quartz holder. The MoO$_3$ powders (0.6 g; Sigma-Aldrich, 99.5%) in an Al$_2$O$_3$ crucible were placed next to the sapphire substrates and S (Sigma-Aldrich, 99.5%) powders were placed close to the furnace open-end at the upstream position, where the schematic illustration of the growth system was described elsewhere.[31] The furnace was first heated to 150 $^\circ$C at 10 $^\circ$C/min rate with 70 sccm Ar at 10 torr and annealed for 20 minutes, then ramped to 650 $^\circ$C at 25 $^\circ$C/min rate and kept for 20 minutes. Sulfur was heated separately by heating belt to 170 $^\circ$C when the furnace reached 400 $^\circ$C. After growth, furnace was slowly cooled to room temperature.

*Selenization of MoS$_2$:* The as-grown monolayer MoS$_2$ single crystal flakes were selenized in a hot-wall furnace at 600 $^\circ$C, 700 $^\circ$C, 800 $^\circ$C, and 900 $^\circ$C, respectively. Briefly, as-grown MoS$_2$ monolayers on sapphire were at the center of the furnace in the quartz tube. The Selenium powders were placed close to the furnace open-end at the upstream position. The furnace was heated to 600 $^\circ$C, 700 $^\circ$C, 800 $^\circ$C, and 900 $^\circ$C at 30 $^\circ$C/min rate and kept for 4 h, respectively. The Selenium powders was heated to 270 $^\circ$C using a separate heating belt. After selenization, the furnace was slowly cooled to room temperature.

*Characterization:* Photoluminescence spectra were excited by green light laser with 532 nm wavelength and 0.9 N.A. of objective (spot size: 0.7 µm). Raman spectra were collected in a NT-MDT confocal Raman microscopic system (laser wavelength 473 nm and laser spot size ~0.5 µm). The Si peak at 520 cm$^{-1}$ was used as reference for wavenumber calibration. The AFM images were performed in a Veeco Dimension-Icon system. The transmittance spectra of the MoS$_2$ flakes were obtained using a JASCO-V-670 UV-vis spec-

![Figure 5. XPS scans for the Mo, S and Se binding energies for the as-grown MoS$_2$ and those after selenization, where the magnitude of each profile was normalized for easier comparison.](image-url)
trophotometer. Chemical configurations were determined by X-ray photoelectron spectroscopy (XPS, Phi V5000). XPS measurements were performed with an Mg Kα X-ray source on the samples. The energy calibrations were made against the C 1s peak to eliminate the charging of the sample during analysis.

Supporting Information

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

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