Ultra-low power threshold for laser induced changes in optical properties of 2D molybdenum dichalcogenides

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Abstract

The optical response of traditional semiconductors depends on the laser excitation power used in experiments. For two-dimensional (2D) semiconductors, laser excitation effects are anticipated to be vastly different due to complexity added by their ultimate thinness, high surface-to-volume ratio, and laser-membrane interaction effects. We show in this article that under laser excitation the optical properties of 2D materials undergo irreversible changes in vacuum. Most surprisingly these effects take place even at low steady state excitation, which is commonly thought to be non-intrusive. In low-temperature photoluminescence (PL) we show for monolayer (ML) MoSe₂ samples grown by different techniques that laser treatment increases significantly the trion (i.e. charged exciton) contribution to the emission compared to the neutral exciton emission. Comparison between samples exfoliated onto different substrates shows that laser induced doping is more efficient for ML MoSe₂ on SiO₂/Si compared to h-BN and gold. For ML MoS₂ we show that exposure to laser radiation with an average power in the μW/μm² range does not just increase the trion-to-exciton PL emission ratio, but may result in the irreversible disappearance of the neutral exciton PL emission and a shift of the main PL peak to lower energy.

Introduction

Atomically thin layers of Van der Waals bonded materials open up new possibilities for physics and chemistry on the nanoscale and for new applications in electronics and photonics [1–7]. Here the group-VI transition metal dichalcogenides (TMDs) of the form MX₂, where M=Mo, W and X=S, Se, are of particular interest: these indirect semiconductors in bulk form become direct semiconductors when thinned down to one monolayer (ML), which makes them especially attractive for optoelectronics [8–12].

The optical properties of TMD MLs are most commonly probed in optical spectroscopy: a laser of suitable energy will create an electron–hole pair (exciton) and subsequently the photoluminescence (PL) emission is monitored. This simple technique led to the discovery of ML MoS₂ having a direct bandgap [13–15]. The optical properties are governed by neutral and charged excitons (trions). There are different physical origins of the resident carriers probed in optical spectroscopy: intrinsic dopants, molecules on the ML surface, carriers trapped at the ML-substrate interface [16–19]. Here we show that the excitation laser itself can have profound impact on the optical properties, in particular on the doping and emission from localized states.

We show that this a general phenomenon for MoX₂ MLs by systematically comparing MoSe₂ ML exfoliated from ultra-pure vapour phase transport (VPT) grown samples with commercial samples. In ML MoSe₂ the sharp exciton emission lines at cryogenic temperatures serve as a sensitive probe of the trion-to-neutral exciton PL emission ratio, which indicates presence/absence of additional carriers. As the Ti-doped sample exfoliated from VPT grown bulk is presumably p-type (confirmed in Hall measurements on bulk) an increase of the trion contribution is
consistent with adding holes. We then show that in these MoSe2 sample systems the effect of laser doping is clearest on SiO2 substrates and much weaker in samples exfoliated onto h-BN and Au. Laser induced doping is also studied in ML MoS2. Here exposure to pulsed lasers leads to irreversible changes in the emission spectrum in vacuum: the neutral exciton signature is lost in PL and the main PL emission is shifted in energy below the initial trion emission. This laser engineering of optical properties for ML MoS2 is demonstrated at \( T = 4 \) K and at room temperature.

MoSe2 and MoS2 MLs exfoliated from different bulk samples

Chemical VPT was used to grow MoSe2 and Ti-doped MoSe2 crystals. Molybdenum (99.9999%), selenium shots (99.9999%) and I2, which acted as a transport agent, were sealed in a quartz tube at \( 5 \times 10^{-5} \) Torr vacuum. The precursors (hot end) were kept at 1085 \(^\circ\) C in a three-zone horizontal furnace while maintaining a 55 \(^\circ\) C temperature difference on the cold end (\( \approx 1030 \) \(^\circ\) C) to initiate nucleation and growth [21], see schematic in figure 1(a). To incorporate Ti into MoSe2, the temperature difference between the two ends of the tube varied from 55 \(^\circ\) C to 65 \(^\circ\) C. For comparison bulk MoSe2 crystals were purchased from two-dimensional (2D) semiconductors. The MoS2 bulk was also supplied by 2D semiconductors. Using a dry-stamping technique [22] MLs from different bulk sources were deposited on either SiO2/Si, h-BN [23] or gold substrates. ML thickness was confirmed by several techniques: in optical contrast measurements (figure 1(b)), in Raman spectroscopy [20] (figure 1(c)) and atomic force microscopy (figure 1(d)). The thickness of MoSe2 MLs measures \( \sim 0.7 \) nm in height, and the out-of-plane (\( A_{1g} \)) Raman peak of MoSe2 softens from bulk (blue dashed line) to ML (red dashed line) as shown in figure 1(c) due to much reduced restoring forces acting on individual ML sheets.

