Synthesis of 2D MoS$_2$(1–$x$)Se$_{2x}$ semiconductor alloy by chemical vapor deposition†

Wenwen Yao, Zhilin Kang, Jiajun Deng, Yan Chen, Qian Song, Xun Lei Ding, Fangchao Lu and Wenjie Wang.

Alloying/doping in two-dimensional (2D) materials is emerging as an increasingly important strategy due to the wide-range bandgap tunability and versatility of these materials. Monolayer 2D transition metal dichalcogenide (TMD) alloy has been investigated both theoretically and experimentally in recent years. Here, we synthesized a bilayer MoS$_{2(1-x)}$Se$_{2x}$ semiconductor alloy via the chemical-vapor deposition technique. The as-grown triangular MoS$_{2(1-x)}$Se$_{2x}$ flakes with size of roughly 10 μm were observed by optical microscope and scanning electron microscope (SEM). The 1.4–1.9 nm thickness of the samples, as measured by AFM, means that bilayer MoS$_{2(1-x)}$Se$_{2x}$ alloys were grown. The characteristic Raman modes related to Mo–S and Mo–Se vibrations were observed in the Raman spectrum. Two emission peaks were respectively found, corresponding to the A and B excitons in the photoluminescence (PL) spectrum. XPS measurements confirmed the Se doping of the alloy. The first-principles calculation results show a contraction of the band gap value with the increase of Se doping in the MoS$_2$ lattice. Compared with monolayer MoS$_{2(1-x)}$Se$_{2x}$ alloy, the band bending effect is more obvious, and the bilayer MoS$_{2(1-x)}$Se$_{2x}$ alloy still shows the direct band gap luminescence characteristic, which has certain guiding significance for the growth of two-dimensional materials and for device preparation.

A variety of methods have been demonstrated in previous studies to synthesize monolayer MoS$_{2(1-x)}$Se$_{2x}$, including mechanical exfoliation of bulk material, gently sputtering, physical vapor deposition, and chemical vapor deposition. Among these methods, the CVD technique is considered a promising method for the controllable synthesis of MoS$_{2(1-x)}$Se$_{2x}$ flakes, particularly for fabricating monolayer MoS$_{2(1-x)}$Se$_{2x}$. Also, theoretical (ab initio) calculations have been performed to reveal the modification of the band structure and bandgap of monolayer MoS$_2$ with Se doping. In order to explore the bandgap difference between bilayer and monolayer MoS$_{2(1-x)}$Se$_{2x}$, the MoS$_{2(1-x)}$Se$_{2x}$ flakes were synthesized by the low-pressure chemical vapor deposition technique. The difficulty in synthesizing MoS$_{2(1-x)}$Se$_{2x}$ bilayer is in controlling the growth parameters in the alloying process, such as deposition temperature, evaporation concentration, and pressure for deposition. The bilayer MoS$_{2(1-x)}$Se$_{2x}$ alloys are found to be achieved easily when $x$ is smaller than 50% in Ar atmosphere.

Experiments

In the present work, MoS$_2$ bilayer and MoSe$_2$ bilayer with controllable morphology and size were firstly obtained using chemical vapor deposition (CVD), and the optical bandgaps of the resulting compounds are 1.53 and 1.82 eV, as given by photoluminescence spectra. Then, we explore the bandgap of MoS$_{2(1-x)}$Se$_{2x}$ bilayer as a function of Se/S ratio. The growth of...
MoS$_{2(1-x)}$Se$_{2x}$ sheets was carried out in a three-zone tube furnace with a 2.5-inch diameter quartz tube, as shown in Fig. 1(a), where different shades of red indicate different temperatures. Sulfur, selenium and molybdenum trioxide precursors were loaded in ceramic boats and were placed from downstream to upstream in the furnace tube, respectively. Argon gas of 200 sccm was provided throughout the experiment. The furnace was heated to 250 °C by heating belt. When the furnace reached 850 °C, the argon gas carries the vaporized selenium, sulfur and molybdenum trioxide to the substrates during the deposition process. After the growth, the furnace was naturally cooled to room temperature. The heating and cooling process of the tube furnace in the experiment is shown in Fig. S1.† More details of the experiment can be seen in the ESL.†

