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Tracking the restructuring of oxidized silver-indium nanoparticles under a reducing atmosphere by environmental HRTEM

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1. Experimental methods for phase identification

During the *in situ* investigation, all nanoparticles experienced more or less rapid evolutions in terms of morphology and mainly atomic arrangements. To better identify the crystallographic phases that formed under different configurations of temperature and atmosphere, we have systematically recorded video sequences using the free video grabber Camstudio v.2.0 (http://camstudio.org/) as preconized previously[1]. Doing so, best frames were extracted, if possible after averaging several consecutive frames to gain in signal-to-noise ratio, in order to allow the easiest identification through analysis of local Fast Fourier Transforms as reported below. In some other cases, single images were directly acquired and Fourier transformed in a similar way. These operations were facilitated by the spherical aberration corrector allowing to maintain a 0.1 nm resolution in the best cases even at the highest temperatures used in this study, i.e. 500°C. Identifying the nature of crystalline structures observed was performed by several methods. The Digital micrograph software (GATAN inc.) is first used for several steps in the data acquisition / interpretation process: i/ recording high resolution images or displaying them to grab movies, ii/ correcting the contrast/brightness/gamma parameters of the images, iii/ filtering to remove the amorphous background in the image, iv/ computing the Fourier transform (FT) of manually selected regions of interest (ROI), and v/ measuring the inter-planar distances and angles from visible diffraction spots in the FT. From the FT images, a home-made software (DIFFWORKSHOP, developed by T.EPICIER at MATEIS Lyon) proposes zone axis solutions taking into account the positions and angles between the different diffraction spots. These solutions were used as input for kinematical simulations with JEMS (simulation package from CIME-EPFL, Lausanne), to definitely confirm the structure.

2. Experimental protocol

Four samples of $In_{75}Ag_{25}$ clusters (deposited on ultra-thin carbon grids) have been elaborated under the same experimental conditions. After air exposure (and thus indium oxidation), each of them has been exposed to various conditions of temperature and hydrogen pressure summarized in figure 2 which show all the applied temperature and pressure for the four samples. Blue numbers represent the hydrogen pressure. An important issue that may influence the reaction mechanisms is radiation damages due to the electron beam, leading to heating, atomic displacements, or radiolysis for high electron doses[2]. A weak electron dose (meaning a spread beam) during acquisitions induces a worst signal-to-noise ratio, but less impact on the nanoparticles structure and evolution. Conversely, a high electron dose leads to a better signal-to-noise ratio but may speed up the reactions, or even introduce short-cuts in the expected phase and nanostructure evolution. In order to avoid as much as possible the artefactuous effects dues to the electron beam, all observations under gas were performed with electron fluxes and doses significantly lower than that used in the last sample (4) depicted in figure 2, where a whole heat treatment was conducted without any gas. This test experiment did not reveal any detectable evolution of the structures and phases present in the nanoparticles, which confirms the essential role played by hydrogen to initiate transformations, and rule out at the same time the hypothesis of a strong and unique influence of the electron beam alone. While the last sample was thus used as a test reference, the first sample (fig. 2.a) was directly exposed to high temperatures and hydrogen pressures. For the second and the third samples (fig. 2.b and 2.c), the role of hydrogen has been investigated by applying high pressures at lower temperatures than the first.