Optical spectroscopy techniques

A purpose-build micro-PL set-up is used to record the PL spectra in the temperature range \( T = 4-300 \) K [24]. The sample is placed on three-axis stepper motors to control the sample position with nm precision inside the low-vibration closed cycle He cryostat. MLs were excited with a linearly polarized cw laser (532 or 633 nm wavelength) or with 1.5 ps pulses at 400 nm generated by a tunable mode-locked frequency-doubled Ti:Sa laser with a repetition rate of 80 MHz [25]. In all cases, the excitation spot diameter is diffraction limited \( \ll 1 \) \( \mu \)m, i.e considerably smaller than the ML size of typically \( \sim 10 \) \( \mu \)m \( \times \) 10 \( \mu \)m. The PL emission is dispersed in a spectrometer (\( f = 50 \) cm) and detected with a liquid nitrogen cooled Si-CCD back-illuminated deep-depletion camera.

Effect of laser radiation on optical properties of MoSe2 MLs

Changes of the optical emission of ML TMDs as a function of laser excitation power have been reported many times in the literature. Here two different

![Figure 1](image-url)
scenarios have to be distinguished. On the one hand, creating more carriers (excitons) will induce eventually interactions between free and localized excitons, trions and resident carriers and possibly result in biexciton formation trions and resident carriers and possibly result in biexciton formation. After exposure, the trion intensity increases. The inset shows that the trion’s dissociation energy increases as a function of the $T/X$ ratio, which is a signature of laser-induced doping of the ML. (b) Same as (a) for a Ti-doped MoSe$_2$ ML (exfoliated from a VPT-grown bulk). (c) Same as (a) for MoSe$_2$ ML exfoliated from a commercial (2D semiconductors) bulk crystal. All samples were mechanically exfoliated on 90 nm thick SiO$_2$ layer on top of a Si substrate.

Our target is to distinguish between these two scenarios. A simple approach is to perform power dependent measurements several times to verify if the laser radiation induced irreversible changes to the spectra. For this we start each experiment with pristine, as-exfoliated flakes that we probe at very low laser power ($\mu$W $\mu$m$^{-2}$). We start with low temperature measurements at $T = 10$ K in vacuum ($10^{-6}$ mbar) on MoSe$_2$ samples grown under controlled conditions and exfoliated onto different substrates for comparison.

Panel (a) of figure 2 shows the PL spectrum using an extremely low excitation power of 40 nW (black curve) of ML MoSe$_2$ exfoliated onto SiO$_2$/Si from a VPT grown bulk sample. The PL spectrum of the pristine sample is dominated by strong and spectrally narrow (FWHM $\approx$8 meV) neutral exciton emission ($X$) at 1.66 eV. A much smaller peak attributed to the trion ($T$) is detected at 1.63 eV. The $X$ and $T$ PL energies are in agreement with standard MoSe$_2$ ML samples [41–43]. The PL FWHM for both transitions of just a few meV are among the best reported in the literature and confirm the excellent sample quality of the pristine flakes. After this initial low power measurement, the laser excitation power at this sample position is increased to 40 $\mu$W and kept constant during 4 min (no measurable evolution is detected for longer times). Directly afterwards, the laser power is lowered to 40 nW, to compare with the black curve before laser treatment, and the PL response is measured (red curve). Remarkably, the trion-to-neutral exciton PL emission intensity ratio $T/X$ has significantly changed, indicating strong doping as a result of the laser treatment. Shown in the inset is the trion’s dissociation energy, defined as the difference between the emission energy of the neutral exciton ($E_X$) and the trion ($E_T$), as a function of the $T/X$ PL intensity ratio. In a simple picture, the trion’s dissociation energy can be written as [44]:

$$E_X - E_T = E_F + E_B^T,$$

where $E_B^T$ is the trion binding energy (typically $\approx$25 meV) and $E_F$ is the Fermi level with respect to the bottom of the conduction band for electrons, with respect to the top of the valence band for holes, respectively. The observed linear increase of $E_X - E_T$ when $T/X$ increases is a signature of an increase of the Fermi level, i.e., of the doping of the ML. Panels (b) and (c) of figure 2 show the laser-induced doping of Ti-doped VPT grown MoSe$_2$ MLs and commercial MoSe$_2$ MLs, respectively. For the different sample sets compared in figures 1(a)–(c), exposure to a 40 $\mu$W excitation during 4 min produces an irreversible change in the $T/X$ spectral weight. We have detected irreversible changes of $T/X$ in vacuum even for powers as low as 1 $\mu$W $\mu$m$^{-2}$. Please note that in many optical spectroscopy measurements of TMDs MLs the...
excitation densities are much larger than the ones used in this study.

Although the doping due to the laser treatment is clearly visible in all panels in figure 2, the nature of the doping (n- or p-type) still needs to be determined. Here the results on the Ti-doped VPT sample give helpful indications in figure 2(b): Hall conductivity measurements on the bulk sample before exfoliation indicate p-doping—we therefore assume that the trion in the pristine sample when deposited on SiO2 is positively charged. The T/X ratio increases gradually as the laser power is increased, which would be consistent with extra holes being created by the laser treatment.

**Dynamics of Laser treatment in ML MoSe2**

The dynamics of this laser doping is shown in panel (a) of figure 3 in real-time for a commercial MoSe2 ML exposed to a cw excitation at 230 μW. The evolution of the X and T integrated PL intensity as a function of time is shown in panel (b), where it can be seen that the X intensity presents a first rapid decrease (within seconds) followed by a second slower decrease in a timescale of several minutes. The trion evolution, in contrast, is marked by an increase on similar timescales. Laser treatment for longer than 4 min did not result in any further, measurable evolution of the PL spectrum. The total PL intensity (Trion + exciton) is decreasing in figure 3(b) as more carriers are added, which might be due to the complex interplay between optically bright and dark state of the trion and exciton [45-47].

**Results for ML MoSe2 on different substrates**

In order to check the applicability of this laser-induced doping of MoSe2 MLs for different device geometries, we also exfoliated MoSe2 MLs onto a few-layer h-BN film [23] and also a 50 nm thick gold film. When deposited onto h-BN, only a very small increase of the T emission was observed after 4 min exposure to a cw laser at 50 μW, as shown in panel (c) of figure 3. When deposited on top of a gold layer, no effect of the laser treatment was observed even after 10 min of exposure to a cw laser at 40 μW. In our experiments the MLs exfoliated onto SiO2/Si showed by far the strongest impact of laser radiation on the optical emission properties.
Treatment of ML MoS$_2$ with cw Lasers

The drastic changes of the emission properties of MoSe$_2$ MLs as a function of laser power raise the question if similar effects can be observed in other materials. Below we show our systematic study on ML MoS$_2$ which confirms the strong impact of the excitation laser on the local doping in the layer. Panel (a) of figure 4 shows the time-evolution of the PL signal from MoS$_2$ MLs at $T = 8$ K when exposed to a cw excitation at $60 \mu W$ at 532 nm. Three distinct PL emission peaks are observed, associated to the $X$ (1.96 eV), $T$ (1.93 eV) and spectrally broad localized emission [48], which peaks approximately at 1.85 eV. Please note that under laser illumination, both the $X$ and the localized emission decrease, whereas the trion increases (panel (b) of figure 4). Again, the dynamics is characterized by a fast and a slow component, of several seconds and several minutes, respectively. This correlation between the localized emission and the neutral exciton peak could not be measured in MoSe$_2$ MLs since in this material there is negligible PL stemming from localized states. Also for ML MoS$_2$ the total PL intensity decreases as for ML MoSe$_2$ in figure 3(b).