Results and discussion

A typical optical image of the as-grown bilayer MoS$_{2(1-0.37)}$Se$_{2(0.37)}$ is shown in Fig. 1(b). It is not difficult to find some dots distributed within the surface of the MoS$_{2(1-x)}$Se$_{2x}$ samples. The bright dot located at the center of the nanoflake indicates the original nucleation sites for the crystals. Similar to the perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) of MoS$_2$, we can conclude that these bright dots coming from PTAS serve as a seeding promoter for the growth of the MoS$_{2(1-x)}$Se$_{2x}$. The shape and scale of MoS$_{2(1-0.37)}$Se$_{2(0.37)}$ are given by the SEM images shown in Fig. 1(b). Unlike SbTe$_2$, α-MoO$_3$ (ref. 23) and Bi$_2$Se$_3$, MoS$_2$ (ref. 25) and MoSe$_2$ (ref. 26) grow in the triangular direction. By controlling the quantity of evaporation source, triangles of MoS$_{2(1-x)}$Se$_{2x}$ with a size >5 μm were obtained. It is noteworthy that the morphology of the material will not be influenced by the composition. As displayed in Fig. 1(c), the thickness and morphology of MoS$_{2(1-0.37)}$Se$_{2(0.37)}$ was further confirmed by AFM technique. The height profile from the Si/SiO$_2$ substrate to the triangular regions falls in the range of 1.4 nm, which is in good relation to the thickness of the MoS$_{2(1-0.37)}$Se$_{2(0.37)}$ bilayer.

Raman spectroscopy (wavelength of laser, 514 nm) was used to investigate the structure of the MoS$_{2(1-x)}$Se$_{2x}$ samples. Two sets of Raman peaks are observed in Fig. 2(a). One set of Raman peaks are MoS$_2$-like peaks around 380–400 cm$^{-1}$, which can be attributed to the E1 2g mode resulting from in-plane vibration and the A$_{1g}$ mode originating from out-of-plane vibration. Also, the intensity of A$_{1g}$ mode is higher than that of E1 2g mode because the intralayer bonding is thought to be strong and predominantly covalent, whereas the interlayer weak bonding is of the van der Waals type. The other set, consisting of 240 and 280 cm$^{-1}$ peaks, corresponds to MoSe$_2$-like A$_{1g}$ and E1 2g modes, but slightly shifts to lower wavenumbers than those of pure MoSe$_2$. Apart from these peaks, the spectrum contains a peak around 300 cm$^{-1}$, which is independent of the composition. It is reasonable to infer that the peak is ascribed to the silicon substrate. It should be noted that the original material MoS$_2$ bilayer has two Raman modes, as earlier reported, and by introducing the Se during the growth process, the synthesized MoS$_{2(1-x)}$Se$_{2x}$ alloy presents two sets of Raman modes. Moreover, with the increasing Se component, the intensity of MoS$_2$-like modes weakens gradually and finally disappears, but the intensity of MoSe$_2$-like modes is enhanced, which agrees with the reported result of monolayer material.

In addition, the kind and intensity of Raman peaks were changed with the introduction of Se to the original MoS$_2$, as shown in Fig. 2(c). All peaks are shifted to lower wavenumbers with increasing Se content, which is consistent with the behavior of monolayer MoS$_{2(1-x)}$Se$_{2x}$. The pristine monolayer MoS$_2$ consists of three sublayers, one layer of Mo atom sandwiched by two planes of sulfur atoms. As the Se atoms substitute for a part of the S sites, the symmetry of original MoS$_2$ crystals is broken due to the larger radius of Se atoms. The original Mo–S and Mo–Mo bond lengths are changed by the distortion, leading to an external tensile stress exerting on the original MoS$_2$ lattice. Therefore, the atomic vibration due to the E1 2g and A$_{1g}$ modes of MoSe$_2$ is softened.

