Supplemental Material

Measurement of local crystal lattice strain variations in dealloyed nanoporous gold

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1. Connection to the main document

In the main part of this letter we show spatially resolved measurements of strain in nanoporous gold. They are based on the evaluation of nano-beam electron diffraction (NBED) patterns acquired in the scanning mode of a transmission electron microscope (TEM) and on the evaluation of high-resolution scanning transmission electron microscope (STEM) images. As the npAu structure is strained in three dimensions and the lattice parameters vary between atomic layers, principally a 3D measurement of atomic positions \cite{S1} would be necessary to describe the complete strain state of the sample. In this supplemental information we show by evaluation of simulated NBED patterns as well as STEM images of test structures, how the experimental results, obtained using methods that cannot resolve strain in three dimensions, can be interpreted. In simulated test structures the 3D strain distribution is known exactly and hence a direct comparison between true strain and measured strain is possible. Furthermore, we show high-resolution TEM images of the npAu ligaments on which experimental measurements of strain have been performed. These images show that at least thin films of contamination are present on the surfaces of npAu ligaments.

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2. Simulation Methods

NBED patterns and STEM images have been simulated with the STEMsim software [S2]. The model structure was built up of 26450 atoms on a regular face-centered cubic (fcc) crystal lattice, periodic boundary conditions in [100] direction, a thickness of 11 atomic layers in the [001] electron beam direction and an extension of 10 nm in [010] scan direction. In scan direction the end of the crystal has a round surface leaving only three atoms in the outmost atomic columns. The test structure was relaxed via an energy minimization using the LAMMPS software [S3] with the embedded atom method (EAM) potential for gold by Foiles [S4]. Atom positions were relaxed until the relative change of the energy was less than $10^{-12}$. The relaxed structure can be seen in Fig. S1(a). As it is known that structure relaxations with the EAM potential seem to overestimate the strain magnitude at the surface [S5,S6], it is not expected that the relaxed structure represents the true strain state in npAu accurately. Nevertheless, this structure should be sufficient to study effects of depth depending lateral lattice parameters on strain measurements. Simulated NBED patterns have been further modified as described in Ref. [S7] in order to obtain simulated diffraction patterns that describe the experiment as accurately as possible.

3. Supplemental results

3.1. Simulation

A scan along the magenta coloured arrow as indicated in Fig. S1(a) has been simulated resulting in a simulated series of NBED patterns, which has been evaluated in the same manner as the experimental ones. The result is shown in Fig. S1(b) by the two dotted curves. The dotted blue curve shows the strain in $<100>$ direction, which is approximately zero because the structure cannot relax in this direction due to the periodic boundary conditions. The dotted red curve shows the strain in $<010>$ direction revealing tensile strain approaching the border of the structure. For comparison the red and the blue lines show the strain which has been calculated by averaging the true strain in the test structure along the electron beam direction. There is a good agreement between both red and both blue curves indicating that the interpretation of experimental results as average strain in the electron beam direction is qualitatively justified in the present case. One aspect that is not recovered by the evaluation of the simulation is the inward surface relaxation of the atomic layer at the border to the vacuum. Thus, as mentioned in section 3.2 of the main document relaxations of single surface layers cannot be measured with this diffraction-based method.

For the interpretation of the result obtained from the evaluation of high resolution STEM images in section 3.2 of the main document, also a STEM image of the test structure has been simulated. The evaluation of this simulated image is shown in Fig. S1(c) and (d). From Fig. S1(d) it is clear that the strain obtained from the high resolution STEM images can be interpreted as average strain in electron beam direction with respect to a certain reference region also quantitatively. Hence, it is clear that the result shown in Fig. 3 of the main document indicates inward relaxation at the curved surfaces of npAu.

In conclusion, both methods measure the strain of the sample averaged in electron beam direction qualitatively. But only the high-resolution STEM method reproduces the numerical value also quantitatively. The disadvantage of the latter is that STEM
Figure S1. Simulation and evaluation of strain measurements. (a) Simulated test structure with depth depending lattice strain. (b) Evaluation of NBED patterns simulated along the line indicated in (a). The evaluation shows that measured strain can be interpreted as average strain in electron beam direction, but strain of single monolayers cannot be resolved. (c) Evaluation of the STEM simulation in the area indicated in (a), inward relaxation of the surface layers is recovered. (d) Comparison of result in (c) with average strain in electron beam direction. Measured strain can be interpreted as average strain in electron beam direction. Strains measured with respect to yellow marked reference regions.

images can be acquired only in a small field of view and of very thin ligaments. For this reason, the NBED-based method is clearly required to analyse larger parts of the sample such as whole ligaments. The problem that NBED cannot resolve strain of single atomic layers has been investigated earlier and can be explained by parts of the electron beam that leak in neighboured atomic columns [S8]. Hence, both methods have their assets and drawbacks, but they complement each other.

3.2. Contamination

Regarding the literature, some publications show TEM images of clean, facettet npAu surfaces [S9–11]. Nevertheless, the problem of contamination especially in the STEM mode is a well-known problem [S12,S13]. Adsorbed molecules might come from sources on the walls of the microscope column and then migrate to the area under electron irradiation [S12]. The layer is than formed by an interaction between the molecules and the electron beam. Even in the TEM mode very often the surfaces are covered at least by a thin layer of unknown adsorbates. The visibility of this layer can be minimized tuning the defocus, nevertheless it is still present. This is shown in Fig. S2. Ligaments are shown here before the measurements of strain. Even at this time a thin layer of adsorbates can be seen. In printed versions of this letter the contamination film might not be visible. For this reason, the facettet crystalline surfaces of the ligaments are marked by the dashed green lines and films of contamination are marked with the dotted yellow lines as a guide to the eye. Figures S2(a) and (c) show the same
Figure S2. High resolution TEM images of npAu ligaments investigated in the main document. As a guide to the eye the crystalline facetted surfaces are marked by dashed green curves, layers of adsorbates are marked with dotted yellow curves. (a) and (c): same ligaments as investigated in Figures 2(a) and (c) of the main document, respectively; (b) representative ligament of sample A as investigated in Figures 2(b) and 3 of the main document.

Adsorbed molecules change the strain state of the nanoporous structure [S14–17]. For this reason, the contamination film seen on the samples could affect the strain state of the samples.
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