Role of defects and phonons in bandgap dynamics of monolayer WS$_2$ at high carrier densities

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Keywords: transition metal dichalcogenides, bandgap renormalization, ultrafast dynamics

Abstract

We conduct ultrafast pump-probe spectroscopy in monolayer WS$_2$ at high pump fluences to gain direct insight into interactions between a high density of carriers, defects, and phonons. We find that defects in the lattice play a major role in determining the relaxation dynamics by trapping the photoexcited carriers and acting as non-radiative recombination centers that emit phonons. In the high carrier density regime explored in our experiments, we observe substantial changes in the transient absorbance signal at unexpectedly long-time delays which we attribute to phonon-induced band gap modification. Our probe frequency dependent measurements and modeling indicate a renormalization of the bandgap by up to 23 meV. These results highlight the importance of defects and phonons for optical applications of monolayer transition metal dichalcogenides.

1. Introduction

Monolayer semiconducting transition metal dichalcogenides (TMDs) are a subclass of 2D materials that retain the honeycomb structure of graphene but offer a direct optical band gap in the visible spectrum. TMDs exhibit strongly bound excitonic states in the visible region of the spectrum [1–3], which opens possibilities for a multitude of opto-electronic device applications. For example, the large photo-absorption cross-section could translate into efficient photovoltaic devices by harnessing photoexcited charge carriers. Conversely, charge carriers can be injected into TMD based p-n junction devices to make visible light sources [4]. However, the room temperature photoluminescence (PL) efficiency of TMD samples is low (∼1%) [5] therefore, photodetectors and light emitting diode devices made using TMD materials suffer from low quantum efficiency. In particular chemical vapor deposition (CVD) grown large area samples are known to contain many defects [2, 6] and the electronic states associated with defect sites act as carrier traps and recombination centers for excitons effectively reducing the PL efficiency [7]. Another important factor affecting the non-radiative recombination rate is carrier-phonon interactions. Apart from reducing the PL efficiency, phonon related effects are also responsible for low mobility and current saturation [8–10].

With consideration of the above discussion, further improvements in device efficiency requires better understanding and control of the many-body interactions involved in the photoexcitation and relaxation processes. Various theoretical efforts have concentrated on modelling lateral thermal conductivity [11–13], phonon relaxation lifetimes [14], phonon-mediated free carrier cooling [15] and phonon-induced band structure changes [16]. Experimental work on TMDs has mostly focused on the study of excitonic interactions in the low carrier density regime [6, 17–20]. The limited studies on carrier-phonon interactions have used Raman spectroscopy [21–23] at low carrier density. Work in the high carrier density regime, above the Mott density, has focused mainly on carrier induced bandgap renormalization (BGR) rather than phonons [24–26]. Understanding the high carrier regime is important to many applications, such as lasers, saturable absorbers, and photodetectors, which are limited by relaxation rates in the materials. Additionally,
this regime offers an area of new and exciting physics, where interesting effects such as population inversion, large BGR, and exciton bleaching can be studied.

In this paper, we employ pump-probe techniques to gain direct insight into the evolution of many-body interactions between carriers, defect states and phonons in WS$_2$. In particular, we utilize high pump pulse intensity to create photo-excited carrier densities an order of magnitude above the Mott density to study the role of carriers, defects, and phonons at these high densities. We find that the relaxation of carriers leads to a rich structure in the transient absorbance spectra due to mechanisms associated with carrier-trapping and recombination via defect states. We discover a long lived BGR at high pump fluences that we attribute to carrier-phonon interactions. We use a simple three-level model to simulate the dynamics of photoexcited carriers and determine the phonon induced BGR and relaxation timescales.

2. Methods

Monolayer WS$_2$ samples were grown using a CVD procedure on sapphire substrates [27]. Individual triangular flakes as seen in figure 1(a) are monocrystalline with no domain walls [27, 28]. The absorbance was obtained by measuring the optical reflectivity of the sample (WS$_2$ on sapphire) compared to the sapphire background. If $n_{\text{sub}}$ is the refractive index of the sapphire substrate, $R_0$ and $R_{\text{sub}}$ are the reflection coefficients from the sample and bare sapphire substrate respectively, we calculate the absorbance, $A_0$, of the sample using the relation [29]:

$$\frac{R_0 - R_{\text{sub}}}{R_{\text{sub}}} = \frac{(1 + n_{\text{sub}})A_0}{n_{\text{sub}} - 1}. \quad (1)$$

The absorbance spectrum of the WS$_2$ shown in figure 1(b) has two peaks at 2.0 eV and 2.4 eV corresponding to the A and B excitons, respectively.

