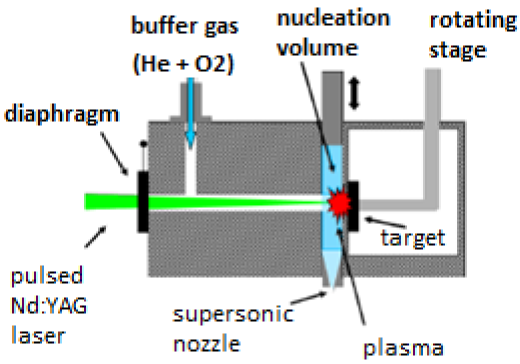
Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

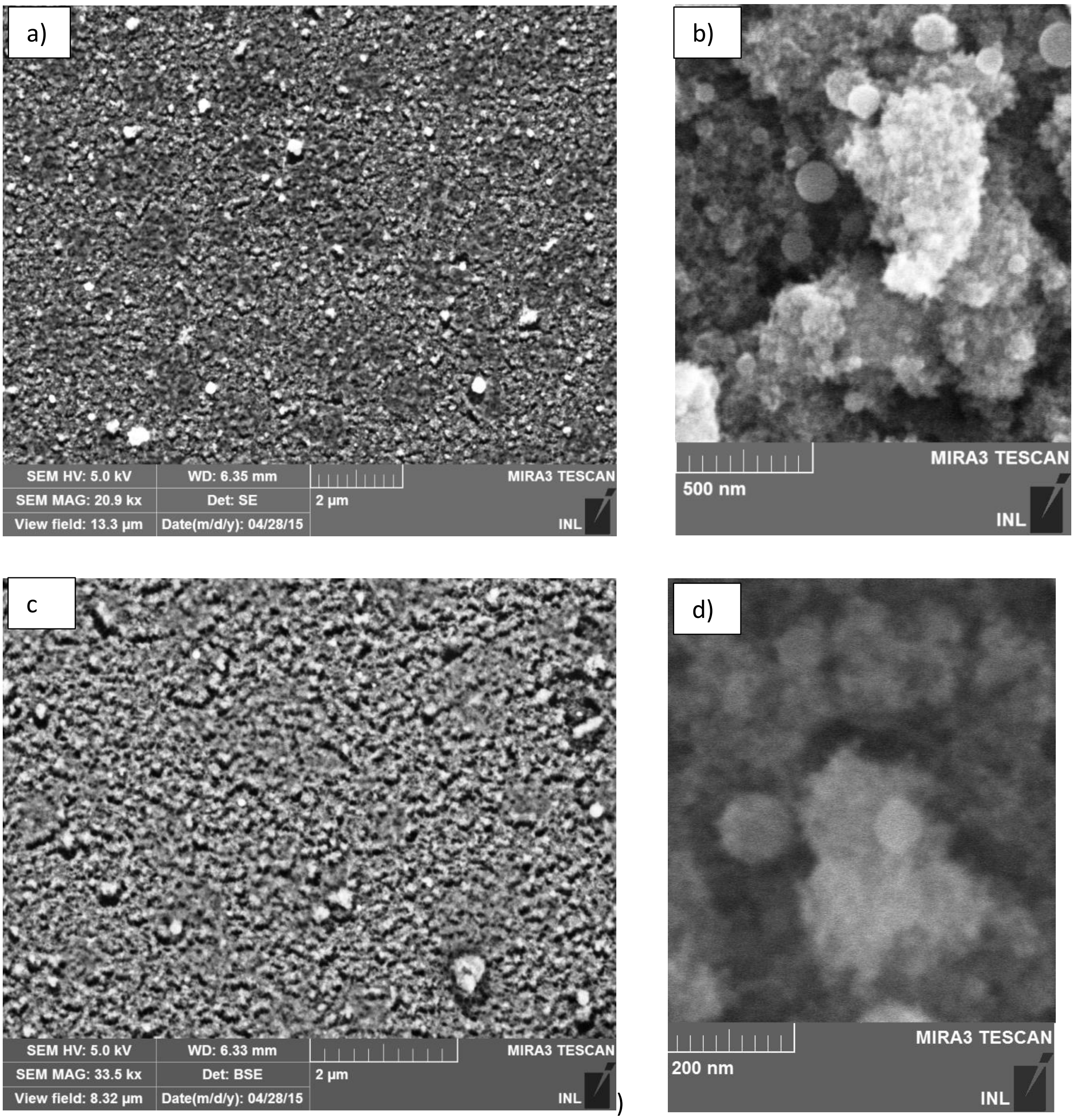
1- Schematics of the nucleation chamber of the LECBD (low energy cluster beam deposition) technique



A plasma is first generated by ablating a target with a high power pulsed (10 Hz repetition rate) doubled (532 nm) YAG: Nd laser. The target is a pellet made of a mixture of ZnO and Ga_2O_3 (99.999% pure each) microscopic powders sintered and annealed at 800°C for 10h. The plasma is first quenched by a constant flux of gas consisting of 75% He and 25% O_2. The buffer gas induces the stabilization of nucleation embryos (dimers and trimers).
On these embryos, atoms from the plasma aggregate according to an accretion process when the plasma expands through a micrometer nozzle while leaving the nucleation chamber at some 20 mbar and reaching the deposition chamber at a few 10^{-7} mbar. This important pressure variation (eight orders of magnitude) located over a very small distance (a few microns from the nozzle) leads to an adiabatic expansion of the plasma leading to the hyperquenching of the nanoparticles produced by accretion. The quenching rate is estimated to about 10^8 K/s. The resulting particles form a supersonic jet which is deposited on silicon substrates

2- SEM images of films assembled from the deposition of GZO nanoparticles

The images were acquired on a FEG TESCAN MIRA 3 SEM, at 5 or 20 kV accelerating voltage (2.4 nm probe) collecting the secondary electrons (a) b) and d)) or backscattered electrons (image c)).

