Raman imaging illuminates 2D materials

Correlative Raman microscopy techniques offer extensive possibilities for characterizing 2D materials in detail.

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Two-dimensional materials are a fascinating new class of semiconductors with tremendous potential for optoelectronics. Here, we illustrate how crystal properties such as layer number, strain, defects and grain boundaries can be characterized by confocal Raman imaging in combination with second harmonic generation and photoluminescence microscopy.

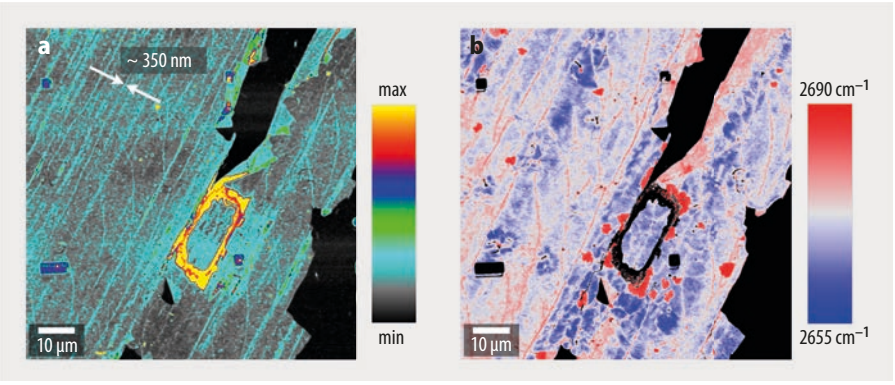

Fig. 1 High-resolution Raman imaging was used to study a graphene sample (100 nm per pixel, 532 nm excitation wavelength). The Raman image of the D-band intensity visualizes crystal defects (a) while the Raman image of the 2D-band frequency shows local strain and doping effects (b).

Two-dimensional (2D) materials, which consist of only one atomic layer or a few layers, are receiving increasing attention due to their unique optical and electronic properties. Prominent examples are graphene, perovskite and transition metal dichalcogenides (TMDs). Their possible applications include the production of light emitting diodes, transistors, photodetectors and photovoltaic cells. The optoelectronic properties of 2D materials depend on crystal features such as layer number, defect density, grain boundaries, doping and strain fields. Non-destructive and fast imaging techniques for characterizing these properties are therefore required in the development and production of high-quality devices. Confocal Raman microscopy (**info box**) is well suited for this task, especially in combination with complementary techniques such as second harmonic generation (SHG) and photoluminescence (PL) imaging.

High-resolution Raman imaging

High spatial resolution is crucial for detecting the finest details of crystal properties. **Fig. 1** presents a Raman measurement of graphene grown by chemical vapor deposition (CVD). It was acquired with a WITec alpha300 *apyron* fully automated Raman microscope equipped with a 532 nm excitation laser. Due to the large area investigated, automatic focus stabilization was used to keep the surface in focus. The Raman image of the D-band intensity visualizes the defect density in the carbon lattice (**Fig. 1a**), as the D-band only appears if defects are present [2]. The observed width of the fine structures is about 350 nm and demonstrates the microscope's high performance, as it is very close to the diffraction-li-

Advanced Raman imaging

The **Raman spectrum** of a substance is as characteristic as a human fingerprint and can be used for chemical identification. It results from the energy shift of light that is inelastically scattered by the molecules in a sample. A **Raman image** is color-coded according to the Raman spectrum measured at each image pixel and thus visualizes the distribution of the sample's chemical components. In addition to molecular identification, crystal properties can also be investigated as they affect a material's Raman spectrum.

In advanced **confocal Raman microscopes**, all optical components are optimized for the highest photon throughput and sensitivity. This makes it possible for high-resolution Raman images to be obtained within minutes, even in three dimensions. Automated Raman microscopes can be placed in environmental enclosures and operated remotely, which allows for measurements under precisely controlled atmospheric conditions [1]. A high degree of automation enables even self-calibration and self-alignment of the system for optimal performance in each measurement.