For the time resolved experiments, 50 fs pulses from a 1 kHz, 800 nm centre wavelength, Ti:Sapphire laser amplifier were frequency doubled to 400 nm and modulated at 200 Hz with a mechanical chopper to be used as the pump beam. The pump fluence was 1500 $\mu$J cm$^{-2}$. Wavelength-tuneable laser pulses ($\sim$50 fs) in the range 600 nm $-$ 650 nm from an optical parametric amplifier (OPA) were used to probe the pump-induced reflectivity changes in the WS$_2$ sample. The FWHM spot size of the laser (3 $\mu$m) was much smaller than the monocrystalline WS$_2$ flakes. The pump and probe beams were cross-polarized to reject the pump scatter at the detector. If $R_0$ and $R(t)$ represent the sample reflectivities measured by the probe in absence of the pump and at time delay $t$ after the pump excitation, respectively, the pump-induced change in reflectivity of the probe beam, $\Delta R(t) = R(t) - R_0$, and consequently the differential reflectivity, $\frac{\Delta R(t)}{R_0}$, can be measured using a lock-in detection scheme. We independently verified that the sapphire substrate shows no pump induced reflectivity changes and the signal we measure is due to the WS$_2$ sample. The differential reflectivity can be converted to pump-induced absorbance change, $\Delta A(t)$, using equation (1).

$$\Delta A(t) = \frac{\Delta R(t)}{R_0} \left( A_0 + \frac{n_{\text{sub}} - 1}{1 + n_{\text{sub}}} \right). \quad (2)$$

3. Results

After photoexcitation, a host of multibody processes dictate the transient change in absorbance, such as phase space filling [30], spectral broadening [31], stimulated emission [32], and carrier-phonon interactions.
Figure 2. Differential absorbance curves for WS$_2$ at probe energies of (a) 1.92 eV (red shifted from A-peak), (b) 2.00 eV (on resonance with A-peak) and (c) 2.07 eV (blue shifted from A-peak) with a pump fluence of 1500 µJ cm$^{-2}$. Calculated differential absorbance curves obtained using our rate equation model are overlaid as solid red lines. Insets: schematic of the transitions and the probe energy, where the black and green lines represent the ground and exciton levels, respectively.

To gain insight into the carrier dynamics, we measure the spectral variation of the transient absorbance near the excitonic resonance by varying the wavelength of the probe beam while keeping the pump wavelength and fluence fixed. The results of time-dependent transient absorption data for three probe wavelengths are shown in figure 2. The data are acquired using probe energies slightly below resonance (figure 2(a)), on resonance with (figure 2(b)) and slightly above resonance (figure 2(c)) of the A exciton in the unperturbed case. From the absorbance of WS$_2$ (figure 1(b)), we estimate an initial photoexcited carrier density of $2 \times 10^{14}$ cm$^{-2}$ in this case, which is above the Mott density at which bound excitons cease to exist [34].

In the short timescale (less than 3 ps), the three curves in figure 2 all exhibit a sharp Pauli blocking dip followed by an increase in transient absorbance. This behaviour corresponds to the following sequence of events. The pump pulse excites carriers into the conduction band which quickly lose energy via intraband scattering within a picosecond. The increase in the population of carriers results in Pauli blocking and reduces the absorption of the probe beam consequently causing a dip in the transient absorbance. The strength of the Pauli blocking dip is determined by the population of carriers within the bandwidth of the probe laser around the excitonic resonance. Thus, the absorbance near time delay zero initially decreases. The carriers are quickly trapped by the defects and localized on the order of 1 – 2 ps [6, 7, 35]. The Pauli blocking dip is then followed by an increase in transient absorbance, which is attributed to the absorption of the probe by the carriers trapped in the midgap defect states [6, 36–40]. All defect-captured carriers represent possible initial states for probe absorption to higher lying final states. This positive absorption competes with the absorption dip due to Pauli blocking. This absorption channel causes an increase in $\Delta A$ that immediately follows the Pauli blocking dip. The existence of defect states responsible for this absorption increase is confirmed in our CVD grown sample in the low temperature (4.3 K) PL spectrum obtained with a monochromatic light source, as shown in figure 1(c). The low fluence of monochromatic light implies low carrier densities and strong tendency towards the formation of excitonic states. The broad peak labelled ‘LE’ (for Localized Excitons) at 1.95 eV represents excitons that are trapped at defect sites [17]. The narrow peak labelled ‘FE’ is the free exciton peak which is blue shifted by about 60 meV from its position at room temperature (RT) due to carrier-phonon interactions. The width of the LE peak in figure 1(c) is indicative of a broad range of defect energies. In TMDs, defects such as metal atom vacancies, chalcogen atom vacancies, oxygen interstitial and grain boundaries have been identified using a variety of techniques such as TEM, XPS, STM, Raman spectroscopy and PL spectroscopy [6, 7, 35, 41–47]. Carrier trapping by defects related to oxygen substitution has been observed in CVD grown TMDs [6, 36, 48]. Typically, carrier trapping by defects is followed by the slow ($\sim 10 – 100$ ps) release and recombination of trapped charges. As we discuss later, in
addition to carrier-induced BGR, phonons emitted during the recombination process play an important role in the BGR, which affects the transient absorption signal at longer pump-probe time delays.

