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Installation of a combined Raman and AFM microscope as a sample environment for nuclear resonance scattering at P01, PETRA III

S. Rackwitz · I. Faus · B. Lägel · J. Linden · J. Marx · E. Oesterschulze · K. Schlage · H.-C. Wille · S. Wolff · J. A. Wolny · V. Schünemann

Abstract A combined Raman and atomic force microscope (AFM) has been installed at beamline P01, PETRA III, DESY in Hamburg and is now available for all users of this beamline. With this unique setup nuclear resonance scattering and simultaneously performed Raman or Atomic Force Microscopy experiments are possible. Here we report on technical details of this new sample environment and on first tests with respect to the study of microstructures of spin crossover materials using ^{57}Fe nuclear resonance scattering.

Keywords Nuclear resonance scattering · Atomic force microscopy · Spin crossover

1 Introduction

In order to enable nuclear resonance experiments like nuclear inelastic scattering (NIS) [1–3] in combination with complimentary microscopic techniques such as Raman- and Infrared (IR) microscopy we have built and tested such sample environments at beamline ID18 of the ESRF [4, 5]. This project was funded by the German Federal Ministry of Education and Research under contract number 05K10UKA and, according to the requirements of the funding agency, the sample environment comprising a dedicated Raman and an IR

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S. Rackwitz (✉) · I. Faus · J. Linden · J. Marx · E. Oesterschulze · J. A. Wolny · V. Schünemann
Department of Physics, University of Kaiserslautern, Erwin-Schrödinger-Str. 46, 67663 Kaiserslautern, Germany
e-mail: rackwitz@physik.uni-kl.de

B. Lägel · S. Wolff
Nano Structuring Center and Research Center OPTIMAS, University of Kaiserslautern, Kaiserslautern, Germany

K. Schlage · H.-C. Wille
Deutsches Elektronen-Synchrotron, Notkestr. 85, 22607 Hamburg, Germany

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microscope was moved to beamline P01, DESY, Hamburg in 2012. In addition, the Raman microscope was upgraded with an atomic force microscope (AFM) which now allows complementary AFM or Raman measurements in combination with nuclear resonance scattering experiments during sample exposure to the synchrotron beam. The AFM allows not only to measure in contact and non-contact mode, it is also equipped with a magnetic force modus (MFM) as well as an option to measure the work function of sample surfaces. In addition tribological properties of the samples surface can be measured via a dedicated friction force modus. These features enable to combine surface sensitive tribological studies with nano-tribological data of ^{57}Fe containing materials, which can be obtained by NIS via the determination of the partial phonon density of states. The MFM is also suited to investigate the influence of the synchrotron beam on the magnetic properties of the sample. With future spot sizes of the synchrotron beam, possibly in the range of some 100 nm, even manipulations of single iron containing objects on the nanometer scale can be performed via the AFM, as has already been shown by combined X-Ray diffraction and AFM experiments in [6].

2 Materials and methods

The Raman microscope (Senterra©, Bruker GmbH; exp. details see [4]) is placed onto a granite block which is located on an active damping table in order to minimize vibrations during the AFM measurement. The AFM head (NEOS©, Bruker GmbH) is connected to a cylinder, which is mounted into the lens revolver of the microscope. Therefore, subsequent AFM and Raman measurements on the same sample spot are easily possible. The AFM enables x-y scans with a maximum area of 41 $\times$ 41 μm^2. The highest achievable experimental resolution in z-direction is 1 nm and the maximal height difference that can be measured is about 2 μm. The back side of the cantilever is mounted directly above an optical fibre. A laser equipped miniaturized Michelson interferometer is used to detect the distance between the cantilever and the fibre. The entire Raman/AFM microscope including the vibration isolation table (see Fig. 1) was centred onto a (5203.80) manufactured by HUBER Diffraktionstechnik GmbH & Co. KG. The 2-circle segment was used to align the samples surface in parallel to the incident synchrotron beam by keeping the surface perpendicular to the AFM head. The height of the table was adjusted to align the sample measuring position of the microscope with the collimated synchrotron beam. The beam collimation was achieved by Kirkpatrick-Baez optics and resulted in a focus spot of approximately 15 $\times$ 30 μm^2.

For the test of this set-up we have prepared microstructures of a spin crossover (SCO) material which is based on $[^{57}Fe(atrz)_3]MSF_2$ (atrz = 4-amino-1,2,4-triazole; MSF = methanosulfonate (CH_3SO_3)). The surface of a $\sim$1 cm^2 Si substrate was pre-patterned by photolithography under cleanroom conditions. Strips having a width and a distance of 15 μm and circles with a diameter of $\sim$10 μm and a distance of $\sim$10 μm were created. The SCO material was dispensed onto the pre-patterned surface and structured with a lift-off technique [7]. The height of the patterned SCO material varied between 80 and 600 nm.