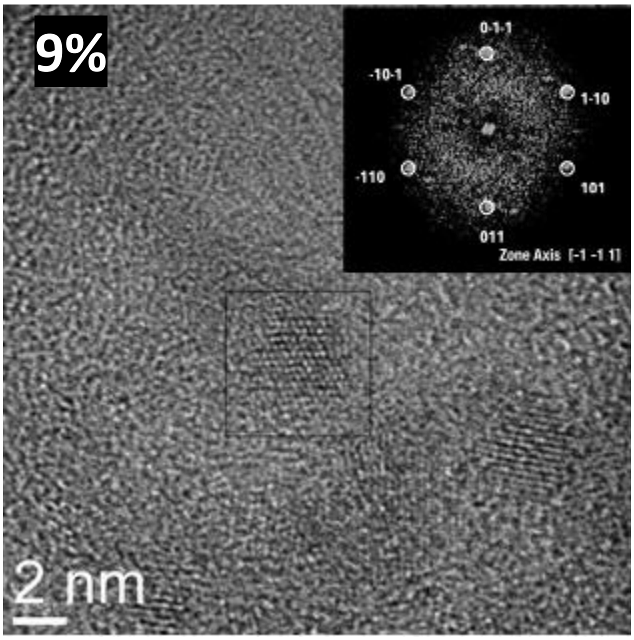


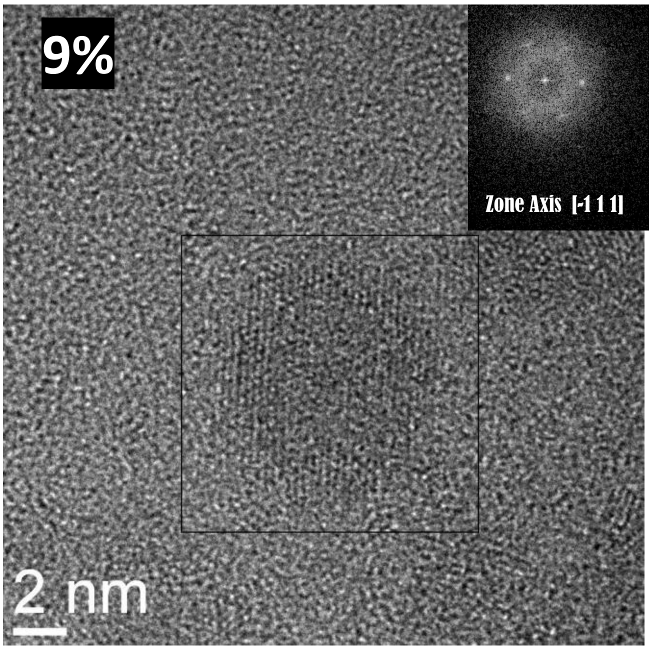
low magnification (a) and high magnification (b) images of a film (43 nm equivalent thickness) of GZO nanoparticles doped at 3%

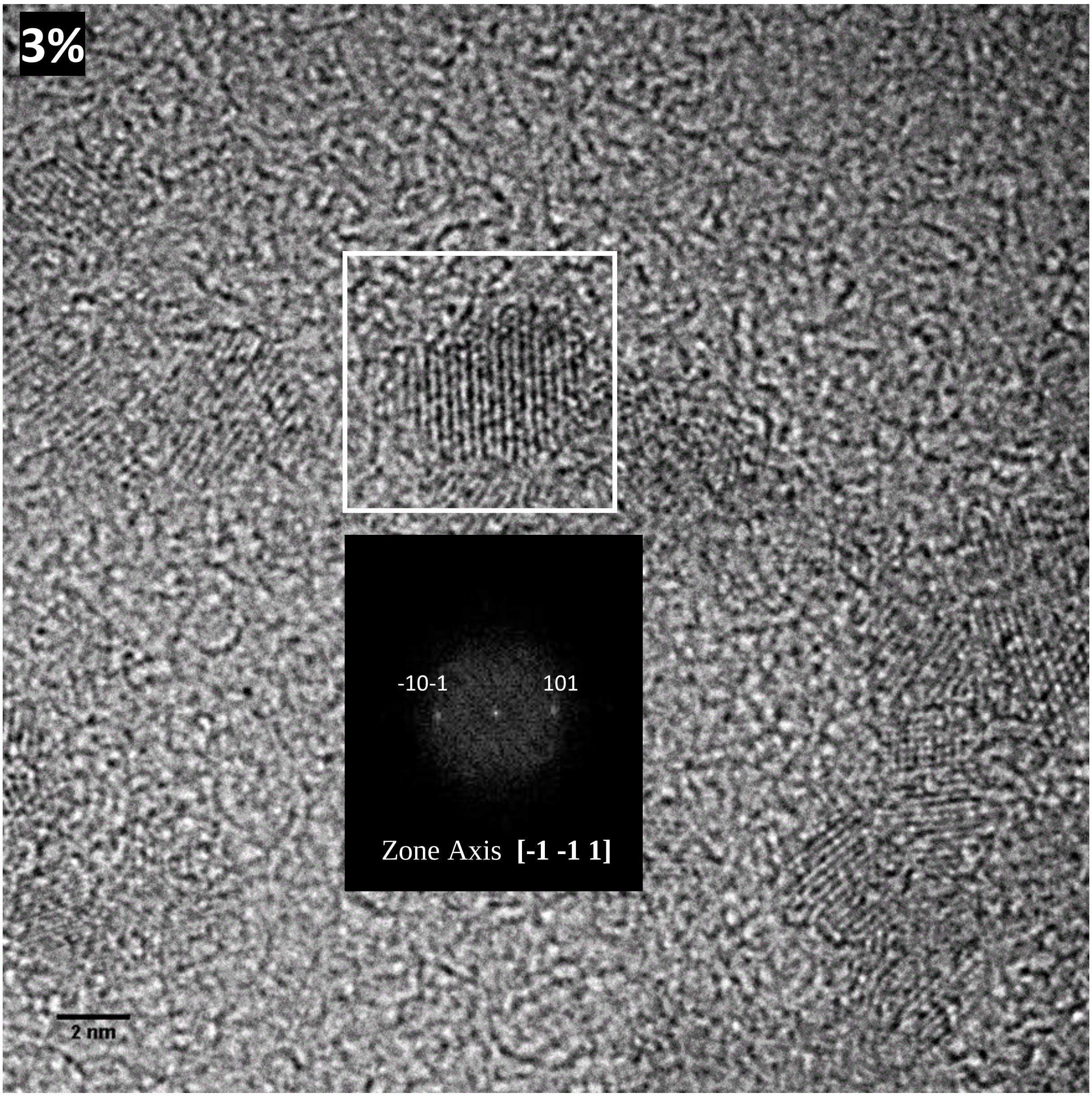
low magnification (c) and high magnification (d) images of a film (90 nm equivalent thickness) of GZO nanoparticles doped at 6%.

