Second-harmonic imaging microscopy for time-resolved investigations of transition metal dichalcogenides

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Abstract

Two-dimensional transition metal dichalcogenides (TMD) have shown promise for various applications in optoelectronics and so-called valleytronics. Their operation and performance strongly depend on the stacking of individual layers. Here, optical second-harmonic generation in imaging mode is shown to be a versatile tool for systematic time-resolved investigations of TMD monolayers and heterostructures in consideration of the material’s structure. Large sample areas can be probed without the need of any mapping or scanning. By means of polarization dependent measurements, the crystalline orientation of monolayers or the stacking angles of heterostructures can be evaluated for the whole field of view. Pump-probe experiments then allow to correlate observed transient changes of the second-harmonic response with the underlying structure. The corresponding time-resolution is virtually limited by the pulse duration of the used laser. As an example, polarization dependent and time-resolved measurements on mono- and multilayer MoS\textsubscript{2} flakes grown on a SiO\textsubscript{2}/Si(001) substrate are presented.

Keywords: second-harmonic generation, pump-probe experiment, transition metal dichalcogenides, time-resolved nonlinear optical spectroscopy, second-harmonic generation imaging microscopy

Supplementary material for this article is available online\footnote{Some figures may appear in colour only in the online journal}

1. Introduction

Two-dimensional (2D) materials have been intensively investigated since the first successful isolation of graphene \cite{1} and this interest has been stimulated further by the discovery of the special properties of single-layer transition metal dichalcogenides (TMD) \cite{2, 3}. Van der Waals coupled 2D materials now span the whole range from metallic over semiconducting up to isolating materials and their combination leads to fascinating opportunities for designing stacked heterostructures \cite{4, 5}. Heterostructures of TMDs have shown promise for various optoelectronic applications (cf. \cite{6} and references therein). Moreover, future applications beyond conventional optoelectronics might be based on the coupled spin and valley physics of TMD monolayers due to their broken inversion symmetry \cite{7}. This coupling allows the excitation of specific spin carriers into a particular valley which has been demonstrated by optical pumping with circularly polarized light \cite{8–10}. These findings pave the way for a new class of prospective devices called valleytronics.

TMD monolayer and heterostructure samples available at the moment are typically smaller than (100 \textmu m)\textsuperscript{2}. Further-
more, they usually exhibit considerable spatial inhomogeneity due to intrinsic defects within the layers or extrinsic inhomogeneity such as substrate roughness, interlayer bubbles or impurities. Therefore, it is particularly important to utilize appropriate imaging techniques for their exploration. Moreover, the energy alignment of TMD heterostructures [11–15] as well as interlayer charge- and energy-transfer processes [16–23] are of particular interest in fundamental and applied research. Due to the van der Waals coupling, arbitrary layer stacking is possible. Rotational misfit between two TMD monolayers of a layered structure results in a corresponding rotation of the hexagonal Brillouin zones of the two layers leading to momentum-mismatched interlayer excitations. Therefore, the stacking influences charge and energy transfer and thereby the performance of the device. It has been shown that the interlayer coupling of homo-stacked layers depends considerably on the respective stacking angles [24–27] and the same should hold for the coupling of hetero-bilayers [28–30]. Indeed, a distinct difference in the exciton recombination of coherently and randomly stacked MoS₂/WS₂ heterostructures was observed [31]. Furthermore, a strong influence of the stacking angle on the formation dynamics of interlayer excitons has been reported recently for WSe₂/WS₂ [23].

Thus, systematic studies are highly needed to investigate how structural characteristics like the stacking angle of 2D heterostructures correlate with other physical properties of the materials such as the existence and dynamics of charge transfer excitons. In this work, we demonstrate that spatially resolved optical second-harmonic generation (SHG), i.e. SHG imaging microscopy, is a powerful experimental technique to perform time-resolved studies in consideration of the material’s structure. It allows studying systematically both the orientation and the charge-carrier dynamics of TMD monolayers and heterostructures with the same experimental setup. In particular, a complementary technique to analyze the stacking of the material is not needed. As an example, we report time-resolved SHG imaging microscopy studies on MoS₂ mono- and multi-layer flakes grown by chemical vapor deposition (CVD) on a 285 nm SiO₂/Si(001) substrate.

