

# Raman spectroscopy of Si(111)-(7x7) surface vibration modes, using a single monochromator with CCD detector

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## Introduction

In solid state physics research, Raman scattering, i.e. inelastic scattering of photons (laser light), is widely applied for investigating not only bulk samples, but also layers, heterostructures and interfaces by means of the characteristic frequencies of their lattice vibrations, called phonon modes. Due to the indirect character of the interaction of the laser light with the phonons, which is mediated by the valence electrons, the resulting Raman scattering efficiency is usually rather low. Therefore, the Raman light intensity is in general far below e.g. photoluminescence. Especially challenging are surface vibrations, because they intrinsically originate from an extremely small scattering volume. Thus, for their observation a high-efficiency monochromator setup and an extremely sensitive detector system are required. We report on the successful observation of well-defined sharp peaks in the Raman spectrum of the (111)-oriented Si-surface under UHV-conditions, which are attributed to surface vibration modes of the (7x7) reconstruction of this surface.

## Experimental Setup

Our optical setup consists of a high-resolution single monochromator SPEX 1000M (focal length 1000 mm, aperture f/8, grating 1200 lines/mm) in conjunction with a Semrock ultra-steep low-pass filter (Type Razor Edge®) for rejecting the elastically scattered laser light. This arrangement constitutes a useful alternative to a double or triple monochromator setup, which may lead to a reduced spectral range for multichannel detection or to a reduction of optical throughput. Detection was performed with a high-efficiency Si-based CCD detector (Andor iDus DU401A-BVF) with an array of 1024 x 127 pixels. The resulting spectral interval for simultaneous detection comprises Raman shift values between ~50 - 100 cm<sup>-1</sup> and ~900 cm<sup>-1</sup>, which implies ~0.9 cm<sup>-1</sup> per pixel. As excitation sources, Ar<sup>+</sup>-ion laser lines at 488 nm and 514 nm were used, which enabled the unambiguous identification of the observed peaks as Raman features. The Si(111)-samples were located in UHV with a base pressure of ~10<sup>-10</sup> mbar, and the Raman scattering experiments were performed in near-backscattering geometry with defined polarization directions of the incoming and scattered light. The incident laser power was 100 mW, and the integration time for the Raman spectra, shown below, was 6 x 300 s.

## Application Note

### Results

Fig. 1a shows in-situ UHV Raman spectra of clean (7x7)-reconstructed Si(111) and unreconstructed Si(111) for reference. Because Raman spectroscopy is not intrinsically surface sensitive, the strongest features originate from bulk Si: the two-phonon signature, dominated by the 2TA(X) peak at 303 cm<sup>-1</sup>, and the one-phonon peak LTO(Γ) at 521 cm<sup>-1</sup>, which exceeds the intensity scale by a factor ~40. Beside these bulk features, additional peaks appear, which are characteristic for the (7x7) reconstruction. These are shown in detail in Fig. 1b as the intensity difference ΔI between the (7x7) and the reference surface. These data were taken from spectra with defined light polarization configurations. The most prominent surface vibrations are located at 251 cm<sup>-1</sup> and 420 cm<sup>-1</sup> and are observed for crossed polarization of the incident and the scattered light. Weaker surface vibration peaks appear between 110 cm<sup>-1</sup> and 140 cm<sup>-1</sup>, essentially for parallel polarization.

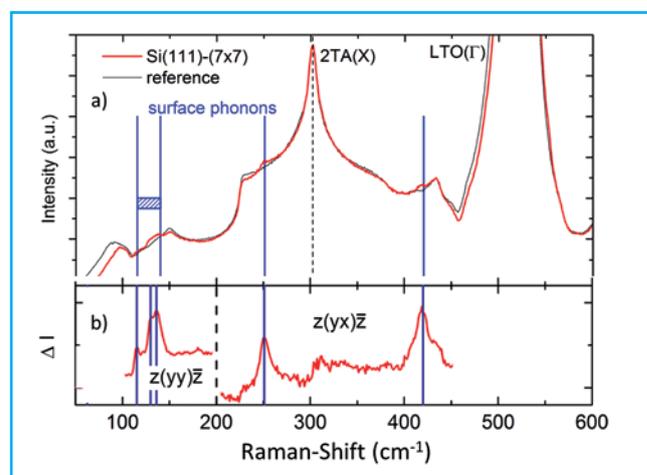


Figure 1 (a) in-situ UHV Raman spectra of the (7x7)-reconstructed clean Si(111) surface and unreconstructed Si(111) for reference (excitation energy = 2.54 eV). (b) Intensity difference ΔI between the (7x7)-reconstructed surface and the reference, taken for crossed and parallel polarization, respectively. Surface phonons at 251 cm<sup>-1</sup> and 420 cm<sup>-1</sup> appear in crossed polarization (Porto notation z(yx)-z), while peaks between 110 cm<sup>-1</sup> and 140 cm<sup>-1</sup> show up in parallel polarization z(yy)-z. The surface peak intensities are ~10<sup>-3</sup> times the one-phonon LTO-peak of bulk Si at 521 cm<sup>-1</sup>.

From comparison with theory predictions [1], the modes at 420 cm<sup>-1</sup> and at 250 cm<sup>-1</sup> are attributed to collective vibrations of the adatoms and the first- and second-layer atoms, and localized adatom vibrations, respectively, while the structures around 120 cm<sup>-1</sup> are

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interpreted in terms of in-plane wagging modes [2]. These Raman peaks constitute the first experimental confirmation of the vibration mode spectrum of the surface atoms, theoretically predicted within the Dimer-Adatom-Stacking fault model (DAS) of the Si(111)-(7x7) surface [1]. Moreover, they allow a significantly refined assignment of the mode frequencies, whose calculated values show a strong spread between the different calculation techniques.

### Conclusion

The employment of a Raman setup, comprising a single monochromator with an ultra-steep low-pass filter and a high-efficiency Si-based CCD detector (ANDOR iDus DU401A-BVF) allowed the detection of surface vibration modes of the (7x7)-reconstructed Si(111) surface, and the high-accuracy determination of their eigenfrequencies, as well as their symmetry properties, although the intensity of these modes was beyond three orders of magnitude below the intensity of the Si bulk phonon Raman peak. In agreement with theory predictions these modes were attributed to localized adatom vibrations, collective vibrations and in-plane wagging modes.

### References

- [1] J. Kim et al., Phys. Rev. B 52, 14709 (1995).
- [2] M. Liebhaber et al., Phys. Rev. B 89, 045313 (2014).

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