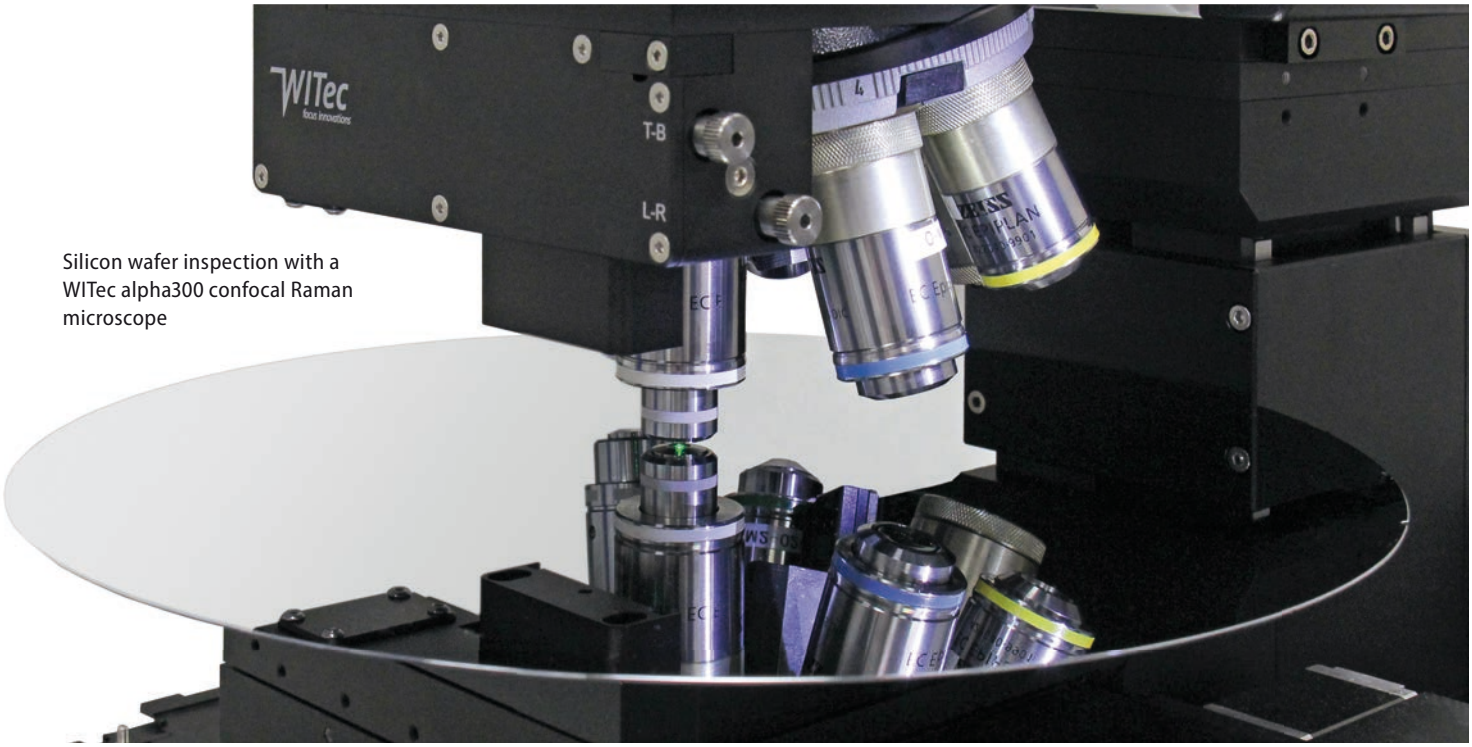


Silicon wafer inspection with a WITec alpha300 confocal Raman microscope

Raman Spotlight on Semiconductors

Correlative Raman imaging can investigate semiconducting materials in great detail.

Eleni Kallis, Thomas Dieing, Hailong Hu, Ute Schmidt, and Olaf Hollricher

Confocal Raman imaging is uniquely capable of characterizing semiconducting materials. It can reveal a sample's chemical composition, identify possible contaminants and visualize strain fields in a crystal, all without damaging the sample. Additional information on, for example, topography or grain boundaries can be acquired from complementary imaging techniques such as atomic force microscopy or second harmonic generation microscopy.

