We report a comprehensive study on the effects of rhenium doping on optical properties and photocarrier dynamics of MoS2 monolayer, few-layer, and bulk samples. Monolayer and few-layer samples of Re-doped (0.6%) and undoped MoS2 were fabricated by mechanical exfoliation, and were studied by Raman spectroscopy, optical absorption, photoluminescence, and time-resolved differential reflection measurements. Similar Raman, absorption, and photoluminescence spectra were obtained from doped and undoped samples, indicating that the Re doping at this level does not significantly alter the lattice and electronic structures. Red-shift and broadening of the two phonon Raman modes were observed, showing the lattice strain and carrier doping induced by Re. The photoluminescence yield of the doped monolayer is about 15 times lower than that of the undoped sample, while the photocarrier lifetime is about 20 times shorter in the doped monolayer. Both observations can be attributed to diffusion-limited Auger nonradiative recombination of photocarriers at Re dopants. These results provide useful information for developing a doping strategy of MoS2 for optoelectronic applications.

1 Introduction

Recently, two-dimensional (2D) transition metal dichalcogenides (TMDs) have drawn considerable attention as new forms of nanoscale materials.1–3 As the most extensively studied member of TMDs, MoS2 has shown several attractive properties such as layer-dependent band structure,4,5 valley-selective optical coupling,6–8 large exciton and trion binding energies,9–11 and strong nonlinear optical responses.12–14 Due to these novel properties, MoS2 has been regarded as a promising candidate for applications in field-effect transistors,15 integrated circuits,16 solar cells,17 photodetectors,17 and light-emitting diodes.18

For device applications, it is necessary to modulate and control the electronic and optical properties of the material. It has been well known that lattice imperfections, such as dopants, often determine the physical and chemical properties of crystalline solids. In the development of the semiconductor industry, doping is widely used to control the type and the density of charge carriers and tailor the charge transport properties. For example, p–n junctions formed by the spatially selective doping of silicon is the cornerstone of modern electronic technology. In developing 2D materials, it has been recognized19 that doping will play important roles to control their electrical,20 optical,21,22 and magnetic properties.23

Electron paramagnetic resonance measurements showed that rhenium is the major type of impurity in naturally occurring MoS2 crystals, with a density in the range of 108–1012 cm−2 per layer.24 Most Re atoms are substitutional dopants at Mo sites and do not migrate, as revealed by scanning transmission electron microscopy measurements.20 They do not alter the atomic structure of the system.25 Controllable Re doping in synthesized MoS2 was also demonstrated.20,26 Substitutional Re dopants give rise to shallow donor states that are about 89 meV below the conduction band in bulk MoS2.24 Therefore, Re-doping is n-type, as confirmed by both transport measurements20 and computational studies.20,27

Despite these efforts to understand various basic aspects of Re dopants in MoS2, their effects on optical properties and dynamical properties of photocarriers have not been studied. Optical properties and photocarrier dynamics are important for most optoelectronic applications. For example, the photocarrier lifetime often limits the efficiency of photovoltaic devices. Here we report a comprehensive study on the effects of Re dopants on Raman scattering, optical absorption, photoluminescence, and photocarrier dynamics of monolayer (1L), few layer, and bulk MoS2. We found that Re dopants with a
concentration of 0.6% induce red-shift and broadening of the major phonon Raman modes, red-shift and broadening of excitonic absorption resonances, 15-fold photoluminescence (PL) quenching, reduction of the photocarrier lifetime by about 20 times, and suppression of exciton formation. These results reveal the important impact of Re doping on the optoelectronic properties of MoS2. This information is valuable for evaluating strategies of modulating electronic and optical properties of MoS2 for targeted applications.

2 Experimental section

MoS2 crystals were acquired from 2DSemiconductors. These bulk crystals were prepared by chemical vapor transport under high vacuum of 10^{-6} Torr and at a high temperature of 1050 °C. Elemental precursors of Mo, S, and Re with 6N purity were used. MoCl5 was introduced as the transport agent to eliminate transition metal contamination. For Re-doped crystals, the dopants were introduced as free materials into the sealed vacuum quartz tube. The mixture was kept at a high temperature for 3 months. The temperature difference between the hot zone (precursor) and the cold zone (product) was 50 °C. The Re doping concentration was 0.6% by weight, which corresponds to 0.516 mol%.