The process described above is highly dynamic as the intraband scattering timescale and defect capture timescale are commensurate (∼1 ps) [2, 49]. We note that there are additional contributions to the dynamics from Auger recombination and carrier-induced BGR. Carrier induced BGR can cause a red shift in the absorption spectrum therefore a decrease in the transient absorbance signal (larger dip) at the location of excitonic resonance [24, 26, 50] with increasing pump fluence. Defect-assisted fast Auger recombination has been proposed as a non-radiative pathway for relaxation in the few-picosecond regime. This partially counters the effect of Pauli blocking (smaller dip).

Overall the experimental data demonstrates that the absorption from defect trapped carriers dominates at high fluences, resulting in a weak dip followed by a fast upswing in transient signal. The upswing in signal does not continue beyond a few picoseconds and the transient absorption reaches a local maximum, from where it starts to decrease again. This behaviour at longer time delays can be seen most clearly in the ‘on-resonance’ (figure 2(b)) and ‘above resonance’ (figure 2(c)) scans. This observation requires a new mechanism as discussed below.

At the high excitation densities used in our experiments, another important mechanism for the spectral shift of the excitonic absorption peak is phonon induced BGR, which is expected to have a later onset, and has not been explored in previous studies. The differential absorbance at the three probe photon energies shows qualitatively different behaviour in the 3 ps to 30 ps delay range. Beyond 30 ps, all curves exhibit a slow (∼100 ps) evolution to the baseline level, which is attributed to trapped carriers being released through non-radiative recombination. This process reduces the population of carriers in the system and the excess energy is released as phonons leading to lattice heating. The timescale of this mechanism is slower than that of carrier trapping and experimentally measured values range from 10 ps to 800 ps [6, 35, 36, 48, 51, 52] depending on the doping levels and defect density of the sample.

The magnitude and sign of the transient absorbance signal between 3–30 ps, and the turning point at ∼20 ps strongly depends on the probe photon energy. This broad feature is positive at a probe energy of 1.92 eV, negative at 2.00 eV and slightly negative at 2.07 eV as seen in figures 2(a)–(c) respectively. The change in sign of ΔA with increasing probe energy indicates an optical BGR effect corresponding to a red shifted absorption profile [31, 50]. However, the late onset of the feature rules out carrier-carrier interactions as a possible cause for BGR since the carrier population is maximum immediately following the incidence of the pump pulse and any carrier induced renormalization must maximize at short (∼100 fs) time delays. The
same argument rules out other carrier-population induced effects such as exciton–exciton annihilation, bi-exciton formation, intra and intervalley dark excitons, stimulated emission etc as the cause of the broad peak near $t \sim 20$ ps.

4. Discussion

Based on the sign and magnitude of transient absorption signals at long time delays, and the arguments presented above, phonon induced BGR emerges as the primary mechanism causing the late onset absorption change is. Phonons are emitted during the relaxation of photoexcited carriers and during the slow non-radiative recombination of carriers at defect sites. There is ample evidence for the existence of phonon induced renormalization in the literature. Calculations predict a large cross section for carrier-phonon interaction in TMDs [16, 19, 33, 53]. *Ab-initio* calculations for MoS$_2$ have predicted a large optical phonon-induced renormalization of the excitonic peak [50]. Previous work has shown a bleaching of the exciton peak lasting $\sim 5$ ps, followed by a long lived red shift of the exciton peak [24]. Multi-phonon assisted recombination at defect sites has been proposed as the mechanism responsible for carrier relaxation in InGaAs/GaAs quantum dots [34, 55]. Recently, a two-level recombination mechanism for defect mediated recombination through phonon emission was proposed to explain the non-radiative recombination rate of excitons in CdTe [56]. Therefore, we invoke phonon-induced BGR to develop a phenomenological description of the probe wavelength dependence observed in the transient absorption results.