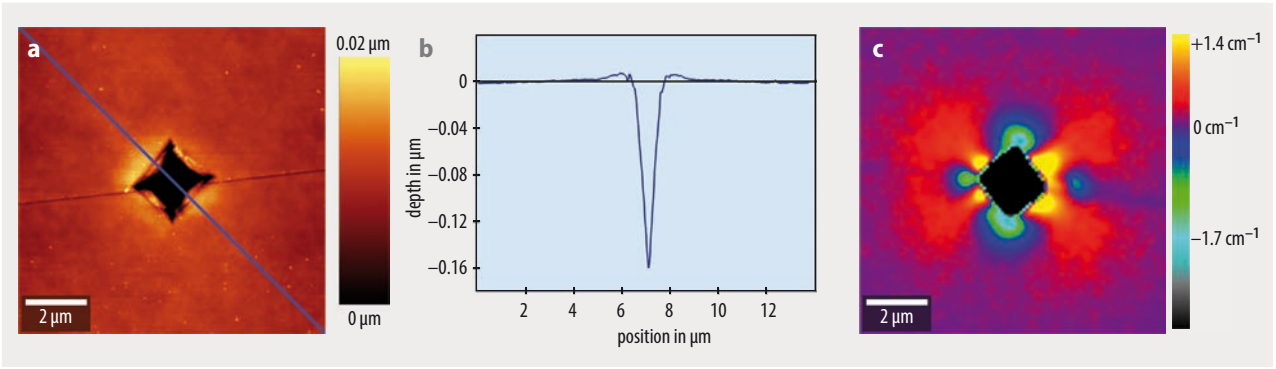
Semiconducting materials are the basis for many electronic and optoelectronic devices such as light-emitting diodes (LEDs), laser diodes, photodiodes, solar cells, and integrated circuits. Prominent examples include silicon (Si), silicon carbide (SiC), gallium arsenide (GaAs), and gallium nitride (GaN), and also many two-dimensional (2D) materials as for instance molybdenum disulfide (MoS_2). During research, fabrication and quality control, the crystal structure, defects and stress fields must be monitored efficiently and without damaging the sample in order to produce high-quality devices. Raman imaging is ideally suited for this task.

Raman microscopy can distinguish between the semiconducting material and possible contaminants and identify them chemically (**info box**). It can also assess crystallinity and reveal stress fields, because crystallographic defects and strain cause broadening and shifting of characteristic peaks in a Raman spectrum. Thus, Raman microscopy enables the comprehensive investigation of semiconducting materials, especially when combined with complementary imaging techniques such as atomic force microscopy (AFM) or second harmonic generation (SHG) microscopy.

Stress in silicon

One aspect of characterizing semiconducting materials is testing their response to deforming forces. In a Vickers test, a square-based diamond pyramid is pushed into the sample material with a controlled force. The physical dimensions of the resulting microindents can be quantified by atomic force microscopy (AFM), while Raman imaging can visualize the stress fields resulting from the deformation [2]. In this example, the indentation was made with a force of 50 mN in a silicon (111) substrate using a Fischer Indentation System (sample courtesy of Helmut Fischer GmbH, Sindelfingen). Raman and AFM images were acquired at precisely the same sample position using a WITec alpha300 RA combined Raman-AFM microscope.

Indentation resulted in a pyramidal indent of 2.6 µm diagonal length and 160 nm depth with protrusions



Sample courtesy of Helmut Fischer GmbH, Sindelfingen, Germany

Fig. 1 Characterization of topography and stress in silicon around a Vickers indent. AFM image of the topography around an indent (a), 10×10 µm². Depth profile along the blue line in the AFM image (b). Raman stress image of the same sample area as in a (c). The shift of the silicon Raman peak at 520 cm^{-1} is color coded.

of about 7 nm in height at the edges, as revealed by AFM (**Fig. 1a, b**). The observed deformations resulted in symmetric stress fields around the indent, which were visualized by Raman imaging. For every recorded Raman spectrum, the relative shift of the silicon peak at 520 cm^{-1} was quantified and color coded in the Raman image (**Fig. 1c**). In silicon, a peak shift of 1 cm^{-1} corresponds to a stress of 435 MPa [2, 3]. Thus, the precision of 0.02 cm^{-1} in this experiment corresponds to a stress sensitivity of less than 9 MPa. The stress fields extended to several micrometers from the actual indent. Tensile strain occurred at the corners of the pyramidal indent (shift to lower wavenumbers, blue/green areas in **Fig. 1c**) and compressive strain along its sides (shift to higher wavenumbers, yellow/red areas in **Fig. 1c**). The example illustrates the usefulness of correlative Raman-AFM measurements for characterizing topography and strain in semiconducting materials.