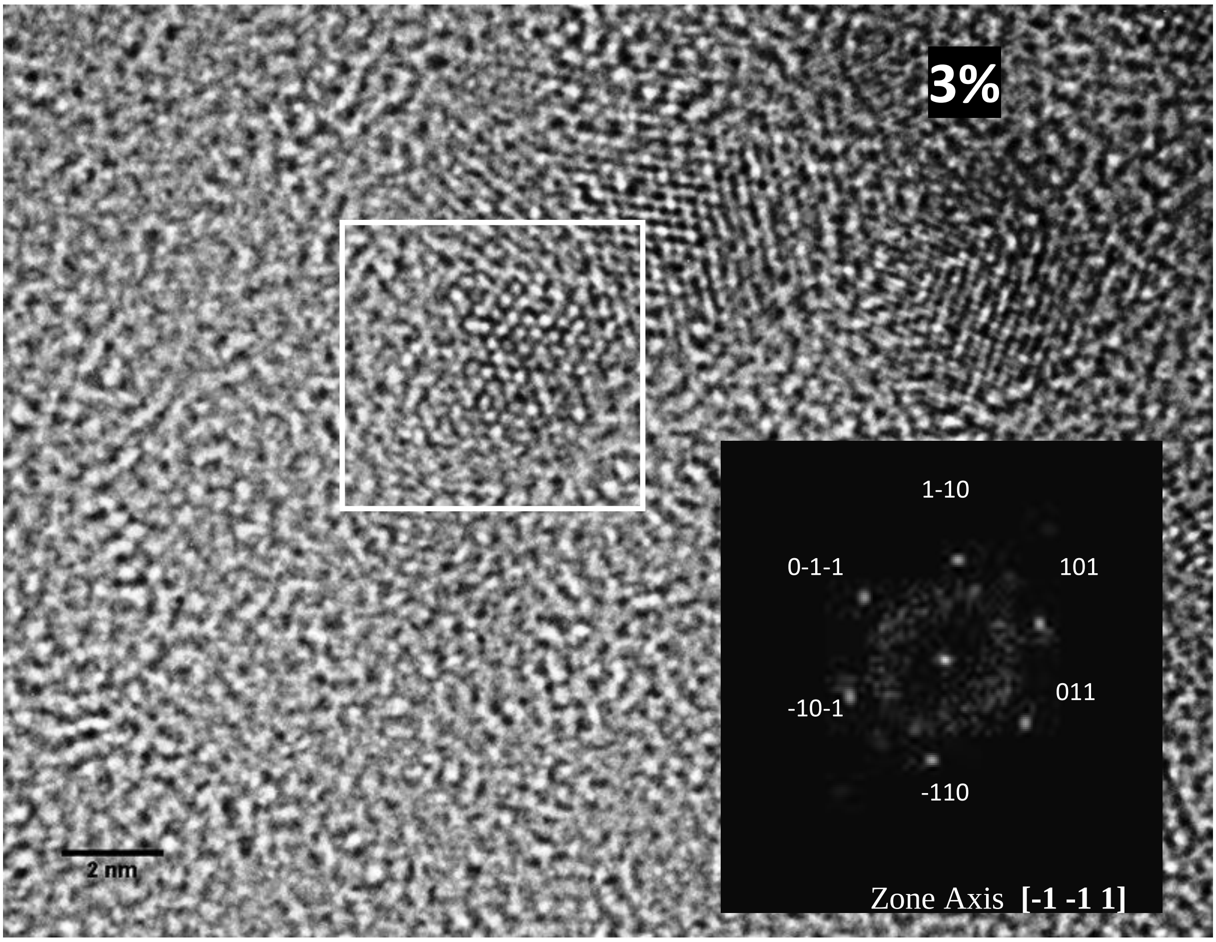
On the high magnification images, the foam-like structure (high porosity) of the films can be seen.

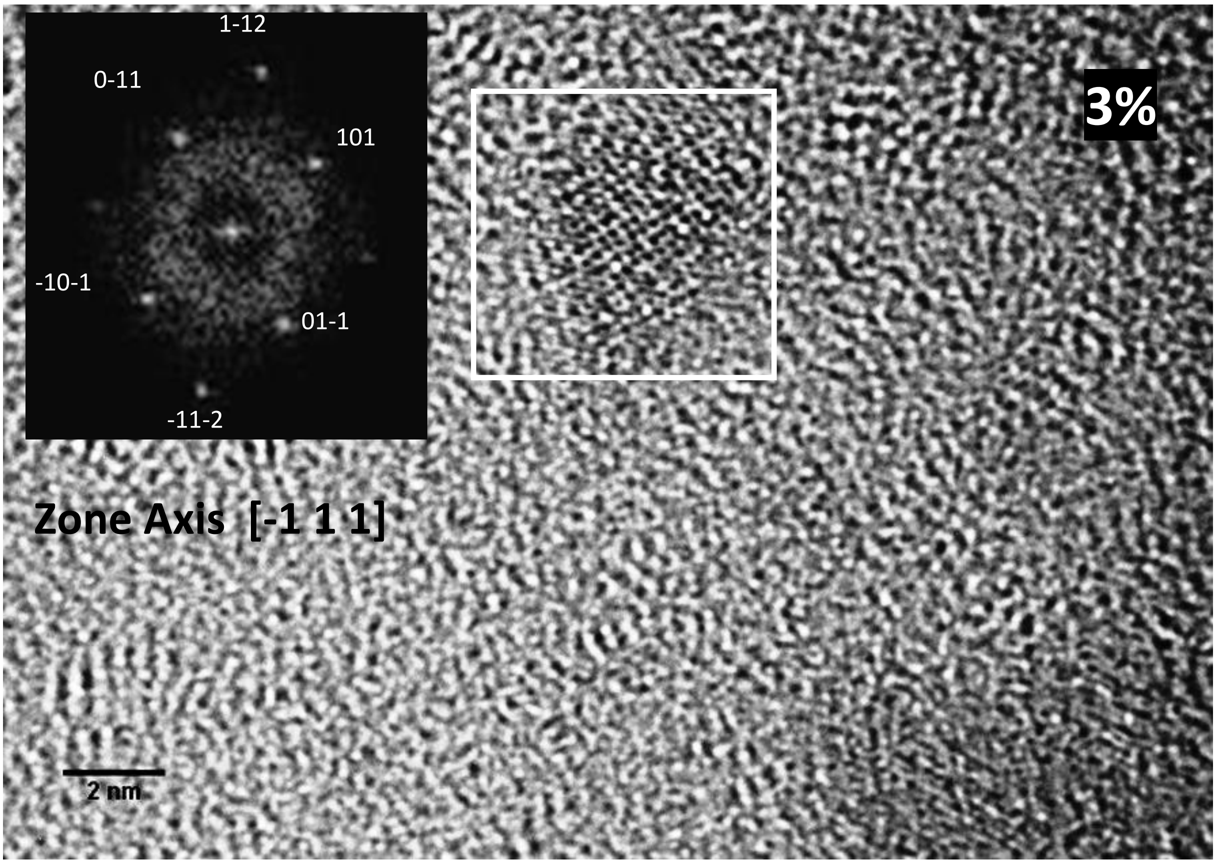
3- HRTEM images of GZO nanocrystals doped at 3%, 6% and 9%. The insets show the FFT of the presented particles. The wurtzite structure is clearly observed.

