Carrier Trapping by Oxygen Impurities in Molybdenum Diselenide

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Supporting Information

ABSTRACT: Understanding defect effect on carrier dynamics is essential for both fundamental physics and potential applications of transition metal dichalcogenides (TMDs). Here, the phenomenon of oxygen impurities trapping photoexcited carriers has been studied with ultrafast pump-probe spectroscopy. Oxygen impurities are intentionally created in exfoliated multilayer MoSe2 with Ar+ plasma irradiation and air exposure. After plasma treatment, the signal of transient absorption first increases and then decreases, which is a signature of defect-capturing carriers. With larger density of oxygen defects, the trapping effect becomes more prominent. The trapping defect densities are estimated from the transient absorption signal, and its increasing trend in the longer-irradiated sample agrees with the results from X-ray photoelectron spectroscopy. First-principle calculations with density functional theory reveal that oxygen atoms occupying Mo vacancies create mid-gap defect states, which are responsible for carrier trapping. Our findings shed light on the important role of oxygen defects as carrier trappers in TMDs, and facilitate defect engineering in relevant materials and device applications.

KEYWORDS: carrier trapping, defect, oxygen impurity, MoSe2

1. INTRODUCTION

In the past few years, layered materials transition metal dichalcogenides (TMDs) have attracted numerous research interests because of their extraordinary properties, such as direct band gap in monolayer samples,1 stable excitons and trions at room temperature,2 superior immunity to short channel effects,3 and strong spin–valley coupling,4 which make TMDs promising for applications in nano- and flexible electronics, photonics, and valleytronics. For many of these TMD-based devices, it is essential to understand the physics of carrier-related interactions5 and to acquire carrier transport properties that determine the key performance metrics (e.g., bandwidth and responsivity), such as carrier lifetime,6 diffusion coefficient,7,8 and mobility.8

Defects inside TMDs or from their environments (substrates and surface adsorbates) can interact with excitons/carriers and significantly affect the functionalities of the electronic devices. For example, the chalcogen vacancy defect9 and its related complex10 are able to activate additional defect-associated photoluminescence (PL) channels, which can decrease the intrinsic exciton PL efficiency. Charged impurity scattering due to either the ionized impurities inside TMDs11 or charge traps at the surface of the substrate12 has been proposed to be the dominant factor for the observed low room-temperature mobility in TMD devices. Charge traps at the TMD-gate insulator interface have also been suggested as the cause of hysteresis in TMD-based field-effect transistors.13 Some defects can also serve as recombination centers, assisting the recombination of the photoexcited excitons/carriers in exfoliated few-layer and multilayer TMDs via Auger scattering.14,15

Even though the defect-trapping effect from oxygen impurities was proposed to be responsible for the previously observed phenomena in chemical vapor deposition (CVD)-grown monolayer and multilayer MoSe2,16 direct evidence and mechanisms about how these impurities are introduced into the samples, and more importantly, their effects on the electronic band structure and carrier dynamics are still not fully understood. In this paper, we intentionally created oxygen defects in exfoliated multilayer MoSe2 by plasma irradiation and then studied and verified the effect of the generated oxygen defects on the photoexcited carrier dynamics with femtosecond...
laser pump-probe spectroscopy. The optical signature of carriers being trapped by mid-gap defects is observed after plasma irradiation, and the defect-capturing-carrier effect increases with oxygen defect density. Our experimental findings, along with a band structure calculation with density functional theory (DFT), confirm the carrier-trapping role of oxygen impurities in MoSe2 and provide important implications for defect engineering in TMD-based devices.

2. RESULTS AND DISCUSSION

2.1. Ar+ Plasma Irradiation and XPS Characterization

Multilayer MoSe2 samples were mechanically exfoliated from the commercial MoSe2 crystal (two-dimensional semiconductors) onto a SiO2/Si substrate using a scotch tape. Because it has been found that the defect-trapping exciton/carrier phenomenon occurs regardless of the sample thickness, indicating that the sample thickness is not a crucial factor, a relatively thick flake [80 nm thickness confirmed by atomic force microscopy (AFM), see Supporting Information] with lateral dimensions >20 μm was chosen to provide large enough sample area for our laser spot (20 μm in diameter).