To understand how phonon induced BGR is responsible for the observed dynamics, we propose a simple three-level model to simulate the dynamics of photoexcited carriers in TMDs. This model allows the magnitude and timescales of various many-body effects to be separated. The energy schematic of our model is shown in figure 3(a). The three states considered are the carriers $|C\rangle$, defect-trapped states $|D\rangle$ and the ground state $|G\rangle$. The various relaxation pathways and associated timescales are shown in figure 3(a). The phonons emitted during defect-assisted recombination are denoted by the red wavy line.

The population dynamics of the photoexcited TMD are described by the system of coupled differential equations:

$$\frac{dn_c}{dt} = \frac{\eta I(t)}{\hbar \omega} - \gamma_{cap} n_c$$  \hspace{1cm} (3)

$$\frac{dn_{cap}}{dt} = \gamma_{cap} n_c - \gamma_{rel} n_{cap}$$  \hspace{1cm} (4)

$$\frac{dn_{ph}}{dt} = \gamma_{rel} n_{cap} - \frac{n_{ph}}{\tau_{ph}}$$  \hspace{1cm} (5)

where $I(t)$ is the incident pump excitation with a 50 fs Gaussian profile centered at energy $\hbar \omega$; $\eta$ is the absorbance of monolayer WS$_2$ at the pump energy; $n_c$, $n_{cap}$ and $n_{ph}$ are the population of carriers in the conduction band, population of carriers in the defect states and phonon population respectively. For simplicity, we ignore the difference between the capture (and release) times of electrons and holes. $\gamma_{cap}$ is the carrier capture rate of defect states, $\gamma_{rel}$ is the carrier release rate from defects which generates phonons and $\tau_{ph}$ is the phonon relaxation time. $\gamma_{cap}$ is fixed at $1.0 \times 10^{12}$ s$^{-1}$ to be comparable to previous studies in TMDs [6, 7]. This parameter only affects the fast dynamics at time delays less than 5 ps and does not affect the behaviour of the model in the later time delay regime where the slower phonon related dynamics are active. As carriers are released and undergo non-radiative recombination, phonons are released. The factor $k$ in equation (5) is a constant giving the number of phonons released per recombination event, and phonon population divided by $k$ can be defined as the number of phonon creation events. The time-dependent evolution for $n_c$, $n_{cap}$ and $n_{ph}/k$ is shown in figure 3(b). Initially, carrier populations reach far above the Mott density, which is approximately $1 \times 10^{13}$ cm$^{-1}$. After approximately 30 ps, the carrier populations have decayed below the Mott density.

After solving the above equations, the differential absorbance is modelled using a linear relation:

$$\Delta A(\omega, t) = \alpha_c n_c(t) + \alpha_{cap} n_{cap}(t) + \cdots$$

$$\Delta A_{BGR}(n_c(t), n_{cap}(t) , \omega)$$.  \hspace{1cm} (6)

Where the coefficient $\alpha_c$ determines the contribution of Pauli blocking and carrier-induced bleaching of the exciton level and $\alpha_{cap}$ determines the defect-induced absorption. The third term in equation (6) is the
contribution to the transient absorbance signal due to BGR from defect trapped carriers and phonons as a function of the populations of the carriers in the defect states, the population of phonons, and the probe energy $\omega$. At long time delays (>30 ps), the BGR due to the population of phonons dominates as the defect trapped carriers are released. Mathematically, this is represented as the unperturbed Lorentzian associated with the absorption profile subtracted from a perturbed Lorentzian which is shifted and broadened by an amount proportional to the populations of carriers and phonons. At each probe energy $\omega$, we sample over a Gaussian distribution to model the probe spectrum. The values of each $\alpha$ coefficient, $\gamma_{rel}$ and $\tau_{ph}$ are varied to simultaneously fit the three experimental data plots in figure 2. The value of the carrier release rate, $\gamma_{rel}$, is obtained as $3.22 \times 10^{10}$ s$^{-1}$ which is a best fit to the data. This value is of the same order of magnitude as that of carrier-capture timescales measured in previous works [6, 35, 36]. We obtain good fits to the data, as shown by the solid lines in figure 2, with the value $\tau_{ph} = 36$ ps for all three probe energies, which is similar to what previous studies have found [51, 52].

Figure 4(a) shows the background subtracted Lorentzian absorbance profile of the A-exciton of WS$_2$ at room temperature (black) and the same peak broadened ($\Delta \Gamma$) and red shifted ($\Delta E$) (orange) due to phonon induced renormalization [16, 31, 48]. The difference between the curves ($\Delta A_{BGR}$) represents the contribution of the third term in equation (6). Looking at figure 4(a), the absorbance at 20 ps is higher for 1.92 eV, and lower for 2.00 eV and 2.07 eV, leading to the maximum and the minima absorbance values around 20 ps in figure 2. The absorbance peak shifts and broadens as the number of phonons induced changes, leading to changes in the differential absorbance as a function of time. The complete differential absorbance as a function of energy and time is shown in figure 4(b). By comparing the values of $\Delta A_{ph}$ at the our probe energies to the value of the phonon-induced renormalization ($\Delta A_{BGR}$) extracted from the model, we deduce a maximum energy shift $\Delta E \sim 23$ meV and broadening $\Delta \Gamma \sim 36\%$ due to BGR.