2. Time-resolved SHG on TMDs

Previous studies already demonstrated that second-harmonic generation is a versatile technique to investigate single- and multilayers of TMDs [32–44]. It has been shown that the SH response of the TMDs exhibits a dramatic odd–even oscillation with the number of layers consistent with the absence (presence) of inversion symmetry in odd (even) layers [32–35]. Rotational anisotropy SHG measurements probing the SH response of TMD monolayers as a function of the crystal orientation reveal the expected three-fold rotational symmetry [33–37]. This allows the determination of crystallographic orientations for single-layer flakes [33–37], domain boundaries and orientations of CVD grown monolayer structures [35, 38, 39] as well as stacking angles of twisted bilayers [40].

While all these examples represent basically static SH experiments for structural characterization of TMD materials, time-resolved SHG has been applied in particular to study the dynamics of various phenomena at surfaces and interfaces of bulk semiconductors. Its sensitivity to symmetry changes and to interface electronic states has been exploited for time-domain investigations of phase transformations [45, 46], of adsorbate reactions [47], of interface-specific electron dynamics [48–50] and to detect transient electric fields at interfaces [51–53]. Those time-resolved experiments on TMD samples have to cope with the small flake/domain size of exfoliated and CVD grown samples available at the moment. Therefore, almost all previous linear and nonlinear optical experiments were performed at normal incidence by means of microscope objectives (∼100) with short working distances and probe beams focused to spot diameter of ≈1 μm. This kind of setup is disadvantageous for time-resolved pump-probe studies like SHG because it makes the non-collinear incidence of pump and probe beam difficult. As the pump beam also generates SH signal, this has to be differentiated from the SH response of the probe beam. Furthermore, the time-resolution is limited due to dispersion of the used optical elements. These difficulties might explain why, to the best of our knowledge, there is only one published time-resolved SHG study on TMDs. Here, the dynamical SH response of single-layer MoS₂ to intense above-bandgap photo-excitation was investigated [41].

SHG imaging microscopy combines the advantages of time-resolved SHG with an optical microscopy setup. The SH response of the sample is imaged optically magnified on a CCD chip. Similar setups have been used to study surface reactions like desorption or diffusion [54–56] as well as electric field distributions and carrier motion [57–60]. SHG imaging microscopy copes with both of the discussed challenges of time-resolved studies on TMDs. On the one hand, the SH response of pump and probe beam can be separated very easily. On the other hand, the time-resolution is virtually limited by the pulse duration of the laser system. The SH response of large sample areas (∼400 × 400 μm²) can be probed without the need of any mapping or scanning. By means of polarization dependent measurements, the crystalline orientation of single-layer flakes and domains, or the stacking angles of heterostructures can be evaluated for the whole field of view. Pump-probe experiments at the corresponding area then allow to correlate observed transient changes of the SH response with the underlying structure. With this technique polarization- and time-resolved measurements can be performed systematically and routinely. SHG imaging microscopy is also suited to study fluorescence dependent phenomena [56].

3. Experimental procedure

The experiments were performed under ambient conditions using 50 fs laser pulses generated by a femtosecond Ti:sapphire laser amplifier system (Coherent RegA) operating at 800 nm with a repetition rate of 150 kHz. The main part of the amplifier output (90%) is used to pump a travelling-wave optical parametric amplifier (OPA) operating in the visible range. The output of the OPA is compressed by a pair
of LaFN28 Brewster prisms. This visible pump beam is then focussed under the angle of 50° onto the sample as illustrated in figure 1. The remaining part of the amplifier output (10%) is used to probe the SH response. Due to the different incident angles the SH signals generated by the pump and the probe beam are spatially separated.

