	Experiment title: Determination of Point Defect Concentrations in Nano-crystalline Pt	**Experiment number**: 20-02/691
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Nano-crystalline metals are generally in a non-equilibrium state after preparation by e.g. magnetron sputtering. The aim of this work was to explore the modification of non-equilibrium point defect concentrations (PDC) and residual stresses during isothermal annealing of nano-crystalline Pt films. The out-of-plane lattice parameter, a, and the thickness, L, of a 40 nm film were measured by XRD (Bragg-Brentano) and XRR, respectively, as a function of annealing time at 130, 200, 300 and 400 °C in an in-situ vacuum furnace at 10^{-6} mbar. In addition, GI-XRD (0.34 °) measurements were done.

For analysis it is assumed that $a(t, T) = a_0 + \Delta a_{th}(T) + \Delta a_{mis}(T) + \Delta a_i(t, T)$, where a_0 is the lattice parameter in the as-deposited state, Δa_{th} is the modification of the lattice parameter due to thermal expansion, Δa_{mis} due to stress resulting from thermal mismatch between substrate (SiO_2) and Pt film and Δa_i due to intrinsic stress, resulting from the production of the film by sputtering. Further, $L(t, T) = L_0 + \Delta L_{th}(T) + \Delta L_{mis}(T) + \Delta L_i(t, T) + \Delta L_V(t, T)$, ΔL_j (j = 0, th, mis, i), are the corresponding quantities of the film thickness and ΔL_V is the thickness change due to a modification in PDC, which becomes not visible in lattice constant changes in first approximation. Note that the determined experimental resolution of the method, given by the maximum error limits of $\sigma(\Delta L/L) < 5 \times 10^{-4}$ and $\sigma(\Delta a/a) < 1 \times 10^{-4}$ is better than initially expected, allowing to determine changes in PDC of about 1×10^{-3}. The modification of PDC as function of time and temperature can be obtained by simply using the formula $\Delta c = \Delta L_V/L_0 = (L-L_0)/L_0 - (a-a_0)/a_0$ (Fig.1(a)).
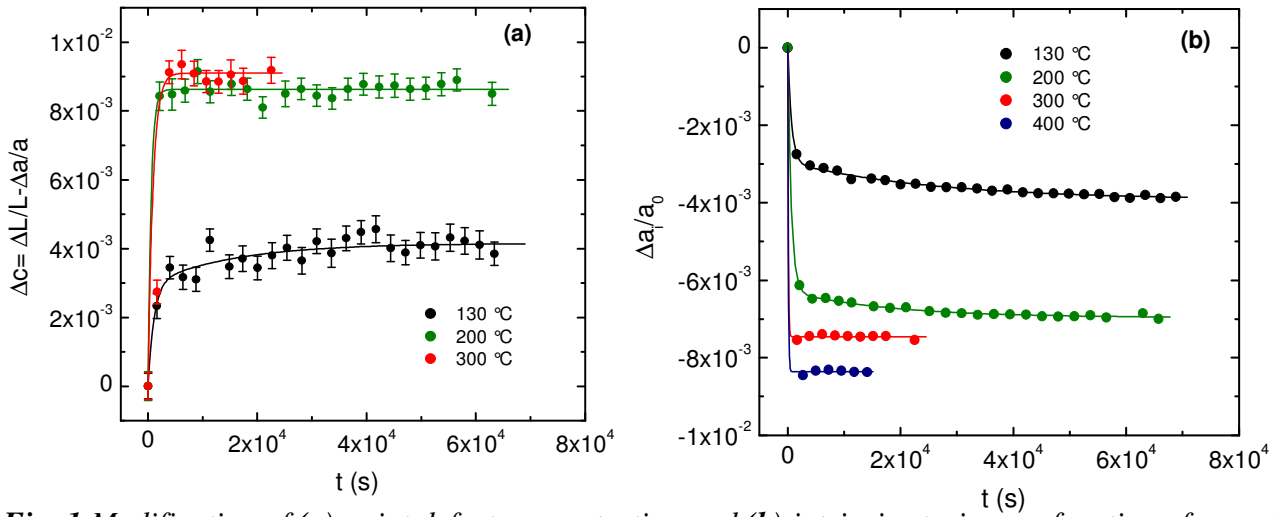
Fig. 1 *Modification of **(a)** point defect concentration and **(b)** intrinsic strain as a function of annealing time. The lines are a guide for the eye. The error limits in **(b)** are smaller than the dots.*

As obvious, for all temperatures we observe a drastic increase of Δc as a function of annealing time, however limited to the first hour of annealing. This can tentatively be interpreted by a process connected with the formation of free volumes, e.g. vacancies during annealing. This is in contrast to initial assumptions, where a reduction of Δc is expected due to vacancy annihilation. A preliminary idea to explain the results is that vacancies are formed to counterbalance the development of stresses during heating to elevated temperatures (see below). A possible influence of an oxide layer forming at the surface is currently discarded by high resolution XPS measurements.

From analysis of a(t,T) closer information on strain modifications can be derived. It is assumed that strain modifications resulting from thermal expansion, Δa_{th}, and thermal mismatch, Δa_{mis}, are time-independent. Detailed analysis (not plotted) shows that during heating up to 400 °C we are in the thermo-elastic range, resulting in the formation of more compressive stresses. Consequently, the observed time-dependence is attributed to the modification of intrinsic strains $\Delta a_i(t, T)$ (see Fig. 1(b)). For T > 200 °C the increase in Δa_i takes place during the first 30 min of annealing (the actual time resolution of the experiment). However, for T $\leq$ 200, the process slows down and becomes visible on a time scale of several hours. The extraction of characteristic time constants is in progress. Further insight into the modification of stresses was gathered from GI-XRD measurements. The discussion is omitted here due to space limitations.

In conclusion, we demonstrated the feasibility of our method for the determination of PDC. For T $\leq$ 200 °C a sufficient resolution can be achieved in order to quantify strain modifications as a function of annealing time. For PDC this can also be achieved for lower temperatures and/or faster data acquisition.