Plasma irradiation is an effective means to generate defects in TMD materials or to reduce the thickness of layered materials. It has been demonstrated that oxygen impurity can be created in MoS2 samples after Ar+ plasma treatment. Initially, the Ar+ plasma generates vacancies and new edge defects, and then the vacancies and the new edges will be occupied or oxidized by oxygen atoms once exposed to air. Following this method, we performed two sequential Ar+ plasma irradiations on our MoSe2 sample using a reactive ion etcher (Plasma-Therm 790 RIE). The recipe used in the plasma treatment is 50 W power, 200 mTorr pressure, 20 sccm Ar flow rate but with 30 s irradiation time for the first treatment and 300 s for the second treatment. To verify the generation of defects, as well as to identify the defect species, we measured the samples with X-ray photoelectron spectroscopy (XPS) after each plasma treatment, as shown in Figure 1. Before plasma irradiation, Mo 3d5/2 and Mo 3d3/2 peaks, located at 228.5 and 231.6 eV, respectively, and Se 3d5/2 and Se 3d3/2 peaks, located at 54 and 54.8 eV, respectively, can be observed. These peak positions agree with the reference values of Mo-Se bonding. After the first plasma treatment (30 s), four new peaks appear, located at around 232.3, 235.4, 58.6, and 59.4 eV. Comparing with the literature results, two of these peaks originate from the electrons in the Mo 3d shell with j = 5/2 and j = 3/2 in Mo–O bonds and the other two peaks from the electrons in the Se 3d shell with j = 5/2 and j = 3/2 in Se–O bonds, respectively. The observation of these peaks indicates that we have successfully created oxygen impurities with chemical bonds to both Mo and Se atoms in the material. After the second plasma treatment, for which the irradiation time is 10 times of the first treatment, the relative intensities of the Mo-Se bonding peaks decrease, whereas those of the Mo-O and Se-O bonding peaks increase. This indicates that more Mo-Se bonds were destroyed and more oxide bonds were created, that is, the density of oxygen impurities increases, with the longer irradiation time.

2.2. Differential Reflection in Pristine Exfoliated MoSe2

The controllable generation of oxygen impurities allows us to investigate their effect on carrier dynamics by directly comparing the differential reflection signals before and after plasma treatments. We measured the differential reflection, \( \Delta R/R_0 = (R - R_0)/R_0 \), with femtosecond laser pump-probe spectroscopy, where \( R_0 \) and \( R \) are the reflections of probe pulse before and after excitation by the pump pulse, respectively. The laser pulses are generated from a Ti:sapphire
femtosecond laser oscillator, with about 100 fs pulse width, 800 nm central wavelength, and 80 MHz repetition rate. Figure 2a shows the obtained ΔR/R₀ signals at different pump fluences before plasma treatments. All of the signals show negative exponential decays. Figure 2b illustrates the carrier generation and relaxation dynamics in bulk MoSe₂. Because the energy difference between the conduction-band minimum and the valence-band maximum at the K point is around 1.51 eV, we can generate and detect electrons and holes in the K valleys nearly resonantly with 800 nm pump and probe pulses, respectively. When probing resonantly, the change in absorption caused by the phase-space-filling effect is mainly due to the change in absorption caused by the phase-space-filling effect. Details about the relation between the differential reflection and the refractive index change can be found in the Supporting Information. The optical penetration depth of our laser in the MoSe₂ material is about 55 nm, comparable to the sample thickness. In this case, the reflection of the multilayer MoSe₂/SiO₂/Si structure needs to be calculated by the transfer matrix method, and the derived expression is

\[
R = \left[ r₁ e^{i(\phi₁ + \psi₁)} + r₂ e^{-i(\phi₂ + \psi₂)} + r₁ e^{-i(\phi₁ + \psi₁)} + r₂ e^{i(\phi₂ + \psi₂)} \right]²
\]

where \( r₁ = \frac{\alpha₁ - \alpha₂}{\alpha₁ + \alpha₂} \), \( r₂ = \frac{\alpha₃ - \alpha₄}{\alpha₃ + \alpha₄} \), and \( \alpha_i = \frac{\rho_i}{\rho_i + i\kappa_i} \) are the complex amplitude of reflection coefficients for air/MoSe₂, MoSe₂/SiO₂, and SiO₂/Si interfaces, respectively; \( \rho_i \) is the complex refractive index of each material (note that positive \( \kappa \) stands for absorption); and \( \phi_i = 2\pi \sigma_i d/\lambda \) is the complex phase shift due to a change in the optical path and the absorption in MoSe₂ or Si.