Monolayer and few-layer samples were obtained by mechanical exfoliation from these bulk crystals using adhesive tape, which were transferred to 0.5 mm quartz substrates for optical measurements. The thicknesses of the samples were determined by their reflection contrasts.28,29 The samples were kept under the ambient conditions at 300 K for all the measurements.

To obtain the absorbance spectrum, reflection contrast measurements were performed. A 800 nm and 100 fs laser pulse from a modelocked Ti-doped sapphire laser was used to generate supercontinuum radiation from a photonic-crystal fiber. This broadband light was focused on the samples on quartz substrates using an objective lens to a spot size of about 2 μm. The reflected light from the sample was collected using the same objective lens and measured by means of a biased Si photodiode. A lock-in technique was used to measure the differential reflection, which is defined as the normalized change of the probe reflection caused by the pump, \( \Delta R/R_0 = (R - R_0)/R_0 \), where \( R \) and \( R_0 \) are the reflection of the probe with and without the presence of the pump beam, respectively.31

3 Results and discussion

3.1 Sample characterization

Fig. 1 shows the optical microscope image of a Re-doped MoS2 flake that was fabricated by mechanical exfoliation and then transferred to a 0.5 mm quartz substrate. The flake contains regions of different thicknesses. We analyzed the green channel contrast across a line over multiple regions [the red
dashed line in Fig. 1(a)]. Here, the contrast is defined as \[ \frac{C(x) - C_s}{C_s} \], where \( C(x) \) and \( C_s \) are the green channel counts of a pixel at \( x \) and the average counts of the substrate, respectively. The result is shown in Fig. 1(b). One can clearly see a step-like contrast variation, with a step of about 11%. Previously, it has been shown that for thin TMD flakes on transparent substrates, the contrast is proportional to the number of layers.\(^{28,29}\) The step of 11% is in good agreement with the previously established values for TMDs.\(^{28,29}\) We note that in other Re-doped MoS\(_2\) samples fabricated (but not used for optical measurements), the minimal contrast is also close to 11%. Hence, it is safe to conclude that the contrast of 11% corresponds to 1L. We can thus identify various regions of the sample as 1L, 2L, 4L, and 5L, as labeled in Fig. 1.

3.2 Raman spectroscopy

The samples were characterized by Raman spectroscopy with a 488 nm and 1 mW laser beam. The red symbols in Fig. 2(a) show the Raman spectra of Re-doped MoS\(_2\) flakes with different thicknesses, as indicated in the legend. For comparison, the Raman spectra of undoped MoS\(_2\) 1L and bulk were also measured under the same conditions. In all the spectra shown in Fig. 2(a), the left and right peaks can be assigned to the in-plane \(E_{2g}^{1}\) (around 380 cm\(^{-1}\)) and out-of-plane \(A_{1g}\) (around 400 cm\(^{-1}\)) phonon modes, respectively, according to previous studies.\(^{32,33}\) To obtain the precise peak position and FWHM of the two modes, each spectrum was fit by the sum of two Lorentz functions, as indicated by the curves in Fig. 2(a). Fig. 2(b) summarizes the peak positions of the two phonon modes. We observe an increase (decrease) of the Raman shift for the \(A_{1g}\) (\(E_{2g}^{1}\)) mode with the sample thickness. This trend is consistent with previous reports on undoped MoS\(_2\).\(^{32,33}\) We find that the \(E_{2g}^{1}\) mode of Re-doped MoS\(_2\) is red-shifted by about 1.1 cm\(^{-1}\) compared to undoped MoS\(_2\), while the \(A_{1g}\) peak is almost unchanged. For the bulk, both modes show red-shifts of about 1 cm\(^{-1}\) with respect to undoped bulk MoS\(_2\).