The specular reflected SH response of the probe beam is imaged optically magnified by a camera lens (NIKON NIKKOR, 1 : 1.4 ED, f = 50 mm) on an electron-multiplied CCD chip (PRINCETON INSTRUMENTS ProEM-HS) with a size of 1024 × 1024 pixels; each pixel covers an area of 13 × 13 μm² on the chip. The camera is sensitive in a spectral range from 300 nm up to 1050 nm and was operated in full image mode. The used magnification was M ≈ 35–40, thus the visible sample region on the CCD was about 400 × 400 μm². The overall resolution of our imaging microscopy setup is better than 4 μm as determined by a standard resolution target [cf. figure S1 in the supplementary material (https://stacks.iop.org/JPCM/32/485901/mmedia)]. Thus, the resolution is close to the diffraction limit of ≈2 μm.

The time-delay between pump and probe beam is varied by a motorized delay stage. The polarization of pump and probe beam can be varied by means of a λ/2-plates. The polarization of the second-harmonic (SH) response is analyzed by a combination of a λ/2-plate and analyzer. Color filters for separation of both the incident ω- and detected 2ω-light have been used (RG715, FBH400-40). The spot diameter of pump and probe beam on the sample (full width at half maximum) were 160 μm and 200 μm, respectively. A combination of λ/2-plate and analyzer enable the continuous variation of the incident pump fluences on the sample. The incident fluence of the 600 nm pump beam was ≈55 μJ cm⁻² and ≈190 μJ cm⁻² for the 800 nm probe beam. Long term measurements with these fluences applied did not exhibit any multishot damage.

The studied TMD sample consists of mono- and multilayers of MoS₂ flakes which were CVD grown on a 285 nm SiO₂/Si(001) substrate [61]. Photoluminescence (PL) measurements of the monolayer flakes exhibit an intense PL peak centered around 1.85 eV indicating low doping during the CVD process and relative low defect density compared to exfoliated MoS₂ as discussed in the supplementary material [62, 63]. Figures 2(a) and (b) show an optical microscope image (×50) in comparison to the respective SHG microscopy image (P-polarized SH component, t_exposure = 300 s) which is intensity-inverted for better comparability. Using a logarithmic color scale, one can differentiate easily between the triangular shaped mono- and multilayer crystals. Monolayers appear in grey color on the bright SiO₂/Si(001) substrate, while the multilayer flakes appear black. They exhibit an up to a factor of 30 times stronger SH response than the monolayer. This is in contrast to the reported negligible SH signals from MoS₂ bulk material [33] which naturally occurs in the inversion symmetric AA’ (2H) stacking. This discrepancy can be explained by an AB (3R) layer stacking which was calculated to have very similar adsorption energy in multilayer growth [64]. Thus, depending on the exact growth conditions, multilayers can grow predominantly AB stacked with the top layer zero degree aligned with the bottom layer [24]. The resulting multilayer structures are primarily non-centrosymmetric and the higher SH intensity can therefore be explained by a constructive interference of the stacked monolayer SH signals.

4. Results and discussion

4.1. Polarization dependent SHG measurements

Previous rotational anisotropy measurements probing the SH radiation component parallel (perpendicular) to the polarization of the fundamental field revealed the expected cos² 3θ (sin² 3θ) dependence [33–38]. Here, θ denotes the angle between the mirror plane in the crystal structure (i.e. the armchair direction) and the polarization of the probe beam. Rotating the sample then allows direct access to the symmetry of the sample and to the crystal orientation [33–38]. However, in order to exploit the advantage of SH imaging microscopy probing a larger surface area at once, the sample position is chosen to be fixed and the polarization of the fundamental is rotated as it has been previously applied on TMD monolayers [39, 41]. As it is known from literature [65] and further derived in the supplementary material, the expected dependence of P- and S-polarized components of the SH intensity on the polarization for normal incidence yield

$$I_P^2(\phi) \propto \cos^2(2\phi + 3\Psi)$$  
$$I_S^2(\phi) \propto \sin^2(2\phi + 3\Psi).$$