Using eq 1, the relative reflection change, \( \Delta R/R₀ \), is plotted as a function of \( \Delta \kappa/\kappa \) in the inset of Figure 2a. It can be seen that the reflection change is proportional to the absorption change with a positive slope. Therefore, the observed negative reflection change means that the absorption in the sample decreases after the pump excitation due to the phase-space-filling effect. When the excited carriers occupy the K valleys and reduce the relevant direct transition probability due to Pauli blocking, absorption of the probe becomes less compared with that before pump excitation. In Figure 2a, there are two decay components in the negative reflection change signals, with the fast one only lasting for several picoseconds and the slow one persisting for several hundred picoseconds. The fast decay component can be attributed to carrier redistribution (mainly from the carrier cooling effect) via intravalley and intervalley scatterings, which are accomplished by numerous processes of carrier–carrier scattering and carrier–phonon scattering, as shown in Figure 2b. The slow decay component depicts the recovery of the reduced direct transition probability back to the unexcited level, which reflects the decrease of the excited carrier population in the K valleys, as also shown in Figure 2b. Note that the \( \Delta R/R₀ \) signal should only be sensitive to the carriers in the K valleys (see Supporting Information for details). The decay rate of the slow component increases with the pump fluences (see the Supporting Information for the normalized \( \Delta R/R₀ \) signals), indicating that many-body effect (very likely the Auger process) is responsible for carrier recombination at high carrier densities.

2.3. Comparison of Differential Reflections before and after Plasma Irradiation. The comparison of \( \Delta R/R₀ \) signals before and after the first and second plasma treatments is shown in Figure 2c. At low pump fluences, one prominent feature of \( \Delta R/R₀ \) after plasma irradiation is the sign change of the signals from negative to positive, indicating that the absorption first decreases and then increases. Such a sign-changing transient signal, that indicates of an initial decrease followed by an enhancement in absorption, has been observed in a number of defected materials, such as low temperature-grown (LTG) traditional semiconductors grown with molecular beam epitaxy (LTG-GaAs, LTG-InP, and LTG-InGaP) and CVD-grown layered MoSe₂ films, and is well-accepted as the signature of defect-capturing-carrier phenomenon. As shown in Figure 2b, when electrons (holes) are just excited into the conduction band (the valence band), the phase-space-filling effect can cause absorption decrease. However, if the material has a considerable amount of mid-gap defects, the excited carriers will be quickly captured and trapped by those...
mid-gap defects. Once the carriers are captured, an additional absorption channel for the probe, that is, the transition from the localized defect states which possess broad moments to high energy states in the conduction band (or the valence band for holes), becomes available, leading to an increase in the absorption. In our previous study,\textsuperscript{16} we have observed the carrier-trapping phenomena only in CVD-grown MoSe\textsubscript{2} films, not in exfoliated flakes. The observed difference between CVD films and the exfoliated flakes comes from the oxygen content that could only be found in CVD samples; hence, oxygen impurities have been proposed to be responsible for carrier-trapping events. Our previous observation also rules out the relevance of Se and Mo vacancies because these vacancies can be found in both exfoliated and CVD-grown TMD materials, with similar density for each vacancy configuration.\textsuperscript{33} Here, the fact that the defect-capturing-carrier signature can again be observed after the generation of oxygen impurities in the exfoliated sample by plasma irradiation serves as a strong evidence that oxygen impurities in MoSe\textsubscript{2} samples are indeed the effective carrier trappers. While the negatively decaying black curve in Figure 2c shows the recombination of free K-valley carriers in the untreated sample, the positively decaying red and blue signals in Figure 2c reflect the process of carrier releasing from the defect states back to the valence band, as shown in Figure 2b.

2.4. Dependence of $\Delta R/R_0$ Signals on the Excited Carrier Density. The $\Delta R/R_0$ signals after the first and second plasma treatments at different pump fluences are shown in Figure 3a,b, respectively. The competition between the trapped carriers and the excess free carriers and the defect saturation effect can be investigated from the pump-fluence-dependent $\Delta R/R_0$ signals. Figure 3a,b shows that the sign-changing signals can only be observed at low pump fluences. As pump power increases, the $\Delta R/R_0$ signals will again become totally negative. This is because when the pump fluence is large enough, the excited carrier density will surpass the defect density, so all of the defects will be occupied, and the effects from excess free carriers will arise. In this case, the final $\Delta R/R_0$ signal is a result of two competing mechanisms: the trapped carriers that contribute positively to the signal via providing additional absorption channels and the excess free carriers that contribute negatively to the signal through the Pauli blocking effect. Obviously when the excited carrier density is much larger than the defect density, the effect from excess free carriers will be dominant and the signal will become totally negative, as shown by the results taken at high fluences in Figure 3a,b. At the highest carrier densities, it can be found that the decay time constants of the later part of the $\Delta R/R_0$ signals in the plasma-treated sample and in the pristine sample are close (see Supporting Information for detail), indicating that the overwhelming excess free carriers recover the system to a condition similar to the pristine case.