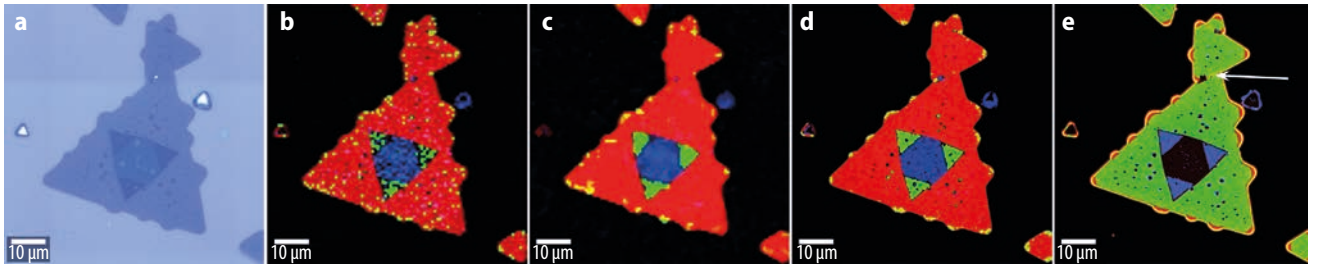

Fig. 2 A Raman imaging investigation of a WSe_2 flake began by first acquiring a white-light image (a). The initial Raman image consists of 10 000 spectra acquired in two minutes (b) and was then smoothed in post-processing (c). A high-resolution Raman image consisting of 102 400 spectra took 17 minutes to be acquired (d). In the photoluminescence image (e), the grain boundary (white arrow) and edge effects are visible. In the Raman images, single layers, double layers and multilayers are color-coded in red, green and blue, respectively. For Raman and photoluminescence, the integration time was 6 ms per spectrum with an excitation wavelength of 532 nm.

mited lateral resolution achievable with a 532 nm laser for excitation and a 0.9 NA objective. The Raman image of the peak position of the 2D-band visualizes local strain and doping effects (**Fig. 1b**), as the frequency of the 2D-band is influenced by local strain and, to a lesser extent, by doping [2].

Ultra-fast Raman imaging

A fast sample overview can be advantageous for initial sample evaluation. The white-light image of a tungsten diselenide (WSe_2) flake indicates areas with different layer numbers (**Fig. 2a**). Raman imaging yields a more detailed characterization. For a first assessment, a low-resolution Raman image (750 nm per pixel) was acquired in only two minutes (**Fig. 2b**) and areas with one, two and multiple layers were identified from the Raman spectra [3]. The different areas are more clearly visible in the smoothed version of this picture, illustrating how an informative overview can be obtained in a very short time (**Fig. 2c**). Recording a high-resolution Raman image (230 nm per pixel) of the same sample area took only 17 minutes and it shows the same structures in greater detail (**Fig. 2d**). Additionally, a photoluminescence image was measured at the same position (**Fig. 2e**). It visualizes rim effects and even a grain boundary between the large and the smaller flake is faintly visible.

Correlative Raman imaging

Comprehensive analyses often call for several imaging techniques, as illustrated using CVD-grown mono-layer molybdenum disulfide (MoS_2). In contrast to the WSe_2 flake (**Fig. 2a**), the white-light image of a mono-layer MoS_2 flake shows no features except for a few bright spots caused by local bulk material (**Fig. 3a**). The material was more closely examined with Raman, SHG and PL imaging using a WITec alpha300 Raman microscope equipped with a 532 nm laser for Raman and PL imaging and a picosecond-pulsed 1064 nm laser for SHG excitation.

SHG is a nonlinear optical process that radiates a photon with twice the frequency of the excitation photon and is sensitive to changes in crystal orientation and symmetry, layer thickness and stacking order [4]. The high-resolution SHG intensity image (**Fig. 3b**) clearly visualizes the grain boundaries in the MoS_2 flake (low SHG signal). In addition, polarization-dependent SHG measurements were performed by rotating the excitation polarization while recording the intensity of the SHG signal component with the same polarization as the incident light. Due to the fully automated polarizer and analyzer of the microscope used, polarization-dependent measurements can be performed automatically within seconds. Polarization series were recorded at three positions on the MoS_2 flake (**Fig. 3b**) and represented in polar plots that depict the recorded SHG signal as a function of the excitation polarization angle (**Fig. 3c**). A particularly symmetric pattern is observed for the position marked in red, indicating little strain in the crystal [5]. In contrast, the other two positions show distinct asymmetric patterns that represent different strain levels.

Raman and PL imaging are frequently used for investigating strain and layer number in TMD crystals [3, 6]. A typical Raman spectrum of MoS_2 shows two prominent peaks, the E_{2g} band originating from an in-plane vibration and the A_{1g} band originating from an out-of-plane vibration (**Fig. 3d**) [3]. The frequency of the E_{2g} mode is particularly sensitive for strain in the crystal [3]. The corresponding Raman image reveals two areas of strong tensile strain, indicated by a pronounced red-shift of the E_{2g} band (**Fig. 3e**). The PL wavelength shows a pronounced red-shift in the same areas (**Fig. 3f**), as it is sensitive to strain as well [6].

Additionally, rim effects around the border of the MoS_2 flake are clearly visible from the pronounced blue-shift of the PL wavelength (**Fig. 3f**).