Grain boundaries in 2D materials

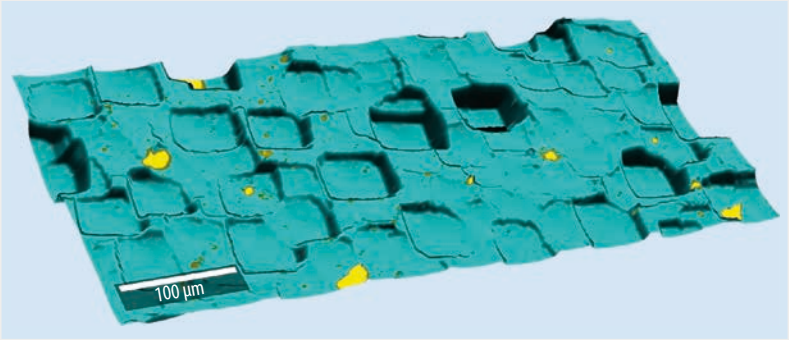
Two-dimensional semiconducting materials, such as transition metal dichalcogenides (TMDs) and perovskite, are the focus of extensive research due to their unique physical and chemical properties and great potential for optoelectronic devices. As grain boundaries can affect the properties of 2D materials, sensitive and fast methods for their visualization are needed. The combination of confocal Raman imaging and second harmonic generation microscopy is able to comprehensively characterize the crystal structure and local strain or doping effects at the grain boundaries of 2D materials. This is illustrated using a sample of single-layer molybdenum disulfide (MoS_2), synthesized by chemical vapor deposition (CVD). The experiments were performed using a WITec alpha300 RA microscope equipped with a 488 nm laser for Raman measurements and a 1560 nm fs-pulsed laser for second and third harmonic generation (SHG and THG) at the Laboratory of Advanced Nanomaterials, Wuhan University in China.

In the optical image, a crack in the crystal is faintly visible, but no other features can be discerned (**Fig. 2a**). For more information, SHG and THG measurements were performed simultaneously (**Fig. 2b, c**). 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 or symmetry, layer thickness and sta-

Confocal Raman Microscopy

The Raman effect is based on the inelastic scattering of light. The interaction of a molecule with photons causes vibrations of its chemical bonds, leading to specific energy shifts in the scattered light with respect to the incident light. The resulting Raman spectrum of a substance is as unique as a human fingerprint and can thus be used to identify chemical components.

In Raman imaging, a confocal microscope is combined with a spectrometer and a Raman spectrum is recorded at every image pixel [1]. The resulting Raman image visualizes the distribution of the sample's compounds. By compiling 2D Raman images from different focal planes, volume scans and 3D images can be generated. Raman microscopy can be combined with other imaging techniques in order to maximize the information extracted from a single sample area. For example, surface structure and chemical composition can be visualized simultaneously (**Fig.**).



Topography and chemical composition of multi-crystalline silicon. Raman imaging reveals contaminants with increased fluorescence signal (yellow) on the silicon (turquoise). The topography was recorded by optical profilometry.

cking order [4]. The SHG image revealed several grain boundaries in the MoS_2 flake (**Fig. 2b**) that were not visible in the optical or THG images.

Further lattice features could be revealed by high-resolution Raman imaging (**Fig. 2d**). The exact positions of the in-plane E_{2g} and out-of-plane A_{1g} peaks (**Fig. 2e**) were quantified for every image pixel by fitting a double Lorentzian function. In the resulting Raman image, the frequency of the A_{1g} mode was color coded (**Fig. 2d**). In all recorded Raman spectra, both the E_{2g} and A_{1g} Raman modes were clearly red-shifted compared to published data on monolayer MoS_2 [5, 6]. This implies that the investigated flake was under strong tensile strain over its entire area. However, the Raman image also revealed local differences, such as areas with reduced stress (yellow in **Fig. 2d**). The example illustrates how correlative SHG and Raman imaging can visualize changes of crystal structure and strain at the grain boundaries of 2D semiconducting materials.

Summary

In summary, the utility of confocal Raman imaging combined with AFM or SHG for non-destructive investigation of semiconductors has been demonstrated. A combination of Raman imaging and AFM characterized stress in silicon caused by mechanical deformation. Raman and SHG imaging investigated crystal structure and strain at the grain boundaries of 2D MoS_2. Confocal Raman imaging's advantages are not limited to semiconducting materials development, but can be applied in many other fields of research, for example polymer research, life sciences and medicine, environmental research and electrochemistry. There are also further useful imaging techniques that can be combined with Raman microscopy, such as scanning electron microscopy (SEM) or photoluminescence imaging.