2.5. Estimation of the Density of Carrier Trappers. Another interesting feature of the $\Delta R/R_0$ signals is the changing trend of the positive plateau values. As the pump fluence increases, the plateau value first increases then decreases and the value around that time delay finally decreases down to the negative region, as marked by the dashed lines in Figure 3a,b. Using the transfer matrix method, with the reflectance at the MoSe\textsubscript{2} surface ($R_0$) and the transmittance into the Si substrate ($T$) known, the absorptance within the MoSe\textsubscript{2} ($A = 1 - R_0 - T$) can be calculated.\textsuperscript{34} With the obtained absorptance and assuming each absorbed photon only generates one electron–hole pair, we convert the pump fluence to the excited carrier density (the validity of this treatment is analyzed in the Supporting Information) and plot the $\Delta R/R_0$ values at time delays marked with dashed lines in a and b, as a function of excited carrier density.
trappers or recombination centers. Thus, the key to answer material, whereas deep mid-gap defects can serve as carrier Shallow defects usually serve as donors or acceptors in a band structure of bulk MoSe$_2$ with O atoms occupying Mo vacancy sites. We have performed DFT calculations to obtain the gap states. We have performed DFT calculations to obtain the creation of oxygen impurities. The density of oxygen impurities reveals the process of the excited carriers being captured by the created oxygen impurities. The density of oxygen impurities can be estimated from the $\Delta R/R_0$ values of the positive plateau, as a function of the density of excited carrier, and the result of the increased defect density in the longer-irradiated sample agrees with the XPS observation. Moreover, DFT calculations show that oxygen atoms in Mo vacancy sites are responsible for the mid-gap defect states that accounts for carrier trapping. Our findings shed light on the understanding of the interaction between charge carrier and oxygen defect in TMD materials and provide important implications for defect engineering in TMD-based devices.

**ASSOCIATED CONTENT**

Supporting Information

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Determination of MoSe$_2$ flake thickness with AFM; analysis of the relation between differential reflection and the refractive index change; analysis of the relative importance of direct transition and indirect transition in the signal detection; normalized $\Delta R/R_0$ signals of the pristine MoSe$_2$; comparison between $\Delta R/R_0$ signals of the pristine MoSe$_2$ and the plasma-treated MoSe$_2$ at high carrier densities; estimation of the excited carrier density; and details of DFT calculation for the band structure of MoSe$_2$ with O atoms occupying Mo vacancy sites. (PDF)

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**CONCLUSIONS**

In summary, we have successfully created oxygen impurities in exfoliated multilayer MoSe$_2$ by Ar$^+$ plasma irradiation. The generation and increase of oxygen defects after each treatment are confirmed by XPS. Transient reflection signals $\Delta R/R_0$ before plasma treatment are composed of two negative fast and slow decays that reflect the inter-/intra-valley scatterings and recombination of the excited carriers. The $\Delta R/R_0$ signals after plasma treatments exhibit a rapid sign change from negative to positive, a signature of defect trapping carriers, revealing the process of the excited carriers being captured by the created oxygen impurities. The density of oxygen impurities can be estimated from the $\Delta R/R_0$ values of the positive plateau, as a function of the density of excited carrier, and the result of the increased defect density in the longer-irradiated sample agrees with the XPS observation. Moreover, DFT calculations show that oxygen atoms in Mo vacancy sites are responsible for the mid-gap defect states that accounts for carrier trapping. Our findings shed light on the understanding of the interaction between charge carrier and oxygen defect in TMD materials and provide important implications for defect engineering in TMD-based devices.

Figure 4. (a) DFT calculation of band structures of bulk MoSe$_2$ without defects and with oxygen atoms sitting in Mo sites. Mid-gap states can be seen clearly when O atoms occupy the Mo vacancies. (b) Atom-projected density of state for MoSe$_2$ with oxygen atoms in Mo vacancy.
The authors declare no competing financial interest.

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**REFERENCES**


