## Mid-infrared detection of 10000 chemical bonds by near-field spectroscopy

Johannes M. Stiegler<sup>1</sup>, Yohannes Abate<sup>2</sup>, Antonija Cvitkovic<sup>3</sup>, Rainer Hillenbrand<sup>1,4</sup>

<sup>1</sup> CIC nanoGUNE Consolider, Avenida Tolosa 76, Donostia – San Sebastian, Spain <sup>2</sup> California State University, 1250 Bellflower Blvd., Long Beach, USA <sup>3</sup> Neaspec GmbH, Bunsenstr. 5, Martinsried, Germany <sup>4</sup> IKERBASQUE, Alameda Urquijo 36-5, Bilbao, Spain <u>j.stiegler@nanogune.eu</u>

The analysis of chemical composition and structure of substances is a major topic in chemical, physical and biological sciences. A powerful and widely used tool is infrared absorption spectroscopy, because of its ability to identify materials by their vibrational mode fingerprint. It can, however, not be applied to study nanoparticles and/or molecules, owing to the extremely small infrared absorption cross-sections and the diffraction limited spatial resolution.

With the help of scattering-type scanning near-field optical microscopy (s-SNOM) [1], the diffractionlimited spatial resolution can be overcome by orders of magnitude. Nanoscale resolved infrared imaging of particles as small as 10 nm has been already demonstrated [2,3], providing information on the dielectric properties of the particles at single wavelengths.

Here we demonstrate spectroscopic infrared imaging of nanopartices and show that the spectral phase contrast in s-SNOM can be employed to determine the spectral absorption characteristics of nanoparticles (Figure). Such infrared fingerprints allow for chemical identification of individual 5 nm silicon nitride particles with an absorption cross-section of 10<sup>-23</sup> cm<sup>-2</sup>. This corresponds to the detection of about 10.000 Si-N stretching bonds, respectively of a volume as small as 65\*10<sup>-24</sup> liters.

Our experimental results are in excellent agreement with calculated absorption spectra based on bulk silicon nitride dielectric data using extended/improved finite dipole model calculations to calculate the near-field response of small nanoparticles. This approach opens the door to nanoscale-resolved chemical imaging on the macromolecular level.

## References

- [1] F. Keilmann, R. Hillenbrand, Philos. T. R. Soc. Lond. A, 362 (2004), 787-805
- [2] Cvitkovic et al., Phys. Rev. Lett., 97 (2006), 060801
- [3] A. Cvitkovic, N. Ocelic, R. Hillenbrand, Nano Lett., 7 (2007), 3177-3181



Spectral s-SNOM imaging of a 10 nm SiN nanoparticle. a) Experimental Setup. b) Experimental image showing an IR phase  $\varphi_2$  image recorded at 950 cm<sup>-1</sup>. c) Measured and d) calculated near-field phase  $\varphi_2$  spectrum of the particle encircled in b), The solid line in c) represents a guide to the eye.