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Report:

Using the coherent x-rays the nanometre-scale dynamics of thin samples can be followed in the time domain using the technique of x-ray photon correlation spectroscopy (XPCS). Due to the coherence of the incident x-rays the scattered radiation shows modulation ("speckles"), which is given by the squared modulus of the Fourier transform of the electron density in the sample. Determining the lifetime of the speckles at a given scattering vector q allows to draw conclusions on the dynamics in the sample.

The main goal of the experiment at hand was to ascertain the process responsible for coarsening of Ag precipitates in silver-doped window glass. Furthermore, by exploiting the small beam diameter, we studied the deformation of initially spherical silver precipitates after irradiation with intense femtosecond laser pulses across the footprint of the laser, therefore as a function of intensity. Finally, we made preliminary measurements concerning the possibility of following atomic diffusion by XPCS.

Fig. 1 shows a detail of the speckled small-angle scattering from the Ag-glass sample at 450°C. The frames were taken with TROÏKA's 1242×1152 direct illumination CCD at a distance of 1.8 m, 5 s exposure per frame, $10 \times 10\,\mu m^2$ slits at an energy of 8 keV. Although the mean radius (determined by a conventional SAXS evaluation) grew by some 30 % during the accumulation of 1000 frames, shown in Fig. 1, the lifetime of the speckles is obviously longer, since they have not been smeared out. The q values shown here correspond roughly to precipitate sizes (≈ 11 nm), so it can be concluded that the precipitates are stationary on these lengths scales within the accumulation time. As a consequence the classical Lifshitz-Slyozov-Wagner mechanism known from metallic systems has to be at work, where the precipitates are fixed in space and coarsening proceeds by diffusion of solute atoms through the matrix from small precipitates to large ones, since for precipitate migration and coalescence to play a role, the precipitates would have to diffuse on the order of the characteristic particle distance within this time window. Measurements at several temperatures yielded the same behaviour. Unfortunately, due to the bad condition of the camera, a more quantitative evaluation of this experiment by temporal autocorrelation functions is not possible, since the corrupted pixels lead to a shift of the baseline.

It has been demonstrated by optical absorption spectroscopy that initially spherical silver precipitates become ellipsoids when irradiated by a single intense femtosecond laser pulse [1]. Since the intensity in such a laser pulse is not homogeneous, it is expected that the morphology of the resulting deformed precipitates reflects this inhomogeneity. In order to clarify this issue, a sample with lines written by a femtosecond laser was prepared. The lines had a spacing of 200 µm. Since with these measurements coherence was not required, the camera was moved into a distance of 80 cm from the sample in order to have the signal on an undestroyed area of the chip, the slits were kept at $10 \times 10\,\mu\mathrm{m}^2$ for optimal spatial resolution. Fig. 3 shows a scan across a line, the steps were 50 µm. The effect is clearly visible, but further measurements have to be done.

Measuring the atomic diffusion step by XPCS was always thought to be impossible with today's third generation synchrotrons. In contrast to conventional small angle measurements, the scattered intensity spreads over a solid angle of 4π, and sensitivity on atomic length scales implies scattering vectors on the order of several Å, i.e. far in the diffuse regime, requiring a high degree of temporal coherence. Using HASYLAB's unscathed CCD camera we tried to compensate for the low scattering intensity (about two photons per hour and pixel) by the sheer number of pixels. As is shown in Fig. 2, indeed, at room temperature the scattered intensity does show a speckle pattern, which is stable over the accumulation time (2.5 h), whereas the dynamics in the sample at 287°C is much faster than the accumulation, because no contrast is left. This is a clear proof that atomic scale XPCS is feasible even at today's x-ray sources.

Figure 1: SAXS of Ag precipitates in glass. Detail of 1000 summed frames, from $q = 0.044\,\mathrm{nm}^{-1}$ (right bottom) to $q = 0.166\,\mathrm{nm}^{-1}$ (left top).

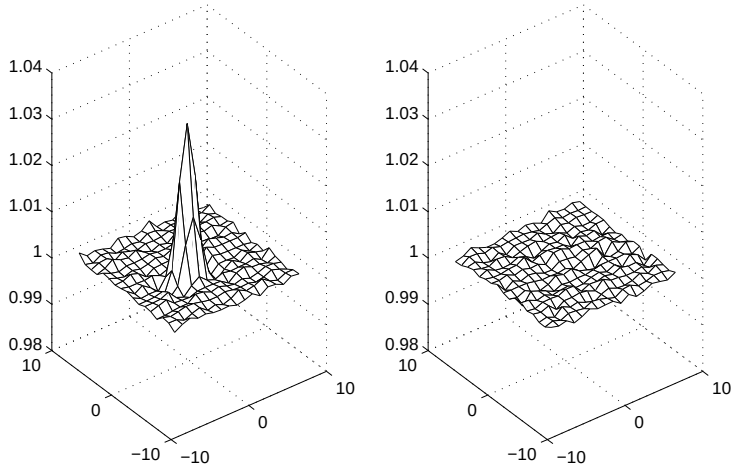

Figure 2: Feasibility of XPCS measurements of atomic diffusion. Pixel-wise q space autocorrelation of summed frames; left: room temperature; right: 287°C. Detector was at $q = 1.4\,\mathrm{Å}^{-1}$.

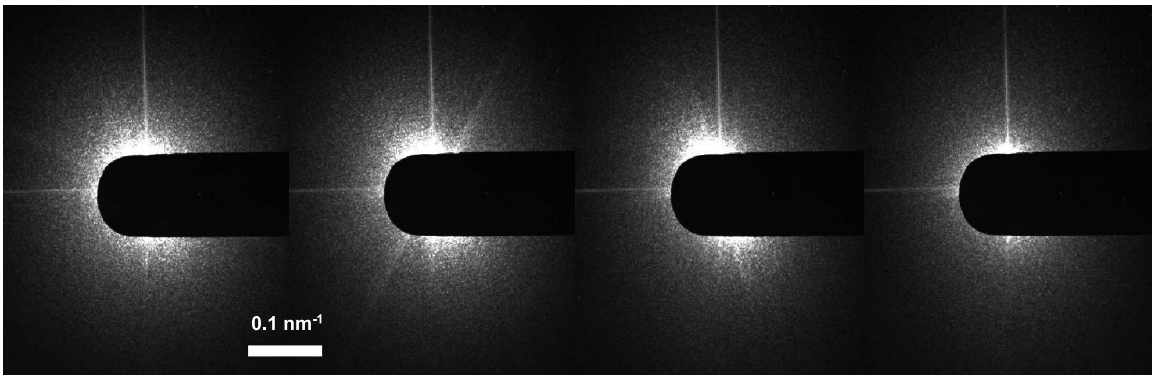

Figure 3: SAXS of Ag precipitates in glass after treatment with fs laser. Scan across line written with the fs laser.

[1] M. Kaempfe, G. Seifert, K.-J. Berg, H. Hofmeister, H. Graener, Eur. Phys. J. D **16**, 237-240 (2001).