Based on previous reports,\(^{34,35}\) the application of strain can red-shift and even split the \(E_{2g}^{1}\) mode of MoS\(_2\) 1L, while the \(A_{1g}\) mode shows no measurable shift. In our Re-doped MoS\(_2\) 1L sample, the red-shift of the \(E_{2g}^{1}\) indicates that the substitutional Re atoms introduce strain to the lattice, as can be expected from their twice-larger atom size. The \(A_{1g}\) mode is strongly coupled to the electrons. The broadening of the \(A_{1g}\) mode can be attributed to the doping carriers introduced by Re.\(^{20}\)

3.3 Steady-state optical properties

We next studied steady-state optical properties of these samples. Fig. 3(a) and (b) show the absorbance spectra of the undoped and Re-doped MoS\(_2\) 1L samples, respectively. For the undoped sample, the A- and B-exciton resonances were clearly observed, which are consistent with previous reports.\(^{36}\) In the

![Fig. 2](image-url)  (a) Raman spectra from regions of different thicknesses of the Re-doped MoS\(_2\) flake (red) and from undoped MoS\(_2\) 1L and bulk samples (black). The blue curves are fits with two Lorentz functions. (b) Peak positions of \(E_{2g}^{1}\) and \(A_{1g}\) phonon modes obtained from the fits. (c) Full width at half maxima (FWHM) of the \(A_{1g}\) peak obtained from the fits.
doped sample, both excitonic resonances are red-shifted and broadened, which could be attributed to the effects of Re-related defect states.\textsuperscript{20,27} Although theory showed that Re dopants introduce deep impurity levels in free-standing MoS\textsubscript{2} 1L,\textsuperscript{37} the dielectric screening of the surrounding materials, such as the substrate, reduces the Coulomb potential and results in shallow energy levels.\textsuperscript{24,37}

Fig. 3(c) shows the PL spectrum of the undoped MoS\textsubscript{2} 1L. Both the peak position and the PL yield are consistent with previous studies on samples of the same type.\textsuperscript{38} The PL spectra of the Re-doped MoS\textsubscript{2} flakes were measured under the same conditions. As shown in Fig. 3(d), the PL yield of 1L is about 15 times smaller than that of undoped MoS\textsubscript{2} 1L. The 2L sample shows a PL peak that is about 10 times weaker than that of the 1L sample. Other doped samples (4L, 5L, and bulk) do not show detectable PL peaks. The thickness dependent PL of the Re-doped samples further confirms that the sample with the smallest optical contrast of 11% is 1L. The strong PL quenching by Re-doping can be attributed to the capture of photocarriers by the defect states and other defect-related non-radiative recombination of photocarriers. Furthermore, it is interesting to note that the PL peak of the Re-doped 1L shows a small blue-shift and no broadening, both in contrast to the absorption measurements. This could be attributed to the different impacts of the dopants on light absorption and emission processes. However, further studies are necessary to fully understand this feature.

\subsection*{3.4 Photocarrier dynamics}

To better investigate the effects of Re-dopants on photocarrier dynamics in MoS\textsubscript{2}, we first studied the photocarrier dynamics in undoped MoS\textsubscript{2} 1L. The sample was pumped by a 388 nm pulse. The differential reflection of a 660 nm probe, tuned to the peak of the A-exciton of MoS\textsubscript{2}, was measured as a function of the probe delay, which is defined as the time delay of the probe pulse with respect to the pump. Fig. 4 shows the results for three different values of the pump fluence. Based on the absorption coefficient of MoS\textsubscript{2} 1L at 388 nm,\textsuperscript{39} a pump pulse with a fluence of 1 \( \mu \)J cm\(^{-2}\) injects a peak carrier density of about \( 2 \times 10^{11} \) cm\(^{-2}\). We find that the decay could be fit by a single-exponential function. The decay constant is independent of the pump fluence, with an average value of 22 ± 3 ps. Since the exciton formation time in TMD 1Ls is as short as 1 ps,\textsuperscript{40–42} the photocarriers are in the form of excitons on a 20 ps time scale. The decay time is thus attributed to the exciton lifetime in undoped MoS\textsubscript{2} 1L.

Next, we studied the photocarrier dynamics in Re-doped MoS\textsubscript{2} 1L. The differential reflection of the 660 nm probe was measured with various values of the 388 nm pump fluence, as shown in Fig. 5(a). Clearly, the signal decays on a much faster time scale. Exponential fits [curves in (a)] were used to determine the decay time constant, which was found to be independent of the pump fluence, as shown in Fig. 5(b) [blue symbol and right axis]. The decay time is about 1 ps, which is about
20 times shorter than that of the undoped sample. We attribute this ultrashort photocarrier lifetime to the efficient Auger recombination of carriers by Re-dopants. The photocarrier lifetime is comparable to the exciton formation time, indicating that the Re-dopants suppress the formation of excitons. The lack of density dependence of the carrier lifetime indicates that exciton–exciton annihilation plays a minor role here.