While the above results are obtained by allowing both the carrier release rate and phonon lifetime to be free parameters as shown by the red point in figure 5, it is also possible to fix the phonon lifetime and repeat the fits. Theoretical calculations have given a large range for the phonon lifetimes [51, 52, 57], and we can explore how our fit quality changes with variation of this parameter. We are able to obtain good fits with a range of phonon lifetimes from 5 – 100 ps. The relationship between the carrier release rate and phonon lifetime along with the residuals from the fits are shown in figure 5. As the phonon lifetime decreases, the carrier release rate must also decrease which essentially ensures that the number of phonons in the system stays roughly constant so that the phonon induced BGR is sufficient to produce the changes in absorption observed in figure 2.

The redshift of the excitonic peak with increasing temperature can be modelled using a variant of the Varshni equation [58].

$$E_X(T) = E_X(0) - S(\hbar \omega) \left[ \coth \left( \frac{\hbar \omega}{2k_B T} \right) - 1 \right]$$

Figure 4. (a) Unperturbed absorbance at room temperature from figure 1(b) (black) and absorbance obtained at maximum renormalization (orange), at approximately 20 ps. (b) Change in absorbance, given by renormalized absorbance minus unperturbed absorbance, as a function of time and energy.
Figure 5. Top: The carrier release rate, $\gamma_{\text{rel}}$, as a function of the phonon lifetime. For each point, the phonon lifetime is fixed and the recombination rate is obtained from fitting the three differential absorbance curves in figure 2 simultaneously. The red point is the best fit leaving the recombination rate and phonon lifetime as a free parameter. The dashed red lines show the best fit region. Bottom: the residual squared for each fit.

Here, $T$ is the lattice temperature, $S$ is a constant proportional to the electron-phonon coupling and $\langle \hbar \omega \rangle$ is the average phonon energy. The parameters, $S = 2.47$, and $E_X(0) = 0.288\text{eV}$, were obtained from cold PL data [59]. At room temperature, the value of the average phonon energy that couples to the carriers, $\langle \hbar \omega \rangle$, is predicted to be close to that of optical phonons in WS$_2$ (50 meV) [16]. Using equation (7), we can calculate the lattice temperature as 500 K. Using the bulk heat capacity value of WS$_2$ [60] and absorbance of WS$_2$ at 400 nm (0.16), if the entire photon energy at a fluence of 1500 $\mu$J cm$^{-2}$ is converted to lattice heating, the increase in temperature is $\sim$800 K. Therefore, we estimate that about a quarter of the excited carriers relax via phonon-mediated recombination as we only observe a 200 K increase in temperature.

5. Conclusions

In summary, the presence of defect states modifies the transient absorbance via carrier-trapping and recombination. The transient absorbance signal is dominated by carrier-carrier interactions at short time delays and carrier-phonon interactions at longer time delays. At the high excitation densities generated in our experiment, phonon-induced BGR becomes significant, leading to a red-shift of the excitonic resonance of up to 23 meV. The phonon-induced effects are delayed compared to carrier-induced effects due to the slow build-up of phonons generated during carrier recombination at defect sites. Using a simple three-level rate equation model, we isolate the phonon-induced contribution to the transient absorbance dynamics. We estimate the relaxation time scale for phonons in WS$_2$ between $20 - 45$ ps. Strong phonon-induced optical BGR has been previously predicted in theory for MoS$_2$ [16]. To our knowledge, ours is the first time-domain measurement of the phonon-induced BGR and phonon relaxation time in TMDs. Our results elucidate the importance of many-body interactions between carriers, defects and phonons in the optical properties of TMD based devices.

Acknowledgments

DG, AD, and AS acknowledge support from NSF award Nos. 1912455 and 1919486. BJL and AB were supported by the US Army Research Laboratory and the US Army Research Office under Contract Grant Nos. W911NF-14-1-0653 and W911NF-20-1-0215. BC and ST were supported by NSF DMR-1552220. JS acknowledges support from NSF award No. ECCS-1708562, Science Foundation of Arizona award No. BSP 0821-17, and AFOSR award No. FA9550-17-1-0215.

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