By exposing different regions of the MoS$_2$ ML to different laser powers, it is possible to control the $T/X$ ratio, and therefore, the doping of the ML. This is demonstrated in panel (c) of figure 4, in which increasing the laser power between 10 and 200 $\mu W$ allows to tune the $T/X$ ratio by almost one order of magnitude. In these experiments we have used different laser power exposure on different sample spots to control the $T/X$ ratio locally. As shown for MoSe$_2$ MLs in figure 2(a), an increase of the trion’s spectral weight is accompanied by an increase of the trion’s dissociation energy. In panel (d) of figure 4, the PL of a MoS$_2$ ML after laser treatment probed subsequently with 0.4 $\mu W$ excitation reveals high doping as inferred from the strong T emission (black curve). By illuminating the same region of the ML with an halogen lamp focused into a spot of $\sim 1 \mu m$, the differential reflectivity of this doped region is obtained. The spectrum plotted in figure 4(d) (red curve) indicates that the $X$ transition is still the dominant absorption mechanism and that no significant shift of the $X$ transition is observed with respect to undoped regions. This suggests that no significant band-gap renormalization is induced by the laser treatment. The same conclusion can be drawn for the MoSe$_2$ MLs studied, as the $X$ peak PL energy (the optical band gap) in figures 2(a)–(c) does not change after the laser treatment.

Figure 4. cw laser treatment of ML MoS$_2$. (a) commercial MoS$_2$ ML exfoliated onto a SiO$_2$/Si substrate. Time evolution of the PL spectrum while being exposed to a cw excitation 532 nm at 60 $\mu W$, revealing $X$, $T$ and localized emission features which evolve over several minutes. (b) $T$, $X$ and localized emission integrated intensity as a function of time for the conditions of panel (a). Both the $X$ and the localized emission decrease as a function of time, while the $T$ gains in intensity. (c) Trion’s dissociation energy as a function of the $T/X$ ratio for a MoS$_2$ ML. The different values of $T/X$ have been obtained by exposing the ML to different laser powers at different positions on the same ML flake. (d) PL spectrum at 0.4 $\mu W$ excitation (532 nm) measured after laser treatment of a MoS$_2$ ML revealing high $T$ emission (black curve). Also shown is the differential reflectivity spectrum (red curve) in which the main absorption is dominated by the $X$ resonance at 1.96 eV, the additional transition at $\approx 2.1$ eV is the $B$-exciton ($X_b$) [13].
Treatment of ML MoS$_2$ with pulsed lasers

Finally, we demonstrate that a further increase of the laser excitation power completely quenches the X emission in MoS$_2$ MLs, as is shown in panel (a) of figure 5. For these more extreme experiments, a pulsed excitation with 80 MHz repetition frequency at 400 nm was used, in contrast to all experiments shown so far carried out with weak cw sources that can be found for example in commercial PL/Raman systems. At the lowest average power used of 0.1 $\mu$W $\mu$m$^{-2}$ (peak power of 600 $\mu$W $\mu$m$^{-2}$), the PL spectrum presents X, T and localized emission. Increasing the average excitation power up to $\sim$25 $\mu$W $\mu$m$^{-2}$ results in a complete disappearance of the X line and a dramatic reduction of the localized emission. Only a broad peak about 20 meV below the T energy is observed, accompanied by a small shoulder at lower energies. The two PL spectra of ML MoS$_2$ before and after laser treatment are totally different. When decreasing the average excitation power back to 0.1 $\mu$W $\mu$m$^{-2}$, a dramatic hysteresis of the PL spectrum is observed, as illustrated by panel (c) of figure 5, similar to experiments using elevated laser power in ML WS$_2$ [28, 36]. Please note that in many studies, the broad peak at $\sim$1.9 eV has been attributed to the neutral exciton emission of MoS$_2$, and that valley-polarization experiments have been often performed with HeNe laser excitation at 1.96 eV, which corresponds to a perfectly-resonant excitation of the neutral exciton transition. These findings demonstrate that for pulsed excitations, a time-averaged power of only a few $\mu$W is enough to change the MoS$_2$ MLs optical properties in a non-reversible way in vacuum. This has to be taken into account when analysing the complex physics probed in time-resolved PL measurements [25, 49], pump-probe [50–53] and Kerr rotations experiments [54, 55], which are often carried out in this excitation power regime.