Here, φ denotes the angle of the polarization with respect to the horizontal and Ψ the angle between the armchair direction of the TMD crystal and the horizontal as sketched in figure 3(b). Thus, instead of the three-fold rotational symmetry, a two-fold polarizational symmetry is expected for normal incidence.
However, if the angle of incidence is $\neq 0$ like in our case, the polarization dependence of the Fresnel factors has to be considered and the equations become more complicated as derived explicitly in the supplementary material. In consequence, the two-fold symmetry is broken and the polarization anisotropy drastically changes with increasing angle of incidence as shown in figure S4. In our case of a small angle of incidence of 18°, the changes are comparably small, but one can clearly observe two pairs of maxima with slightly different heights in the polarization dependence shown in figure S5. The experimental data can be well described by the extended formalism to determine the crystal orientation. The polarization anisotropy for different crystal orientations $\Psi$ is visualized in figure S6 of the supplemental material simulating our experimental conditions. Please note, that because of the three-fold rotational symmetry of the TMD monolayers, SHG without phase information does not deduce opposite crystal orientations. Consequently, it only determines domain orientations modulo 60°. The consistency of our evaluation has been confirmed by comparison with optical microscopy (cf. section 5 in the supplemental material). The mean value for the deviation of the extracted crystal orientations yields $0.8^\circ \pm 0.4^\circ$ and this accuracy probably could be further improved by longer exposure times and/or smaller angular steps. For the determination of stacking angles in TMD heterobilayers, the polarization anisotropy of at least two regions (i.e. two monolayer regions or the heterobilayer plus one monolayer region) has to be evaluated, since the SH response from the heterobilayer represents a coherent superposition of the SH fields from the individual layers [40].

A movie of the polarization dependent SHG microscopy measurements showing the P-polarized SH component ($t_{\text{exposure}} = 60$ s) for varying polarization of the fundamental from 0° to 360° in steps of 3° can be found in the supplementary material. Figure 3 shows the corresponding polar plots of the SH intensity of (c) three mono- and (d) three multilayer regions marked in the SHG microscopy image (a). According to the derived equations, the crystal orientations $\Psi$ of these MoS$_2$ mono- and multilayer flakes can be evaluated from the observed phases $\Delta \Psi$ of their polarization anisotropy by a corresponding fit. The crystal orientation can also be extracted for every pixel by an automatized fitting routine which is further described in the supplementary material. The result is illustrated in figure 2(c). The crystal orientation for each individual flake including overlapping domains and growth errors like twins can be easily identified. One has to point out that the determination of the crystal orientation or stacking angles by means of SHG originates directly from the symmetry properties of the TMD layers. Neither a complementary experimental technique nor further modelling is needed for the evaluation. This is in contrast to similar considerations for graphene which is, by the way, not accessible by SHG due to its inversion symmetry. Instead, the stacking of bilayer graphene has been studied systematically for example by the combination of structural and optical experimental techniques like transmission electron microscopy and Raman spectroscopy [66, 67].

4.2. Time-resolved SHG measurements

The results of a time-resolved pump-probe SHG experiment on the same surface area as in figure 3(a) are shown in figure 4. The used pump-wavelength of 600 nm (2.07 eV) was chosen to be slightly above the B-exciton resonance of MoS$_2$ (2.02 eV) [20] for generation of A- and B-excitons to gain access to the full domain of possible decay channels. The observed transients for both MoS$_2$ monolayers and multilayers show an ultrafast pump-induced decrease of the SH response and a subsequent relaxation on a picosecond timescale. The relaxation dynamics considerably differ between mono- and multilayers. The spatial resolution of SH imaging microscopy is particularly advantageous to monitor directly the homogeneity of the TMD monolayers and heterostructures after photoexcitation. As illustrated in figure 4(a), the individual monolayer flakes reveal a homogeneous SH response, and the same holds for the transient changes of the monolayers due to photoexcitation. Figures 4(b) and (c) display SH images at pump-probe delays of 0 ps and 12.5 ps which were normalized to an average of ten images at negative delays. While normalization improves the visibility of small pump-induced changes, it also amplifies the overall noise level. Thus, the noisy appearance
of the monolayer flakes in the normalized images is caused by their lower SH signal and not due to sample degradation. In comparison to the rather homogeneous transient changes of the monolayer flakes, the dynamics of the multilayer flakes exhibit clear inhomogeneity within the flakes such as the apparent differences for the inner and outer part of the multilayer flake at ROI 4. Appropriate regions of interest are therefore chosen to evaluate the transient change for a homogeneous area.