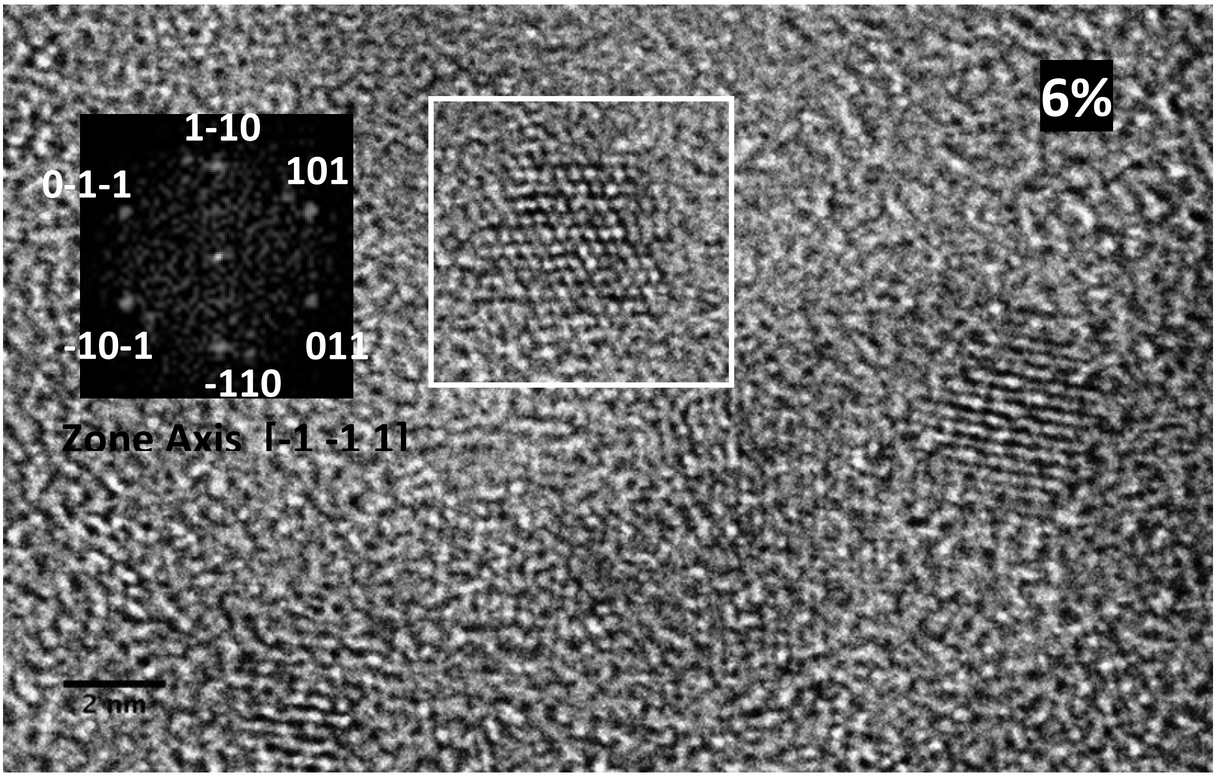


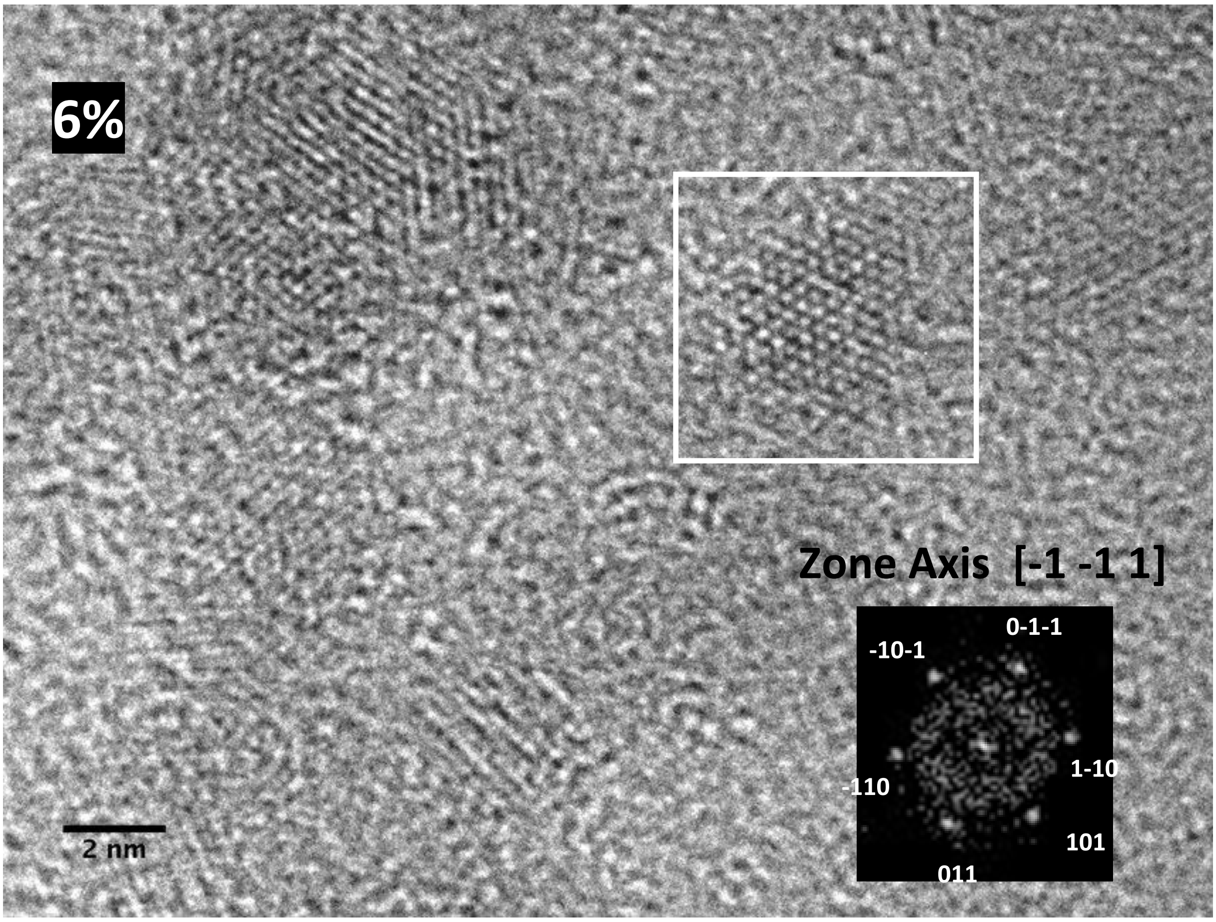



3%
-10-1
101
Zone Axis [-1 -1 1]
2 nm


3%
1-10
0-1-1
101
-10-1
011
-110
Zone Axis [-1 -1 1]
2 nm

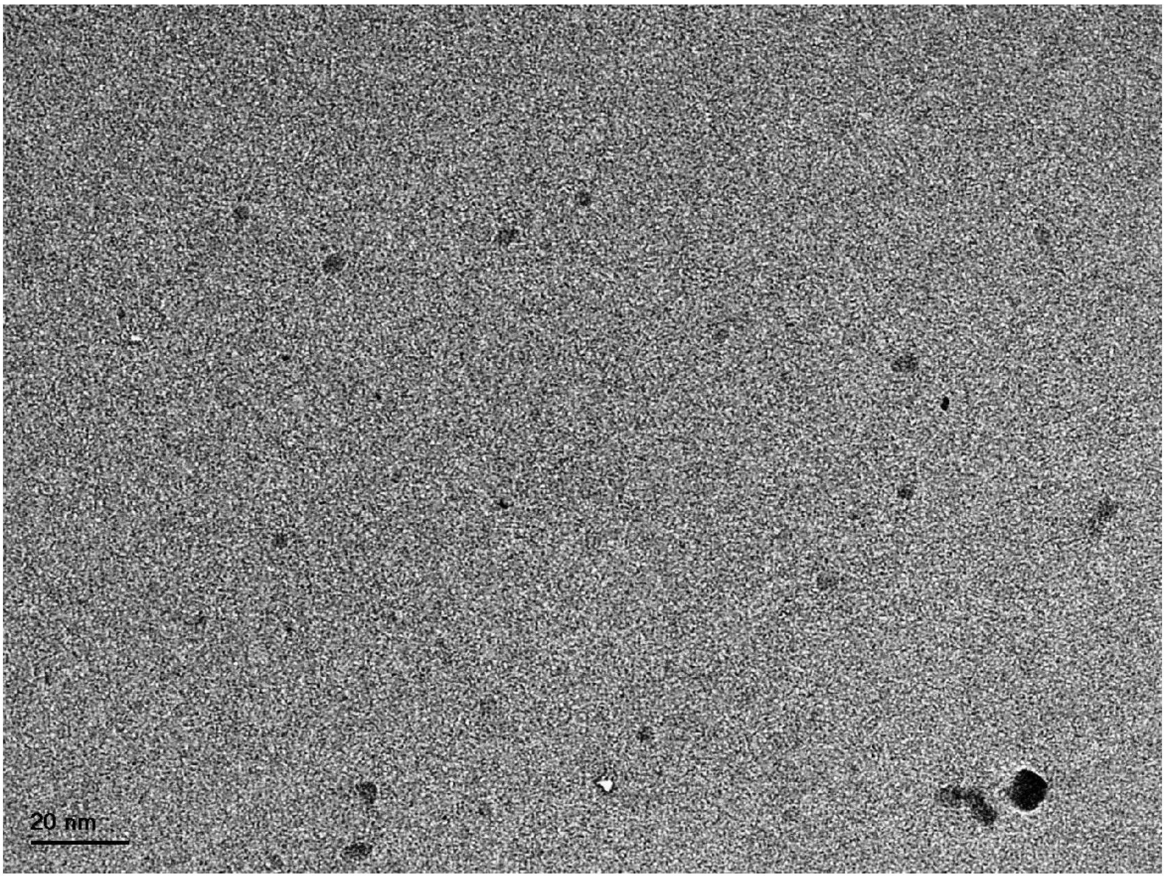

1-12
0-11
101
-10-1
01-1
-11-2
3%
Zone Axis [-1 1 1]
2 nm

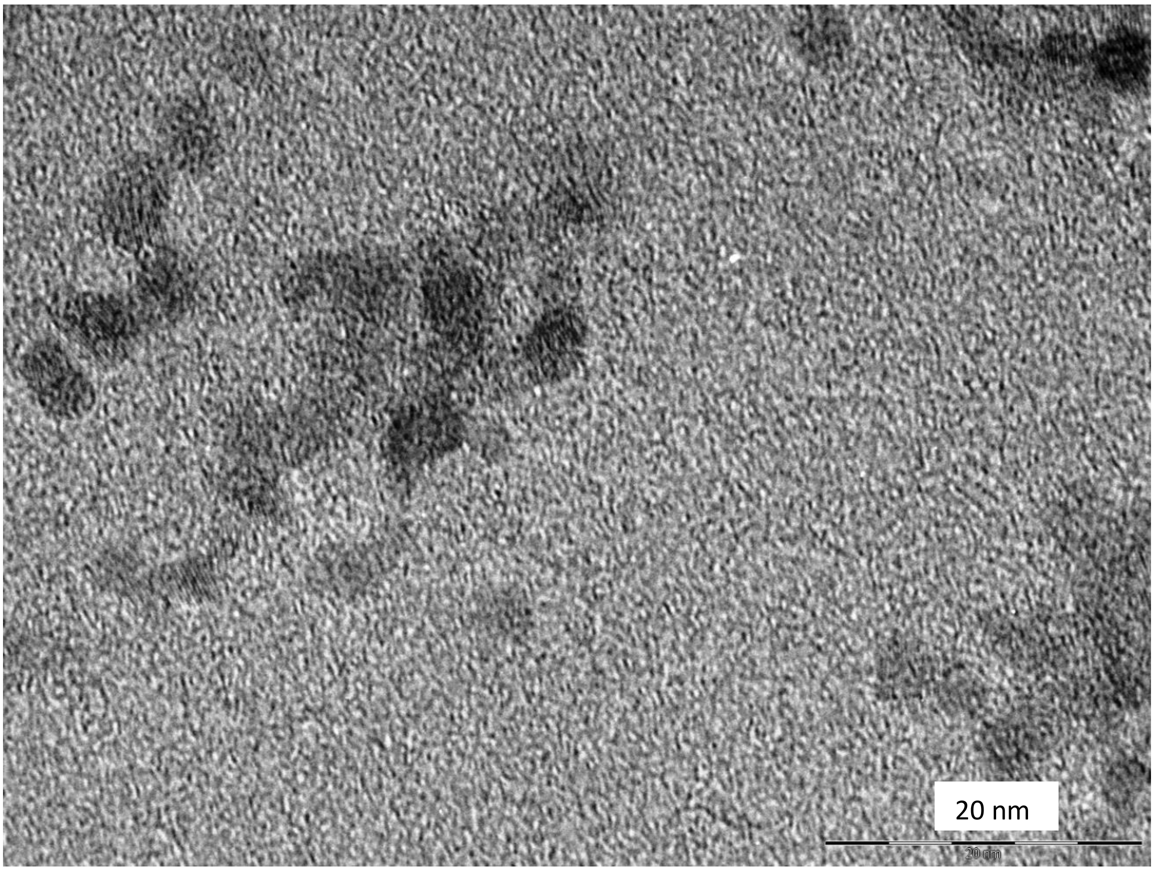

6%
1-10
0-1-1
101
-10-1
011
-110
Zone Axis [-1 -1 1]
2 nm


6%
Zone Axis [-1 -1 1]
0-1-1
-10-1
1-10
-110
101
011
2 nm

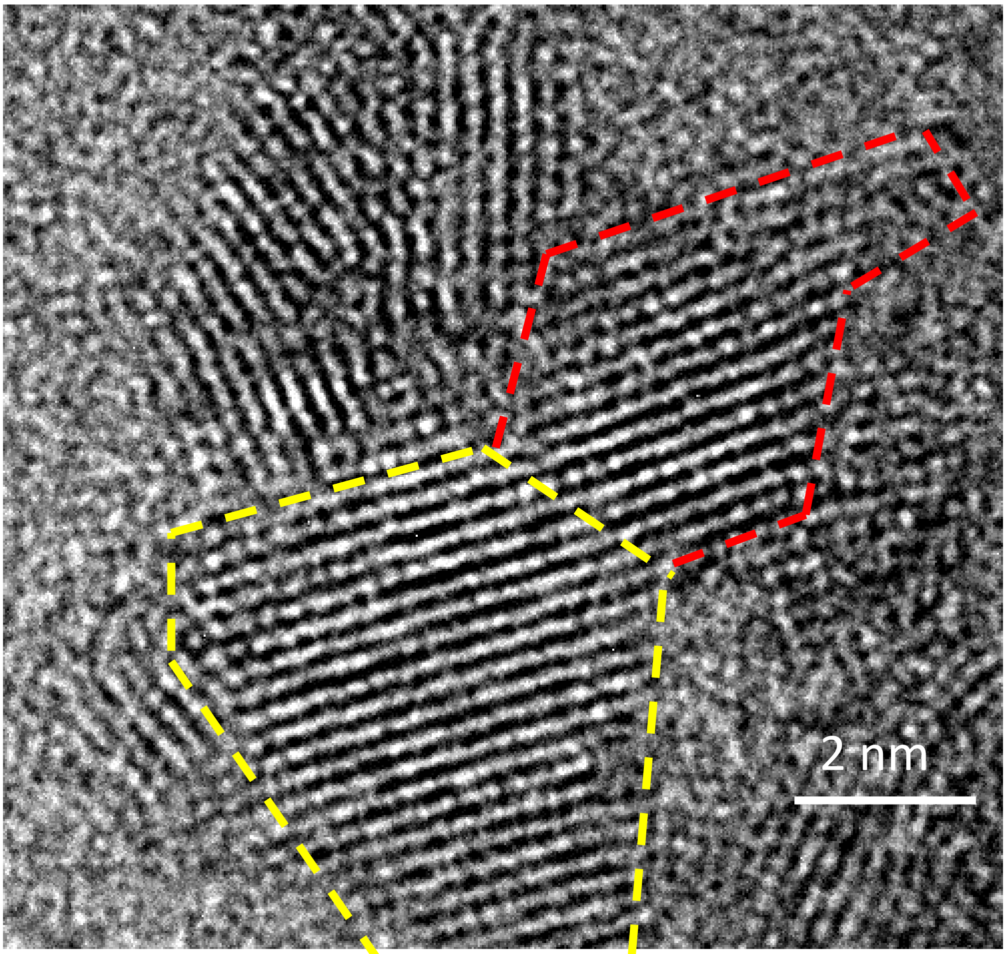