Photoluminescence measurements were performed to study the optical properties of as-grown MoS$_{2(1-x)}$Se$_{2x}$. We control the composition of the alloy by adjusting the amount of reactants Se, S and MoO$_3$. The photoluminescence spectra of the bilayer MoS$_{2(1-x)}$Se$_{2x}$ ($x = 0–1$) are shown in Fig. 2(b). In comparison with monolayer MoS$_{2(1-x)}$Se$_{2x}$, all bilayer alloys have two PL peaks originating from the direct excitonic transition at the K-point of the first Brillouin zone. The peak located at the higher wavelength is generally termed as exciton A, and the other at the lower wavelength as exciton B. The difference between these PL peaks can be inferred from the spin–orbit coupling of the valence band. The plots of A and B exciton energy of bilayer MoS$_{2(1-x)}$Se$_{2x}$ with different Se contents ($x$) are displayed in Fig. 2(d). The results reveal that the emission energy can be continually tuned from 1.82 eV (680 nm) to 1.53 eV (810 nm). We find a decrease of the optical bandgap with Se content increasing in the bilayer MoS$_{2(1-x)}$Se$_{2x}$ alloy, which is similar to monolayer MoS$_{2(1-x)}$Se$_{2x}$. However, the bandgap bowing effect is more obvious than that in monolayer MoS$_{2(1-x)}$Se$_{2x}$. There is no doubt that the redshift of PL peaks is related to the band structure variation via Se introduction to MoS$_2$. According to the
molecular orbital theory, the non-bonding d bands of MoS$_2$ are mainly derived from the Mo-d$_{xz}$, Mo-d$_{yz}$, and Mo-d$_{z^2}$ orbitals. Mo and S atoms are coordinated through ionic-covalent interaction. With Se introduction into MoS$_2$, the strong covalent effects in MoS$_2$(1-x)Se$_2$x subsequently occur, resulting in the non-bonding d bands broadening and, thus, the band gap reduced. Beyond the optical properties based on PL, we evaluated the stoichiometric features of bilayer MoS$_2$(1-x)Se$_2$x.

According to the following formula, a quadratic rule is introduced to describe the relationship between bandgap and x value of the ternary alloy:

$$E_g(x) = xE_g(MoSe_2) + (1 - x)E_g(MoS_2) - bx(1 - x),$$

where $E_g(x)$ is the bandgap of the alloy. We can firstly estimate the x of as-grown MoS$_2$(1-x)Se$_2$x. In bilayer MoS$_2$(1-x)Se$_2$x, we choose B exciton energy in the PL spectrum as $E_g(x)$, and b is the bowing parameter of MoS$_2$(1-x)Se$_2$x, approximated to 0.05. The calculated x values are approximately equal to 0.20, 0.22, 0.41, and 0.50. On the other hand, X-ray photoelectron spectroscopy (XPS) was adapted to characterize the chemical composition of crystals. In Fig. 3, the XPS spectrum of as-grown MoS$_2$(1-x)Se$_2$x is displayed. The Mo 3d, S 2p, and Se 3d regions of the XPS spectra for MoS$_2$(1-x)Se$_2$x with different Se composition can be deconvoluted into various peaks. The Mo 3d window (Fig. 3(a)) consists of Mo$^{4+}$ 3d$_{5/2}$, Mo$^{4+}$ 3d$_{3/2}$, Mo$^{6+}$ and S 2s, and the corresponding binding energies are 229.5, 232.6, 235.7 and 226.8 eV, which is in good agreement with the previous literature. The presence of Mo$^{4+}$ 3d$_{5/2}$, Mo$^{4+}$ 3d$_{3/2}$ and S 2s is due to Mo 3d spin–orbit splitting in the formation of MoS$_2$ and MoSe$_2$. The reason for Mo$^{6+}$ in the energy spectrum may be the presence of MoO$_{3-x}$S$_x$ in the reaction system. MoO$_{3-x}$S$_x$ may be derived from incomplete vulcanization (or selenization) of metal Mo during the heating process, or it may be generated by the partial decomposition of MoS$_2$(1-x)Se$_2$x deposited during the cooling process. The S 2p doublet is shown in Fig. 3(b), and it exhibits two peaks located at 162.4 eV and 163.6 eV, corresponding to S 2p$_{3/2}$ and S 2p$_{1/2}$ components, respectively. Further, as displayed in Fig. 3(c), the Se 3d spectra can be deconvoluted into two peaks at 54.9 eV and 55.7 eV, corresponding to Se 3d$_{3/2}$ and Se 3d$_{5/2}$ components, respectively. The orbital binding energy diagram of S 2p and Se 3d with doping concentration is shown in Fig. S2.† From the XPS results, we analyze the Se/S ratio by eqn (2),