In order to maximize the signal detection for NIS the silicon wafer was placed directly onto the detector (avalanche photo diode (APD)). To minimize the attenuation of the inelastically scattered radiation the silicon substrate was thinned via a defined etch process with KOH which at the end lead to a 3 $\times$ 6 mm^2 window with a 30 μm thick membrane. The SCO microstructures investigated here have been prepared directly onto this 30 μm membrane of the silicon substrate.

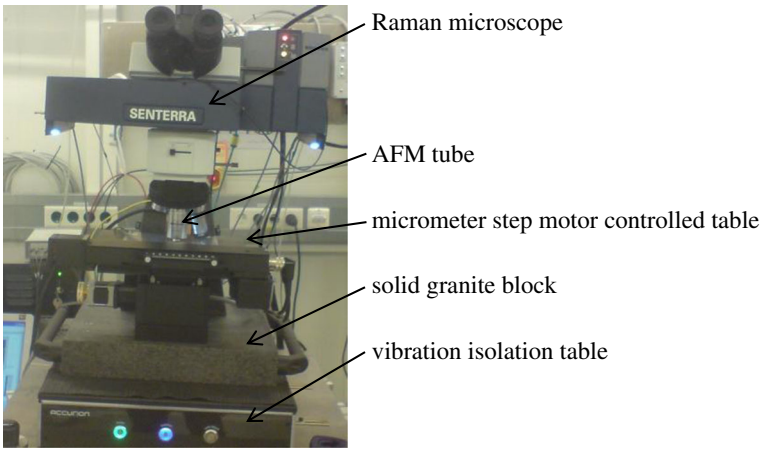

Fig. 1 Picture of the Raman/AFM microscope installed at P01, DESY, Hamburg, during experiment number I-20110655. The vibration isolation table is mounted on a 2-circle goniometer as mentioned in the text

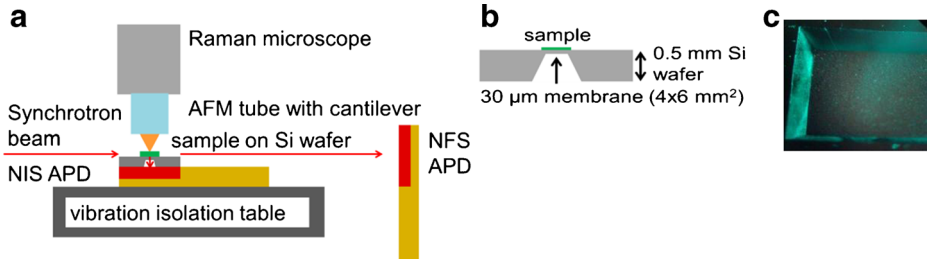

Fig. 2 **a** Raman/AFM setup for NIS/nuclear forward scattering (NFS) detection. The sample including the Si substrate was put directly onto the APD. This allowed the simultaneous application of NIS/NFS and AFM in order to study the surface of the sample (see Fig. 3). For the temperature controlled NFS measurements (see Fig. 4) a mini cryostat (Linkam®) was placed on the microscope stage instead of the NIS APD. **b** The newly designed 0.5 mm thick Si wafer with a 30 µm membrane and a schematic view of the cross section and **c** a picture of the etched window

In order to follow the spin crossover process of the SCO microstructures the samples have been mounted on a mini cryostat (Linkam®) and temperature controlled NFS experiments have been performed at 283 and 243 K, respectively.

3 Results and discussion

Figure 3a shows an optical view of a microstructured silicon membrane with SCO strips on top. This microstructure has been investigated by means of AFM with the collimated synchrotron beam on the sample. No electronic artefacts could be recognized when the synchrotron beam hit the sample during the AFM scans for a scanning time of ∼30 min. The analysis of the so obtained AFM picture displayed in Fig. 3b shows that the strips which are ∼15 µm wide have a height of only ∼120 nm. Figure 3c exhibits NIS data which have

