Optical imaging of strain in two-dimensional crystals

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Strain engineering is widely used in material science to tune the (opto-)electronic properties of materials and enhance the performance of devices. Two-dimensional atomic crystals are a versatile playground to study the influence of strain, as they can sustain very large deformations without breaking. Various optical techniques have been employed to probe strain in two-dimensional materials, including micro-Raman and photoluminescence spectroscopy. Here we demonstrate that optical second harmonic generation constitutes an even more powerful technique, as it allows extraction of the full strain tensor with a spatial resolution below the optical diffraction limit. Our method is based on the strain-induced modification of the nonlinear susceptibility tensor due to a photoelastic effect. Using a two-point bending technique, we determine the photoelastic tensor elements of molybdenum disulfide. Once identified, these parameters allow us to spatially image the two-dimensional strain field in an inhomogeneously strained sample.

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The properties of materials can be strongly influenced by strain. For example, local straining techniques are employed in modern silicon field-effect transistors to reduce the carrier effective mass and increase the carrier mobility\(^1\). In optoelectronics, strain can be used to transform indirect band gap semiconductors into direct gap materials with strongly enhanced radiative efficiencies, or to tune the emission wavelength of light emitters\(^2\text{–}^5\). While silicon typically breaks at strain levels of ~1.5%, two-dimensional (2D) atomic crystals\(^6\) can withstand strain of >10%\(^7\text{–}^8\), making them promising candidates for stretchable and flexible electronics\(^9\). Their high flexibility further allows for folding or wrapping them around (lithographically defined) nanostructures to induce spatially inhomogeneous atom displacements. This provides an opportunity to modify their electronic structure such that excitons can be funneled into a small region of a layered semiconductor\(^10\text{–}^11\) to form exciton condensates, improve solar cell efficiencies, or realize single photon emitters\(^12\text{–}^15\).

In order to better understand and improve the performance of devices, analytical tools are required that are capable of noninvasive strain imaging at the submicron scale. Traditionally, X-ray diffraction (XRD) is employed, but submicron spatial resolution can in most cases only be achieved by the use of coherent radiation, e.g., from a synchrotron\(^16\). High-resolution transmission electron microscopy (TEM) based techniques\(^17\) rely on precise measurements of atom column positions, but they offer only a small field of view and are invasive, as they require thin specimens. Electron backscatter diffraction (EBSD) techniques\(^18\) can overcome some of those limitations, but require flat surfaces and comparison of the experimental data with simulations to analyze the complex diffraction patterns. Optical techniques, such as micro-Raman\(^19\text{–}^21\) and photoluminescence (PL)\(^10\text{,}^22\text{,}^23\) spectroscopy, offer an interesting alternative. They are noninvasive, allow for large-area imaging with submicron spatial resolution and are simple to set up.

Strain-induced second harmonic generation (SHG) has been investigated for decades\(^24\) and has been employed to generate frequency-doubled light in centrosymmetric materials, such as silicon\(^25\text{–}^30\). The second harmonic response in these works is typically described by a phenomenological modification of the nonlinear susceptibility of the unstrained material\(^31\text{–}^35\). In a more thorough theoretical investigation, Lyubchanskii et al. demonstrated that strain and nonlinear susceptibility are connected via a photoelastic tensor\(^36\text{,}^37\).

Here, we adapt this theory and determine, to our knowledge for the first time, all photoelastic tensor elements of a material from SHG. Once identified, these parameters allow us to spatially map the full strain tensor in a mechanically deformed 2D material with a spatial resolution below the diffraction limit of the excitation light. As a representative example, we present results obtained from MoS\(_2\) — a layered transition metal dichalcogenide (TMD) semiconductor\(^38\text{,}^39\). Our technique, however, is not only limited to 2D materials, but is applicable to any thin crystalline film. It establishes a novel optical strain probing technique that provides an unprecedented depth of information.

### Results

#### Theoretical description

SHG is a nonlinear optical process in which two photons with the same frequency \(\omega\) combine into a single photon with double frequency, as schematically depicted in Fig. 1a. As only non-centrosymmetric crystals possess a second-order nonlinear susceptibility, SHG in 2H-stacked TMDs requires odd layer thickness\(^31\text{–}^35\). Figure 1b shows a microscope image of a mechanically exfoliated MoS\(_2\) flake on a Si/SiO\(_2\) (280 nm) wafer.

The corresponding SHG signal amplitude in Fig. 1c shows the expected layer dependence and quadratic scaling behavior with excitation power (see Supplementary Fig. 2). The polarization dependence of the SHG intensity, plotted in Fig. 1d, reflects the underlying \(D_{3h}\) symmetry of the TMD crystal\(^31\text{–}^35\). The spatial resolution of our specific setup (280 nm full-width-at-half-maximum (FWHM)) was determined from a line scan across an edge of the MoS\(_2\) flake (Fig. 1e). Spatial features below the diffraction limit of the excitation wavelength can thus still be resolved, due to the nonlinear nature of the SHG process. Details of the experimental setup can be found in the Methods section and in Supplementary Fig. 1.