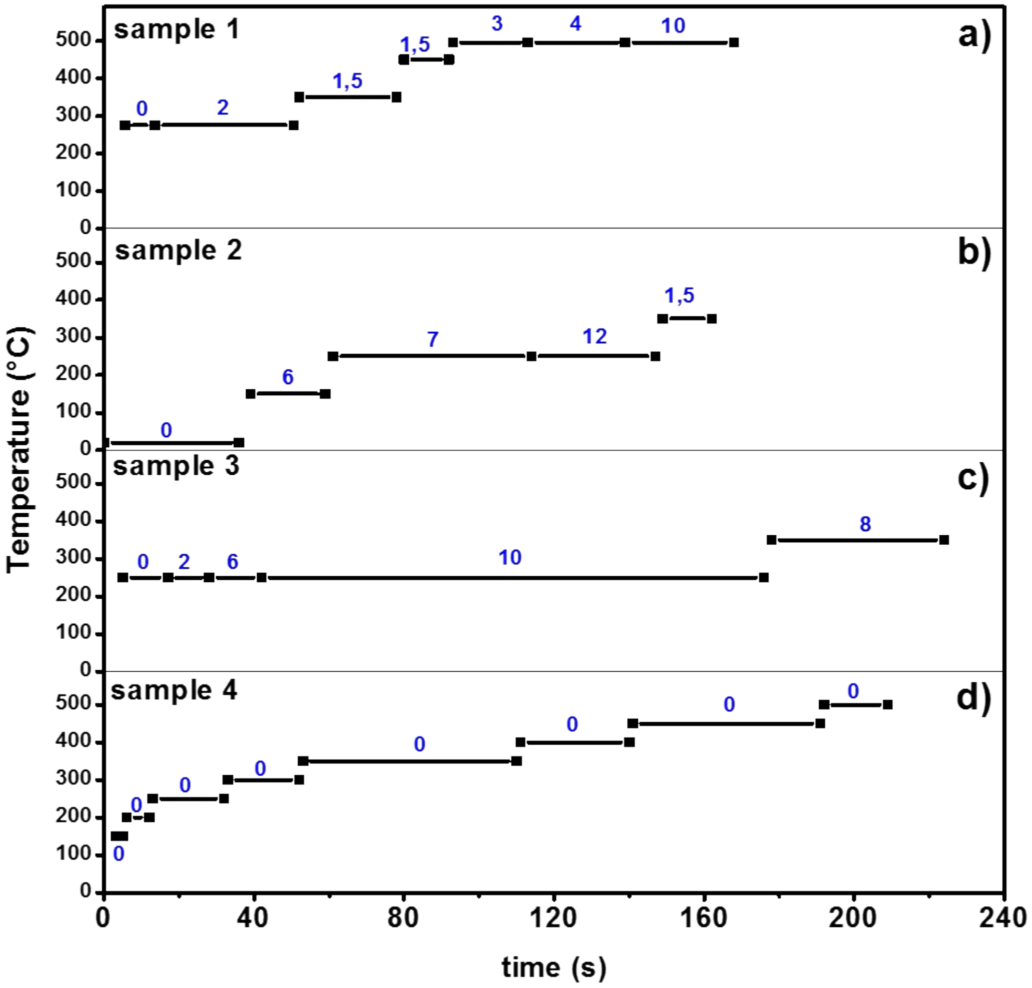


Fig. SI1. Exposure times of environmental treatments for all sample. Blue numbers represent the applied hydrogen pressure. Each of the (T,P) couples have been investigated. The first sample (a) has been used for quickly probing hard conditions (temperature and pressure). High hydrogen pressures at lower temperatures have been explored on the second (b) and third (c) samples. The last sample (d) has been used as a control sample, by increasing the temperature without hydrogen to evidence the need of hydrogen to start structural changes.

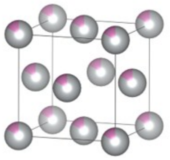
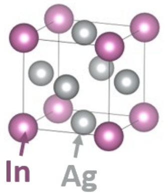
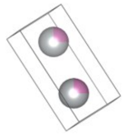
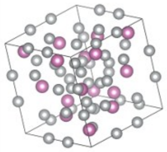
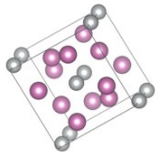
	α	α’	ζ	γ	ϕ
					
Space group name	F m -3 m	P m -3 m	P 63/m m c	P -4 3 m	I 4/m c m
Crystal system	Cubic	Cubic	Hexagonal	Cubic	Tetragonal
Composition range at 25°C (%In)	0-20%	25%	27-29%	33.5%	66.5%
Composition range at 25°C (%In)	0-20%	187°C	25-43%	312°C	166°C
Cell parameters at 25°C	a = 4.08 Å(0%) a = 4.14 Å(20%)	a = 4.14 Å	a = 2.95 Å(27%) c = 4.78 Å(27%) a = 2.96 Å(29%) c = 4.78 Å(29%)	a = 9,92 Å	a = 6.88 Å c = 5.62 Å
Cell parameters at 320°C	a = 4.08 Å(0%) a = 4.14 Å(20%)	187°C	a = 2.94 Å(25%) c = 4.79 Å(25%) a = 3.00 Å(40%) c = 4.75 Å(40%)	312°C	166°C

Table 1. Crystalline parameters of Ag-In alloys. Some parameters (limit domain, cell parameters) are given at 25°C and 500°C. Data have been taken from Campbell et al. for both **α** and **α’** cubic phases,[3] Campbell et al. and Satow et al. and for **ζ** hexagonal phase,[3,4] Brandon et al. for **γ** cubic phase[5] and Havinga et al.[5] for **ϕ** cubic phase.[6] Yellow cases indicate that the phases do not exist at 500°C. Inserted temperatures represent the existence limit of each concerned alloys.

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