The different monolayer flakes (ROI 1–3, figure 4(d)) exhibit very reproducible transients with an initial pump-induced decrease of the SH signal of about 6% followed by a bi-exponential recovery. As determined from a rate-equation model the fast decaying component corresponds to an averaged time-constant of \( \tau_1 = 1.9 \pm 0.7 \) ps, followed by a second slow component with a time-constant of \( \tau_2 = 48.5 \pm 2.1 \) ps. In direct comparison, the multilayer flakes (ROI 4–6, figure 4(e)) show a slightly larger variance with regard to the initial drop (\( \sim 3–6\% \)) as well as the following dynamics. Most likely, this variance can be attributed to a certain thickness variation of individual multilayer flakes. For all multilayer transients, however, a clear mono-exponential recovery can be observed. The corresponding averaged time-constant is determined to be \( \tau = 3.2 \pm 0.9 \) ps.

In linear optical spectroscopy, a sub-picosecond initial decay of the transient absorption signal from TMD monolayers has been observed upon ultrafast interband excitation (3.18 eV), which was attributed to the formation of excitons from electron–hole pairs [68]. Accordingly, this fast decay is absent, if the pump pulses are tuned to the exciton resonances, like in our case, and the excitons are directly injected [68]. Furthermore, thermalization and energy relaxation processes of non-thermal carrier distributions were reported to appear on even shorter time scales [69] and should play a minor role for resonant exciton injection. We therefore attribute the fast initial decrease of the SH response to pump-induced changes in the second-order nonlinear susceptibility, e.g., due to the pump-induced depopulation of the valence band associated with the generation of excitons. The subsequent progression is then interpreted as exciton relaxation. Please note, that no pump-induced changes have been observed for different TMD monolayers, if the pump photon energy is tuned below their A-exciton resonance (not shown). Further evidence for our attribution is given by fluence dependent measurements, which exhibit a linear increase of the initial signal change with increasing applied pump power (cf. insets of figures 4(d) and (e)) [70]. Beside this linear increase, the dynamics of the SH transients do not show any dependence on the applied pump fluence. The latter would have been expected for higher exciton densities for which exciton–exciton annihilation was shown to dominate the decay of the exciton population [71]. We therefore attribute the observed lifetimes of the SH signals as defect-mediated non-radiative recombination in accordance with previous studies on MoS2 monolayers [72–74].

The determined time-constants of the MoS2 monolayer compare very well with excitonic lifetimes obtained from linear optical spectroscopy [72, 73]. However, the overall number
Figure 4. Time-resolved SHG from MoS$_2$ monolayer and multilayer flakes upon 600 nm excitation at an applied laser power of 10 mW ($F_{\text{pump}} = 55 \mu J cm^{-2}$). (a) SH image of the same area as shown in figure 3 at a pump-probe delay of $-2.5$ ps. (b) and (c) show normalized SH images at different pump-probe delays of 0 ps and 12.5 ps, respectively. The two images are normalized to an average of ten images at negative delay times, i.e. before excitation, and therefore share the same color scale. Dark blue color represents a pump-induced decrease in intensity, light blue signifies no change. At temporal overlap (b), a clear decrease of the SH intensity is observed for all MoS$_2$ flakes. After 12.5 ps (c), the intensity of all flakes has recovered to some extent, in particular in the center of the multilayers flakes. (d) and (e) show the averaged SH intensities of the individual regions in dependence of the pump-probe delay for monolayers (ROI 1–3) and multilayers (ROI 4–6), respectively. The grey arrows mark the temporal position of the images (a), (b) and (c). The insets show the fluence dependence of the initial decrease of the SH intensity ($\Delta$SHG) as indicated by the arrow in (d).

and values of reported time-constants for MoS$_2$ monolayers differ quite strongly [18, 41, 71–73, 75–80]. Single- [41, 76, 78], bi- [18, 71, 73, 75, 77, 79] and tri- [72, 80] exponential behavior has been reported. The value of the shortest time-constant ranges from 500 fs up to 100 ps and that of the longest time-constant from 15 ps up to 500 ps.