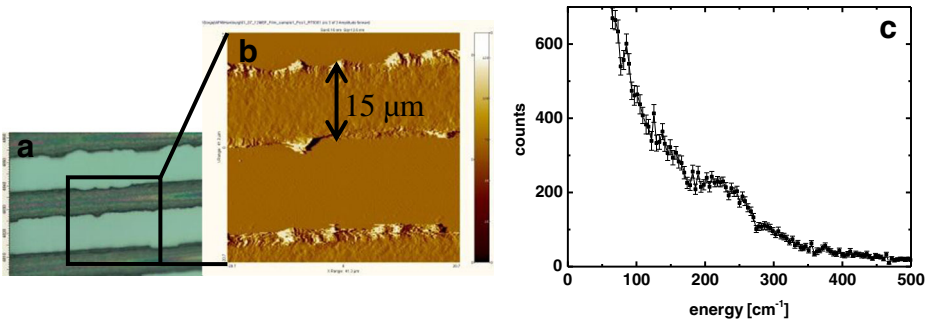

Fig. 3 **a** Optical view and **b** the AFM picture of microstructured $[Fe(atrz)_3](CH_3SO_3)_2$strips, 15 µm wide and ∼120 nm thick. **c** NIS data of the $[Fe(atrz)_3](CH_3SO_3)_2$ microstructures taken at room temperature with the set-up displayed in Fig. 2

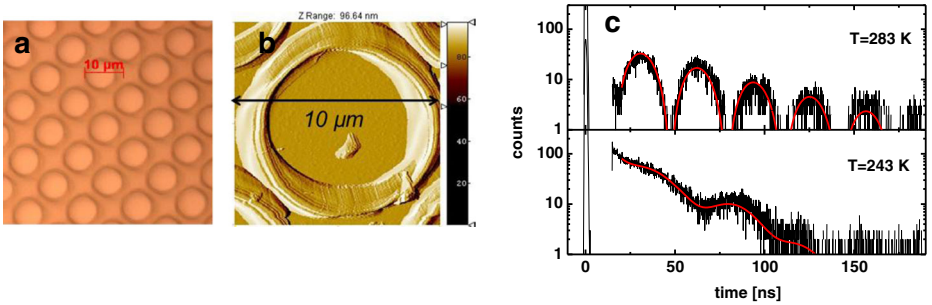

Fig. 4 **a** Optical view and **b** an AFM picture of microstructured $[Fe(atrz)_3](CH_3SO_3)_2$ rings with 10 µm in diameter and a height of ∼100 nm both taken at room temperature. **c** NFS data for the $[Fe(atrz)_3](CH_3SO_3)_2$ microstructures (600 nm in height) at 283 and 243 K, respectively. The change of the beating indicates a spin crossover process from $S = 2$ to $S = 0$. The solid line is a simulation with parameters explained in the text

been collected with this set-up in the configuration shown in Fig. 2. It should be noted that the count rate in the elastic channel was approx. 75 s^{-1} which normally allows collecting a reasonable NIS data set within 4 to 8 h. The NIS data displayed in Fig. 3c show an unusual broad band within the energy region of 120 to 280 cm^{-1}. This is neither caused by the sample environment nor by the sample itself: It turned out that, due to problems with the high resolution monochromator, its instrumental function was unusually broad and we therefore did not observe a more detailed NIS pattern of the high-spin ($S = 2$) state of the sample as in previous experiments [8]. Since P01 at PETRA III is now equipped with a different high resolution monochromator users of this new sample environment can now expect much better resolved NIS data.

Figure 4a shows another type of SCO microstructures which have been prepared in the same way as the stripe type microstructures discussed above. The diameter of the microstructured rings is ∼10 µm and their height was determined to be ∼100 nm with the NEOS©-AFM (see Fig. 4b).

That these SCO microstructures are indeed capable of the spin crossover effect is shown by the temperature dependent NFS data displayed in Fig. 4c. At T = 283 K a periodic beating is observed which is characteristic for a quadrupole splitting of $\Delta E_Q = 2.73$ mms^{-1} typical for a high-spin (HS) site. Cooling to T = 243 K leads to a complete different

NFS time pattern which could be reproduced by a simulation using the software Motif [9] assuming the presence of 22 % HS sites and 78 % low-spin (LS) sites with the parameters $\Delta E_{QHS} = 2.91\ mms^{-1}$, $\delta_{HS} = 1.07\ mms^{-1}$, $\Delta E_{QLS} = 0.21\ mms^{-1}$ and $\delta_{LS} = 0.5\ mms^{-1}$.

The presented NFS experiments show that the microstructured $[Fe(atrz)_3]MSF_2$ is capable of undergoing a spin crossover. Obviously, this property is retained after the coating and drying procedure of the material during the microstructuring process. This is a promising step on the way to the fabrication of SCO microstructures with even smaller lateral dimensions in the nanometer regime.

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