Many experiments on MoS$_2$ with pulsed or cw excitation are carried out at room temperature [56]. We demonstrate the effect of the excitation laser on the optical spectrum also at $T = 300$ K in vacuum conditions, as shown in panel (b) of figure 5. A clear redshift of the PL peak position is observed and also a hysteresis of the PL at the lowest power used is evident (panel (d) of figure 5). Also shown in this panel is the PL spectrum obtained after letting ambient air back inside the cryostat. The PL intensity increase and the PL maximum shifts back to the neutral exciton emission. After averaging over several MoS$_2$ MLs, it is found that the PL intensity after this cycle is smaller than the intensity obtained on pristine samples in air. This finding suggests that the laser induced changes...
are partially reversible once the ML interacts with the molecules present in air. It should be noted that testing the reversibility of laser treatment by air exposure is more difficult in MoSe₂ MLs since in this material the T emission is not easily detected at room temperature.

**Discussion**

There are several physical processes that can contribute to the modification of the Trion-to-neutral exciton PL emission ratio due to laser treatment. Behind this lie the different physical origins of excess carriers coming from doping of the TMD material, charges trapped at the ML-substrate interface and molecules on the ML surface.

One possibility is that the laser induced changes are purely electronic i.e. due to optical ionization of impurities. These effects can have lifetimes from fractions of second to days [57]. These physical processes were initially uncovered by Staebler and Wronski in hydrogenated amorphous SiO₂ [58]. A possible explanation for the observed phenomena is that the additional charges are optically created from defects in the SiO₂ substrate and are subsequently transferred to the TMD ML. In addition, charges trapped at defects could be optically activated in the TMD ML itself, as suggested by photoconductivity measurements [59]. A charge transfer from SiO₂ to the TMD ML could be suppressed by insertion of an h-BN layer in between [60], which might explain the absence of optical doping for this particular sample in figure 3(c). Molecules present in air can interact with TMD MLs, particularly on defect sites [61], changing the free carrier concentration in the ML. This can explain the observed partial reversibility of this optical doping effect once the MLs are exposed to air.

In figure 3 we see that the laser treatment does not modify the emission for ML MoSe₂ exfoliated onto h-BN or gold. Since the thermal conductivities of h-BN or gold are much larger than that of SiO₂ (κ(SiO₂-amorphous) ≈ 1 − 2 W m⁻¹ K⁻¹, κ(h-BN) ≈ 300 W m⁻¹ K⁻¹ [62] and κ(Au) ≈ 300 W m⁻¹ K⁻¹ [63]), possible thermal effects needs to be considered. For example, the contact between the ML and a good thermal conductor may facilitate heat dissipation and as a consequence prevent the laser-induced doping of the ML. While thermal effects such as local heating may result in defect formation/modification, we can rule them out in our experiments and point to photo-ionization effects as the main mechanism for the observed optical changes, as the neutral exciton transition energy did not shift measurably for ML MoSe₂ [64] or gold are much larger than that of SiO₂ [65]. These physical processes can have lifetimes from fractions of second to days [57]. These physical processes were initially uncovered by Staebler and Wronski in hydrogenated amorphous SiO₂ [58]. A possible explanation for the observed phenomena is that the additional charges are optically created from defects in the SiO₂ substrate and are subsequently transferred to the TMD ML. In addition, charges trapped at defects could be optically activated in the TMD ML itself, as suggested by photoconductivity measurements [59]. A charge transfer from SiO₂ to the TMD ML could be suppressed by insertion of an h-BN layer in between [60], which might explain the absence of optical doping for this particular sample in figure 3(c). Molecules present in air can interact with TMD MLs, particularly on defect sites [61], changing the free carrier concentration in the ML. This can explain the observed partial reversibility of this optical doping effect once the MLs are exposed to air.

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