4- Low magnification TEM images of GZO nanocrystals

The samples differ by the amount of particles deposited per unit surface.



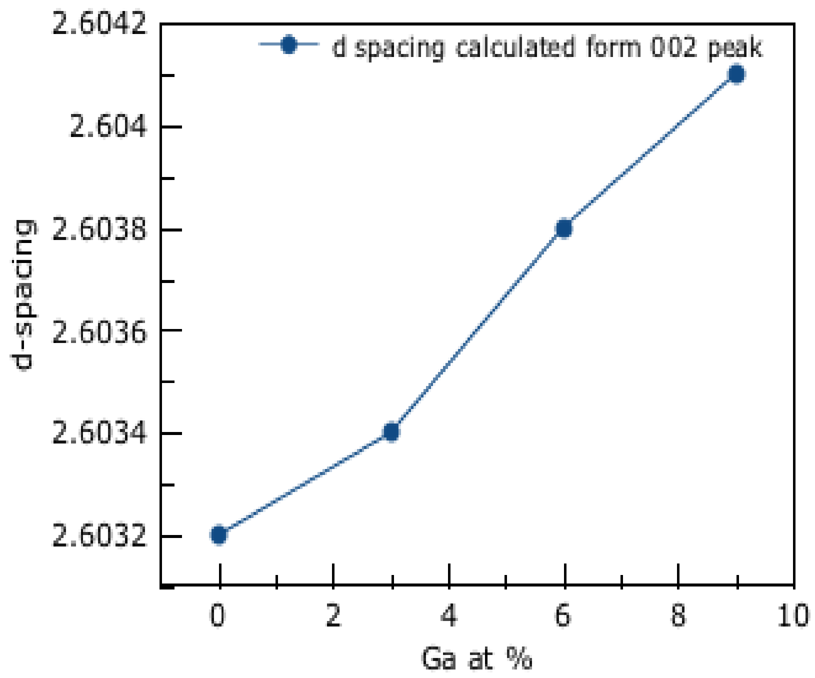


4- Example of oriented attachment of GZO nanocrystals



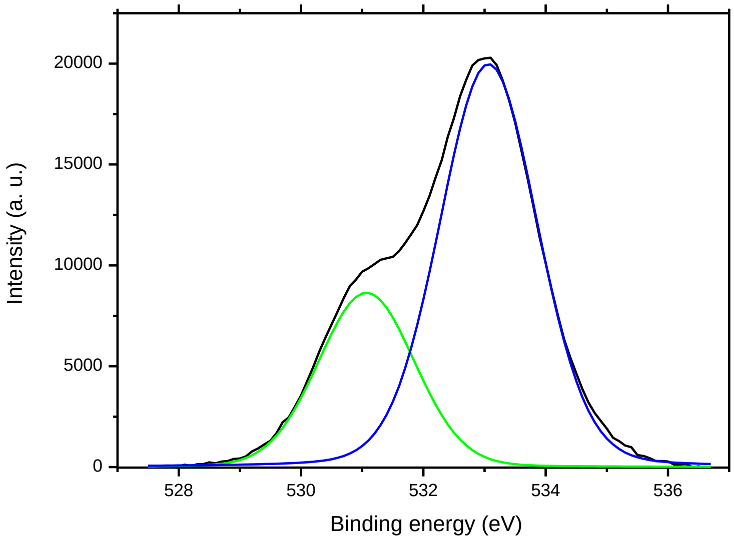
Two facetted uncapped nanocrystals can be distinguished, sharing a common face. The oriented attachment leads to epitaxy when the faces are commensurable and to defects such as twin boundaries or dislocations