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Authors

Eleni Kallis, **Thomas Dieing**, **Ute Schmidt**, **Olaf Hollricher**, WITec GmbH, Lise-Meitner-Str. 6, 89081 Ulm, Germany, phone: +49 731 140 700, www.WITec.de, Eleni.Kallis@WITec.de; **Hailong Hu**, WITec GmbH Beijing Representative Office, #507, Landmark Tower 1, 8 North Dongsanhuan Road, Chaoyang District, Beijing, PRC. 100004, China

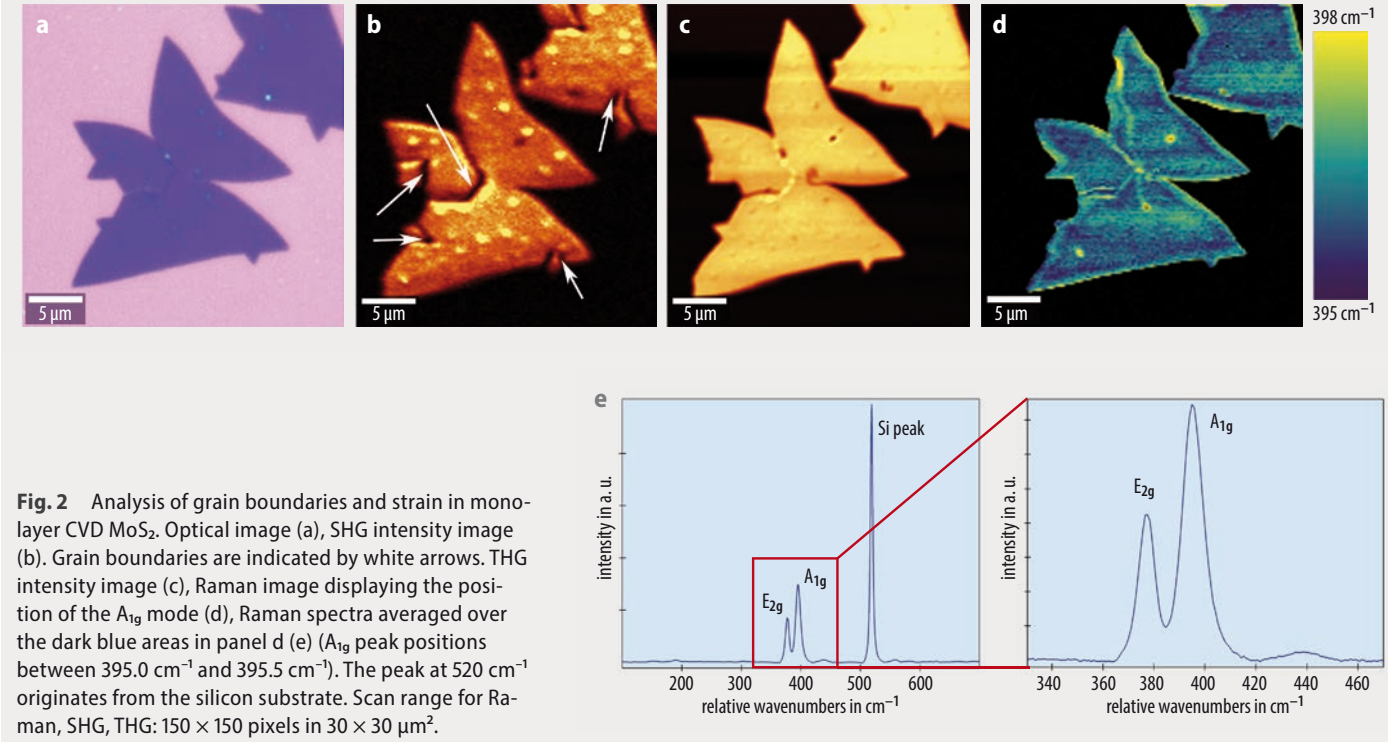

Fig. 2 Analysis of grain boundaries and strain in monolayer CVD MoS_2. Optical image (a), SHG intensity image (b). Grain boundaries are indicated by white arrows. THG intensity image (c), Raman image displaying the position of the A_{1g} mode (d), Raman spectra averaged over the dark blue areas in panel d (e) (A_{1g} peak positions between 395.0 cm^{-1} and 395.5 cm^{-1}). The peak at 520 cm^{-1} originates from the silicon substrate. Scan range for Raman, SHG, THG: 150 × 150 pixels in 30 × 30 $µm^2$.