For the MoS$_2$ multilayer, we observe that the overall decay is clearly faster than the monolayer decay. Experimental studies comparing directly the dynamics of MoS$_2$ mono- and multilayers are rare and, furthermore, report contrary effects: Shi et al observed slightly smaller time-constants of few-layer systems without discussing the physical origin [72]. In contrast, Wang et al found a strong increase of the time-constants with increasing layer number, which was attributed to enhanced surface recombination due to larger defect density of surface layers in multilayer samples [74]. The observed difference in the multilayer dynamics of our study and the work by Wang et al might be caused by the different stacking configuration (3R vs. 2H) or different defect densities due to the different preparation methods (CVD vs. exfoliation). While the former is less likely because of the very similar bandstructure of the 3R- and the 2H-configuration [3, 81], it seems reasonable that the defect density in the CVD grown multilayer is more homogeneous than for the exfoliated sample. Due to the indirect bandgap of multilayer MoS$_2$ optical excitation results in momentum indirect excitons with the electrons and holes located at the $\Sigma$- and the $\Gamma$-point, respectively [3, 81]. The bands at these points consist of hybridized states and are therefore delocalized over multiple layers, which enables effective interlayer charge transfer [82, 83]. Therefore, the fast decay of
the exciton population in the multilayer could be facilitated by vertical transport across the layers resulting in a faster trapping compared with the monolayer.

Thus, the values and trends in the dynamics of MoS$_2$ mono- and multilayer systems reported in literature deviate considerably from each other. While the reasons for these differences remain ambiguous, they might be explained especially by varying sample quality and among other things also by the use of different substrates, different temperatures, different pump- and probe energies and laser fluences, and of course, also by systematic effects of the applied techniques. From this lack of clarity for these quite simple 2D mono- and multilayer systems, one might anticipate the complexity for 2D heterostructures and corresponding devices. Thus, systematic time-resolved studies on monolayer and heterostructure systems are mandatory in identifying the genuine physical effects and understanding the underlying mechanisms. Consequently, this knowledge will facilitate the further development and improvement of prospective applications based on 2D materials.

Overall, SHG imaging microscopy enables such systematic investigations of µm small 2D monolayers and heterostructures on various substrates. It is universally applicable to all materials without inversion symmetry. The underlying substrate should ideally generate no SH light, but the substrate can of course strongly modify the dielectric environment of the 2D structure which will also affect the SHG intensity (cf. supplementary material). One particular advantage of our imaging microscopy over scanning techniques is the large field of view allowing the simultaneous evaluation of several flakes or spatially inhomogeneous structures. The intrinsic sensitivity of SHG to symmetry changes, electronic states or transient electric fields permits a plethora of time-resolved studies such as ultrafast charge transfer within TMD heterostructures and its correlation to the layer stacking. Especially by applying the particular strengths of polarization-resolved measurements in combination with time-resolved experiments unique opportunities arise for misaligned heterostructures. Since the signals from the individual monolayers can be isolated, the investigation of directional interlayer charge transfer becomes feasible which is not directly accessible by linear optical pump-probe techniques.

5. Conclusion

We have introduced time-resolved SHG imaging microscopy for the investigation of monolayers and heterostructures of two-dimensional transition metal dichalcogenides. For single- and multilayer MoS$_2$ flakes grown on SiO$_2$/Si(001) crystalline orientations are evaluated from polarization dependent measurements. Time-resolved experiments exhibit an ultrafast pump-induced decrease of the SH response in both systems while their relaxation behavior differs considerably. From the corresponding time-constants the transient changes are attributed to the generation and relaxation of excitons. The results demonstrate that SHG imaging microscopy is a powerful method to investigate the dynamics of charge carriers and excitons of TMD heterostructures by systematic pump-probe experiments of spatially inhomogeneous samples. The observed transient changes of the second-harmonic response can be readily correlated to the stacking of the material.

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