otherwise. Because of their erratic shapes, these nanocrystals may actually be the result of oriented attachment of several smaller nanoparticles.

5- Inter-reticular spacing d of (002) planes as a function of the Ga content



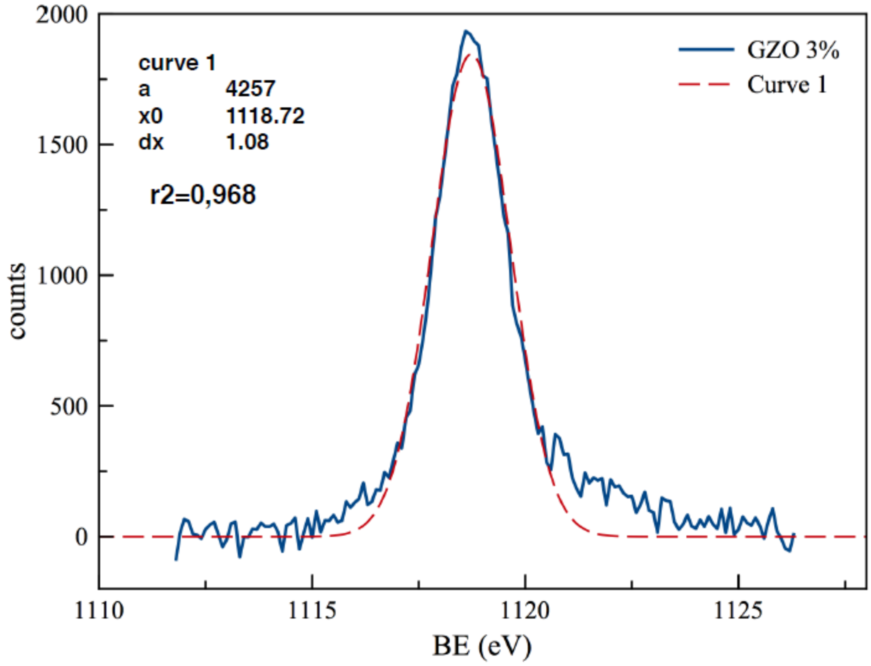
As the Ga content increases, the d-spacing very slightly increases due to the small mismatch of radius between Ga and Zn. The small increase might also be caused by some Ga atoms mis-incorporated at interstitial sites.