We will now discuss how SHG can be used to measure strain in 2D TMDs, or thin crystals in general. Polarization resolved SHG reflects the lattice symmetry of the probed crystal, where the relation between SHG intensity and crystal lattice is given by the second-order nonlinear susceptibility tensor \(\chi^{(2)}\). Strain deforms the crystal lattice and therefore also influences \(\chi^{(2)}\) breaking the symmetry in the SHG polarization pattern, as illustrated in Fig. 2. This effect is described by an Ansatz which...
Depending on the coordinate system, the strain tensor and the incident electric fields, \( P^{(2)}_r(2\omega) \propto X_{ijk}^{(2)} E_i(\omega) E_j(\omega) \). In our polarization resolved SHG measurements we chose a linear polarized incident electric field under an angle \( \phi \) and analyze the SHG signal with same polarization. \( P^{(2)}_r(2\omega) \) is the parallel polarization which corresponds to that signal and the square of it is proportional to the measured SHG intensity:

\[
I^{(2)}(2\omega) = \frac{1}{4} (A \cos(3\phi) + B \cos(2\theta + \phi))^2, \tag{4}
\]

with \( A = (1 - \nu)(p_1 + p_2)(\varepsilon_{xx} + \varepsilon_{yy}) + 2\chi_0 \) and \( B = (1 + \nu)(p_1 - p_2)(\varepsilon_{xx} - \varepsilon_{yy}) \). \( p_1 \) and \( p_2 \) are the photoelastic parameters, \( \varepsilon_{xx} \) and \( \varepsilon_{yy} \) denote the principal strains, \( \theta \) is the principal strain orientation, \( \phi \) the polarization angle, and \( \chi_0 \) the nonlinear susceptibility parameter of the unstrained crystal lattice.

Photoelastic tensor measurement. The effect of strain on SHG is determined by the photoelastic parameters, which depend on the specific material. We determine these parameters for monolayer MoS\(_2\) by applying different levels of uniaxial strain using a two-point bending method (Fig. 3a), and measuring the polarization resolved SHG signal. For that, MoS\(_2\) on a flexible substrate with length \( L \) and thickness \( d \) (see Methods for sample preparation) is clamped between two points and the distance \( a \) between them is controlled by a motorized linear actuator. At distances \( a < L \) the sample is bent, which causes tensile strain in the MoS\(_2\) layer. Assuming a circular bending profile of the flexible substrate, the resulting uniaxial strain \( \varepsilon_{xx} \) for a chosen distance \( a \) is then given by the relation \( \sin(\varepsilon_{xx}/L/d) = \varepsilon_{xx}a/d \), which we solve numerically (see Supplementary Fig. 3).

Fitting the SHG patterns at different known strain levels with Eq. (4), allows us to determine the photoelastic parameters \( p_1 \) and \( p_2 \). Experimentally, we find that the SHG intensity under varying uniaxial strain is constant in the uniaxial strain direction (\( I^{(2)}(\phi = \theta) = \text{constant} \)), which indicates that the two photoelastic parameters are connected by Poisson’s ratio: \( p_1 = \nu p_2 \). This relation simplifies the nonlinear fitting procedure and, as shown in Fig. 3b, the measured polarization resolved SHG data from strained MoS\(_2\) flakes can be fitted accurately with the linear strain consideration in the nonlinear susceptibility tensor (1). In Fig. 3c the photoelastic tensor parameters are plotted for two different samples for tensile strain values up to \( \sim 1\% \). Both parameters are constant over this range, confirming the theoretically predicted linear relation between strain and nonlinear susceptibility (Eq. (1)). Using a Poisson ratio of \( \nu_{MoS_2} = 0.29 \) and an unstrained nonlinear susceptibility of \( \chi_0 = 4.5 \text{ nm/V}^2 \), we determine the photoelastic tensor parameters of MoS\(_2\) monolayers as \( p_1 = -0.68 \pm 0.07 \text{ nm/V/\%} \) and \( p_2 = -2.35 \pm 0.25 \text{ nm/V/\%} \).

Strain imaging. Having extracted these parameters, we can now employ SHG spectroscopy to locally probe inhomogeneous strain fields in MoS\(_2\) monolayer samples. As discussed before, due to the nonlinear nature of SHG, the spatial resolution is higher than that obtained by linear optical strain mapping techniques, such as PL or Raman spectroscopy. However, recording a high-resolution strain map, where each strain value is determined by a full polarization scan, is extremely time consuming. We thus determine the strain from the SHG intensities at the three AC directions (\( \phi = 0^\circ, 60^\circ, 120^\circ \)) of the MoS\(_2\) crystal only. Using this method, we first record one complete polarization resolved measurement to determine the crystal orientation. Thereafter, for each location we acquire three SHG signals at the angles noted above, from which we
determine the local strain. By taking the square root of the measured SHG intensity, being proportional to the second order polarization $P(\phi) \propto \pm (I(\phi))^{1/2}$, we obtain a system of equations with three unknowns—$A$, $B$, and $\theta$—presented in the Methods section. This equation system is analytically solvable and yields:

$$A = \frac{2}{3}(P_0 + P_{60} + P_{120}),$$

$$B = \frac{1}{3}(P_0^2 + P_{60}^2 + P_{120}^2 - P_0P_{60} - P_0P_{120} - P_{60}P_{120})^{1/2},$$

$$\theta = \frac{1}{2} \arctan \left( \sqrt{3} \frac{P_0 - P_{60}}{P_0 - P_{120}} \right),$$

with $P_0 > P_{60}, P_{120}$.

$A$ and $B$ are directly related to the principal strain values $\epsilon_{xx}$ and $\epsilon_{yy}$ (see Eq. (4)), and $\theta$ is the rotation of the principal strain coordinate system relative to the crystal lattice. Uniaxial strain can then be determined as $\epsilon_{\text{ua}} = \epsilon_{xx} - \epsilon_{yy}$ and biaxial strain as $\epsilon_{\text{bi}} = \epsilon_{yy}$, since we chose $|\epsilon_{xx}| > |\epsilon_{yy}|$. The relative error of the photoelastic tensor elements $p_1$ and $p_2$ is directly connected to the error of the calculated strain $\delta \epsilon = \frac{\delta p_1}{p_1} \epsilon = \frac{\delta p_2}{p_2} \epsilon$. In our measurement, the relative error of the photoelastic tensor components is $\sim 10\%$, which is also the uncertainty of the measured strain values. The uncertainty of $p_1$ and $p_2$ mainly stems from our two-point bending technique, which does not fix the strained samples as well as three-point or four-point bending methods. It could thus be improved by employing more sophisticated straining techniques.

We finally present an illustrative application example of the SHG strain mapping technique. Using a PC (polycarbonate) based pick-and-place technique, we transferred a mechanically exfoliated MoS$_2$ monolayer flake onto a 115 nm high lithographically defined structure on a Si/SiO$_2$ substrate, shown as scanning electron microscope (SEM) image in Fig. 4 (inset). The force applied during the transfer technique causes the MoS$_2$ to be strained by the non-flat surface. A strain map is then recorded using the technique described above, and the resulting local uniaxial strains $\epsilon_{\text{ua}}$ are plotted as vectors in Fig. 4. Since all uniaxial strain values are positive we conclude that only tensile strain is present, which makes sense because the relaxed MoS$_2$ is spanned over the lithographic structure. Also contaminations on the substrate (e.g., in the lower right corner) lead to strained MoS$_2$ areas.

**Discussion**

In summary, we have presented a method that allows to extract the full strain tensor by means of polarization resolved SHG measurements. Using a two-point bending technique, we determined the photoelastic tensor elements for monolayer MoS$_2$. Once identified, these parameters allowed to spatially map the strain field in an inhomogeneously strained sample with $280 \text{ nm}$ spatial resolution. Determination of the local strain tensor via

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**Fig. 3** Photoelastic parameters. a Schematic illustration of two-point bending method (top: side view; bottom: top view). AC armchair direction, ZZ zig-zag direction. b SHG patterns for applied tensile strains of 0.1, 0.5, and 0.95%. (symbols: measurement data; line: fit) c Photoelastic parameters $p_1$ and $p_2$ for monolayer MoS$_2$ as determined from measurements on two different samples (plotted in different colors). Left panel: strain dependence; right panel: histogram of measurement data.

**Fig. 4** Strain imaging. Uniaxial strain map of MoS$_2$ monolayer flake (filled color) on a lithographically defined structure (dashed lines). Arrows: measured uniaxial strain field. Inset: SEM image of sample. Scale bars, 1 $\mu$m.
three polarized SHG measurement points enables for efficient and fast strain field imaging over large sample areas, providing an unprecedented depth of information. Our method supplements and extends established optical strain measuring methods, such as Raman and PL spectroscopy. Due to the insensitivity of the SHG response to free carriers in TMD monolayers\(^5\), our technique is less prone to artefacts that arise from local doping. Moreover, using this technique, it may be possible to image transient crystal deformations on a sub-picosecond timescale.

**Methods**

**Experimental setup.** For SHG measurements we use a femtosecond Ti:


down the MoS\(_2\) monolayer, another SU-8 coating is spun on top. The SU-8


data that support the

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Author contributions
L.M., M.M.F. and T.M. conceived and designed the experiment. L.M., M.M.F. and S.W. built the setup and carried out the measurements. M.M.F., L.M., S.W., M.P. and D.K.P. fabricated the samples. L.M. and M.M.F. analyzed the data. L.M., M.M.F. and T.M. prepared the manuscript. All authors discussed the results and commented on the manuscript.

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