![Fig. 2](image-url) (a) Raman spectra and (b) PL spectra of the bilayer MoS$_2$(1-x)Se$_2$x (x = 0.00–1.00); (c) plots of MoS$_2$(1-x)Se$_2$x Raman modes with Se composition increasing; (d) plots of A-exciton and B-exciton energy of MoS$_2$(1-x)Se$_2$x.
\[ Se = \frac{(I_{Se} \times F_S)}{(I_S \times F_{Se})} \]

where the \( F_S \) and \( F_{Se} \) are the relative sensitivity factors for S 2p3/2 (0.4453) and Se 3d3/2 (0.8493); \( I_S \) and \( I_{Se} \) represent the areas of the S and Se peaks. The Se content \( x \) was estimated to be 0.20, 0.23, 0.37 and 0.55, corresponding to the Se/S ratios of 0.40 : 1.60, 0.46 : 1.54, 0.74 : 1.26 and 1.10 : 0.90, respectively. As compared with the \( x \) value obtained from the band gap (B exciton) by formula (1), the XPS results are in good agreement with the theoretically calculated value, as displayed in Fig. 4. The good agreement also indicates that the B exciton energy can be used to estimate the band gap of bilayer MoS\(_{2(1−x)}\)Se\(_{2x}\).

In order to further understand the properties of bilayer MoS\(_{2(1−x)}\)Se\(_{2x}\) semiconductor alloy with different Se doping concentrations, we chose VASP (Vienna \textit{ab initio} simulation package) for density functional theory (DFT) calculation and used the Perdew–Burke–Ernzerhof (PBE) functional to evaluate the band gap changes of the doped alloys.\(^4\) The 4 × 4 × 2 supercell was selected for the study of the pristine bilayer MoS\(_2\), which contains 96 atoms (32 Mo atoms and 64 S atoms). The side and top views of the atomic structure of MoS\(_{2(1−0.37)}\)Se\(_{2(0.37)}\) are shown in Fig. 5(a) and (b), respectively. MO, Se and S are represented by purple, green and yellow, respectively. The results of DFT calculation show that the bilayer MoS\(_2\) is an indirect band gap semiconductor with a band gap value of 1.70 eV, as seen in Fig. 5(c), which is consistent with a previous report.\(^4\) The direct bandgap of bilayer MoSe\(_2\) is 1.42 eV, which is lower than the 0.28 eV of bilayer MoS\(_2\). The band structures calculated at \( x = 0, 0.20, 0.37, 0.55 \) and 1 are shown in Fig. 5(d), and with the increase of Se doping content, the band gap value of bilayer MoS\(_{2(1−x)}\)Se\(_{2x}\) alloy has a decreasing trend corresponding to the PL spectrum shown in Fig. 2(b), but the band gap values are slightly lower than the experimental values. From the band structure theory, when Se enters the MoS\(_2\) lattice, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) approach the Fermi level, resulting in band gap value decrease, which is a contraction of the band gap value.\(^3\) Compared with monolayer MoS\(_{2(1−x)}\)Se\(_{2x}\) alloy, the band bending effect of bilayer MoS\(_{2(1−x)}\)Se\(_{2x}\) alloy is more obvious,\(^4\) and the bilayer MoS\(_{2(1−x)}\)Se\(_{2x}\) alloy still shows the luminescence characteristic of direct band gap, which benefits the electronic structure research of 2D materials.
Conclusion

We have demonstrated an approach for preparing bilayer MoS₂ using low-pressure chemical vapor deposition. Then, by introducing the Se component in the growth process of MoS₂, MoS₂(1 - x)Seₓ bilayers with various Se contents were synthesized. The formation of triangular-shaped microcrystals was confirmed by SEM, AFM, Raman, PL and XPS measurements. Because the MoS₂ lattice is modified by Se doping, the grown alloys possess bandgaps between the values characteristic of bilayer MoS₂ and MoSe₂. The two sets of Raman modes and two PL peaks of bilayer MoS₂(1 - x)Seₓ are consistent with the variation trend of the properties of monolayer MoS₂(1 - x)Seₓ. Furthermore, we regard the B exciton energy as the bandgap of MoS₂(1 - x)Seₓ ranging from 1.82 eV to 1.53 eV to estimate the x values, which is in good agreement with the XPS result. Additionally, we also use first-principles calculations to confirm the experimental results. With the addition of Se to bilayer MoS₂ lattice, the band gap decreases. Changing of the Se/S ratio in growth crystals results in the band structure and bandgap adjustment, which provides a promising approach to produce 2D crystals with fancy properties in particular applications. The application of layered MoS₂(1 - x)Seₓ could be further considered in later papers.

Conflicts of interest

There are no conflicts to declare.

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