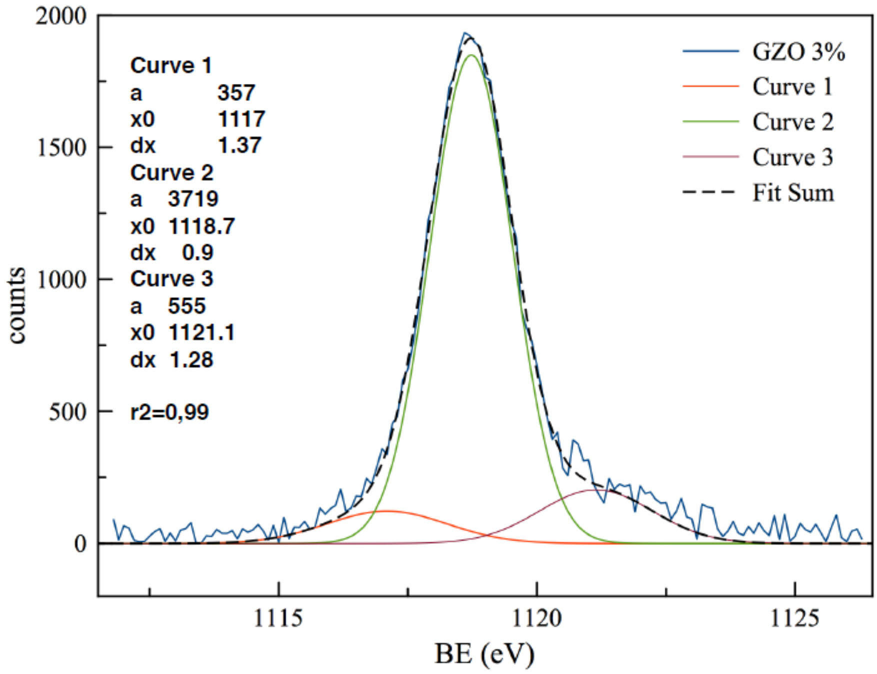
6- XPS of O1s peak of 3% GZO nanocrystals



The O1s peak is made of two contributions; a low energy one peaking at 531 eV corresponding to O atoms in bulk ZnO and a high energy one corresponding to O atoms close to the surface or contamination species at the surface, in a perturbed environment. The intensity ratio of the two peaks is 2.4.

7- XPS of Ga2p3/2 peak of 3% GZO nanocrystals





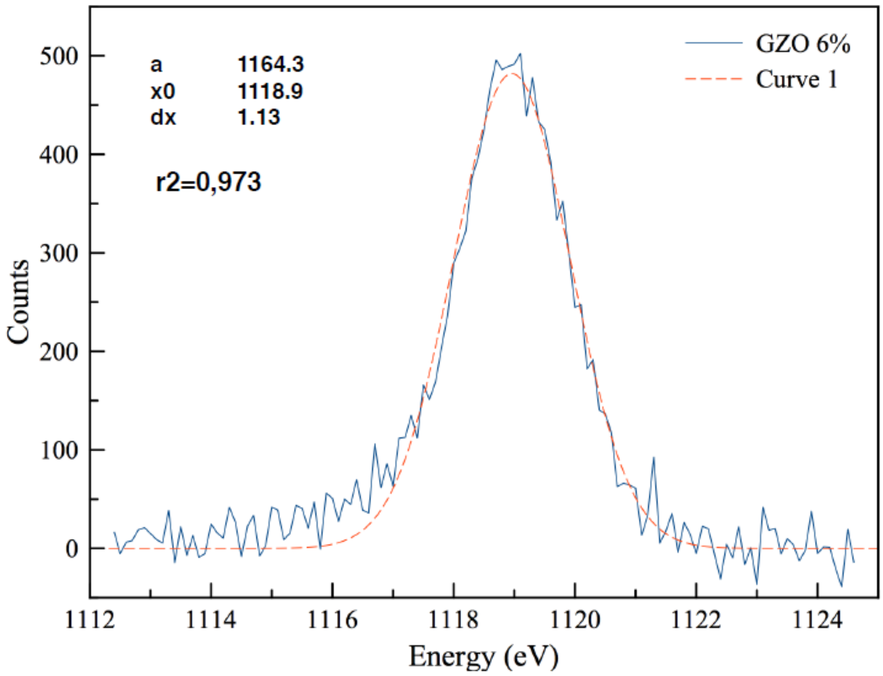
Upper graph: fitting to the Ga 2p3/2 peak using one Gaussian contribution. The main feature is reproduced but the tails (at low and high energies) are not reproduced.

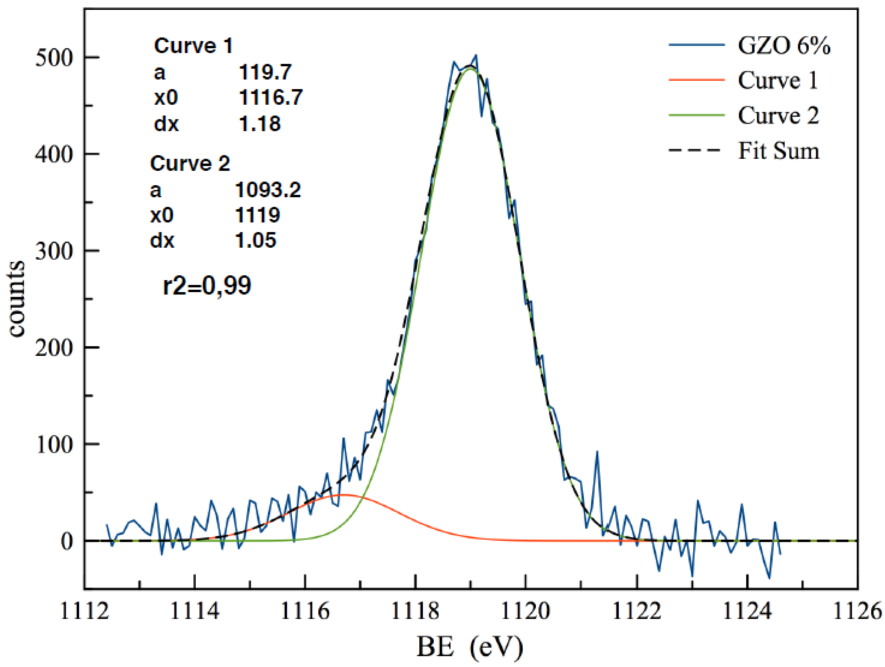
Lower graph: when using three contributions, the fit procedure is more accurate (R^2 goes from 0.968 to 0.99). a stand for area, x0 is the position of the maximum and dx the Half-Width-at-Half-Maximum.