Summary and outlook

Correlative Raman, PL and SHG imaging yields complementary information for characterizing 2D materials by visualizing diverse crystal features without damaging the sample. High-end microscopes are optimized for high resolution and speed and are automated for user-friendliness.

In addition to the presented techniques, Raman microscopy can be combined with further imaging methods. For example, atomic force microscopy (AFM) and scanning electron microscopy (SEM) both provide very detailed structural information about a sample's surface. Integrated Raman-SEM microscopes allow the correlation of chemical and structural information from precisely the same area of interest. Similarly, the combination of Raman and AFM microscopes provides information on chemical composition, surface structure and properties such as adhesion and stiffness. Furthermore, Raman imaging can be combined with scanning near-field optical microscopy, fluorescence microscopy and time-correlated single photon counting for time-resolved imaging. All of these techniques are useful for characterizing 2D materials and thus, the integration of several techniques in one microscope significantly accelerates such studies.

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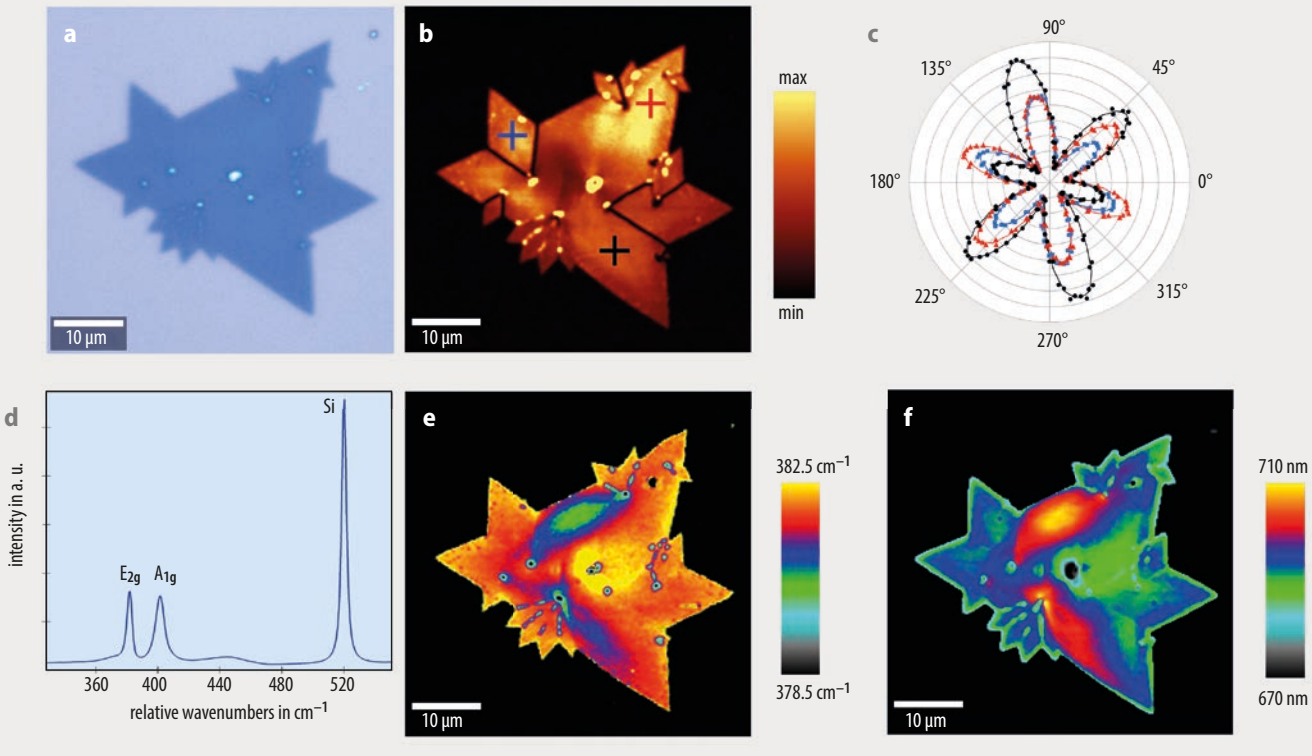

Fig. 3 Single layer MoS_2 was investigated using different methods: white-light image (a) and the SHG intensity image with 200 nm per pixel (b). Polarization series were automatically recorded at the three marked positions to extract polar plots of the SHG signal as a function of the excitation polarization angle (c). The intensity refers to the SHG component with the same polarization as the incident light. The Raman spectrum of MoS_2 on a silicon substrate (d) yields a Raman image that displays the E_{2g} mode frequency (200 nm per pixel) (e). The PL image shows the peak emission wavelength (200 nm per pixel) (f).