The red symbols (left axis) of Fig. 5(b) show the peak signal as a function of the pump fluence (bottom axis) and injected carrier density (top axis). The data can be fit using a saturation model, \( \Delta R/R_0 \propto N/(N + N_{\text{sat}}) \), where \( N \) is the injected carrier density and \( N_{\text{sat}} = 1.8 \times 10^{11} \text{ cm}^{-2} \) is the saturation density. To ensure that the probe senses the carrier-induced change of the A-exciton resonance, we repeated the measurement with different probe wavelengths and with a pump fluence of 1.4 \( \mu \text{J cm}^{-2} \). As shown in Fig. 5(c), the signal is only significant when the probe is near the exciton resonance. Both positive (photobleaching) and negative (photon-induced absorption) signals were observed. This is similar to the results from undoped MoS\(_2\).

Finally, we repeated the measurement on a Re-doped MoS\(_2\) bulk sample. The results are summarized in Fig. 5(d)–(f). The decay of the signal is found to be slightly slower than that of the 1L sample, and is still independent of the pump fluence, as shown in (d) and (e). The peak signal is proportional to the injected carrier density (e), and depends sensitively on the probe wavelength (f). These results strengthen our conclusion that Re-dopants significantly reduce the photocarrier lifetime in MoS\(_2\).
The 20-fold reduction of the photocarrier lifetime by Re dopants is well consistent with 15-fold PL quenching. The difference could be attributed to various processes associated with the steady-state and dynamical measurements. Furthermore, the picosecond carrier lifetime is also consistent with the carrier transport properties that was previously studied. With a lattice constant (Mo-Mo) of 0.32 nm and a weight doping concentration of 0.6%, the average distance between two dopants is on the order of 10 nm. Considering the diffusive motion of photocarriers, the average distance an electron–hole pair travels in time \( \tau \) is \( D \tau = L^2 \), where \( D \) is the diffusion coefficient of the photocarriers. Using \( L \approx 10 \text{ nm} \) and \( \tau \approx 1 \text{ ps} \), we find \( D \approx 1 \text{ cm}^2 \text{s}^{-1} \). Previous measurements have shown that for TMD 1Ls, the exciton diffusion coefficient is on the order of 10 \( \text{cm}^2 \text{s}^{-1} \). Since the Re-dopants are expected to reduce the mobility and the diffusion coefficient of the sample by introducing additional scattering mechanisms, we find that the picosecond photocarrier lifetime is reasonably consistent with the diffusion-limited Auger recombination at Re sites.

The reported effects of Re doping on photocarrier dynamics and optical properties of MoS_2 are important for developing doping strategies for optoelectronic applications. It is also useful for understanding behaviors of nominally undoped MoS_2, since Re is the most common impurity in MoS_2. Furthermore, the effective control of photocarrier lifetime by Re doping can be utilized in developing fast optoelectronic devices. It was known during the development of GaAs-based optoelectronic devices that an ultrashort photocarrier lifetime can be advantageous for some applications. For example, low-temperature-grown GaAs thin films with a photocarrier lifetime of less than 1 ps can achieve high-speed terahertz emitters and detectors, because the carriers injected by the femtosecond gating pulse can quickly recombine. Low-temperature-grown Be-doped InGaAs/InAlAs multiple quantum wells with a short photocarrier lifetime can achieve ultrafast optical switching. Hence, Re-doped MoS_2 can be explored for 2D-material-based high-speed optoelectronic devices.

4 Conclusion

We have performed a comprehensive study on the effect of Re dopants on optical properties and photocarrier dynamics in MoS_2 monolayer, few-layer, and bulk samples. We found that with 0.6% (weight) Re doping, MoS_2 maintains its lattice structure and band structure, evident from the Raman, absorption, and photoluminescence spectra that are similar to those of undoped samples. Re dopants introduce lattice strain and charge doping, which are probed by the red-shift and broadening of the phonon modes in Raman spectra. Compared to the undoped samples, we observed a 15-fold PL quenching in the Re-doped MoS_2 monolayer. The photocarrier lifetime was reduced to 1 ps, which is about 20 times shorter than that in the undoped monolayer. Similarly short photocarrier lifetime was also obtained in a doped bulk sample. These results are valuable for evaluating strategies for modulating electronic and optical properties of MoS_2 for targeted applications.

Conflicts of interest

There are no conflicts to declare.

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