Three contributions are necessary to properly fit the data. The prominent one, centered at 1118.9 ± 0.2 eV, is attributed to Ga^{3+} ions bonded to O. This contribution is often seen in Ga_2O_3 oxides or other oxide environment [1,2]. Thus, it is hard to tell on this simple observation whether these ions are in substitution of Zn^{2+} in the wurtzite ZnO structure or not. A previous study concentrating on Ga doped ZnO nanowires [3] assigned a contribution at 1117.7 eV to Ga^{3+} ions in substitution of Zn^{2+} ions. Our results on nanoparticles do not lead to the same observation but are in agreement with the work by Bhosle *et al.* [4]. The second one, peaking at 1116.8 ± 0.2 eV, can originate from metallic Ga at 1117 eV [2, 5]. It is worth noticing that its intensity is about one tenth of the prominent contribution. A third minor contribution is observed only for the 3% doped GZO nanoparticles, peaking at 1121 ± 0.2 eV. This contribution can hardly be assigned to Ga since no contribution has been reported at an energy higher than 1119 eV and no hypothesis is proposed yet.

[1] M. Passlack et al. J. Appl. Phys. 1995, **77**, 686-693
[2] G. Cossu, G.M. Ingo, G. Mattogno, G. Padeletti, G.M. Proietti, Appl. Surf. Sci. 1992, **56**, 81
[3] S.K. Lim, S. H. Hong, S-H. Hwang, S. Kim, H. Park, J. Mater. Sci. Technol. 2013, **29**, 39-43
[4] V. Bhosle, A. Tiwari, J. Narayan , J. Appl. Phys. 2006, **100**, 033713
[5] C.D. Wagner, Discuss. Faraday Soc. 1975, **60**, 291

8- XPS of Ga2p3/2 peak of 6% GZO nanocrystals



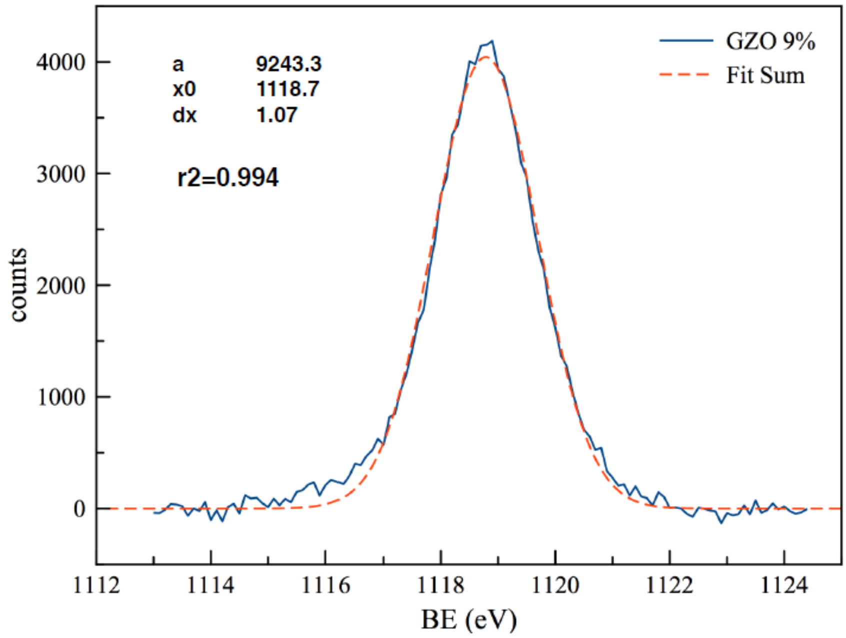


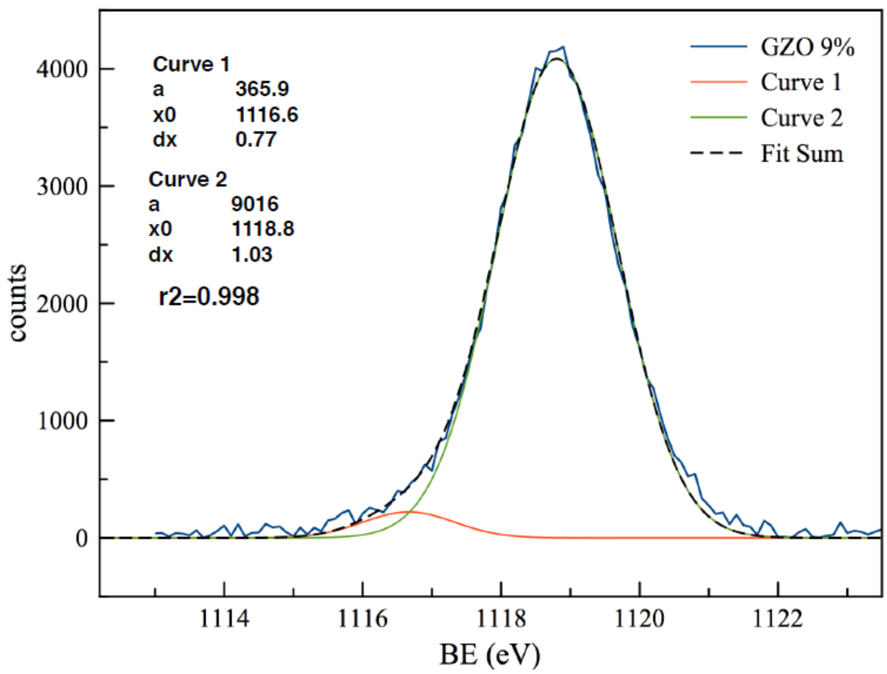
Upper graph: fitting to the Ga 2p3/2 peak using one Gaussian contribution. The main feature is reproduced but the tail at low is badly reproduced.

Lower graph: when using two contributions, the fit procedure is more accurate (R^2 goes from 0.973to 0.99). a stand for Area, x0 is the position of the maximum and dx the Half-Width-at-Half-Maximum.

The same conclusion as for the 3% doped GZO nanoparticles holds.

9- XPS of Ga2p3/2 peak of 9% GZO nanocrystals





Upper graph: fitting to the Ga 2p3/2 peak using one Gaussian contribution. The main feature is reproduced but the fit to the tail at low can be improved.

Lower graph: when using two contributions, the fit procedure is more accurate (R^2 goes from 0.994to 0.998). a stand for Area, x0 is the position of the maximum and dx the Half-Width-at-Half-Maximum.

The same conclusion as for the 3% doped GZO nanoparticles holds.

The one peak fit is already satisfactory revealing the negligible influence of the pure Ga contribution.