Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2017

SUPPORTING INFORMATION

Control of the compensating defects in Al-doped and Ga-doped ZnO nanocrystals for MIR plasmonics

M. H. Hamza Taha¹, O. Boisron², B. Canut¹, P. Melinon², J. Penuelas³, M. Gendry³ B. Masenelli^{1*}

¹ Univ Lyon, INSA-Lyon, ECL, UCBL, CPE, CNRS, INL-UMR5270, F-69621, Villeurbanne, France
² Univ Lyon, Univ Lyon 1, CNRS, ILM-UMR5306, F-69622, Villeurbanne France.
³ Univ Lyon, ECL, INSA-Lyon, UCBL, CPE, CNRS, INL-UMR5270, F-69134, Ecully, France

*corresponding author: <u>Bruno.masenelli@insa-lyon.fr</u>; +33 4 72 43 74 72



S1 : High resolution TEM image of AZO nanocrystals. The FFTs of selected nanocrystals are displayed and confirm the wurtzite structure.



S2: large scan X-ray diffractograms of AZO nanocrystals synthesized in O-rich (top) and O-poor (middle) conditions along with that of undoped ZnO nanocrystals (bottom). No peak other those from wurzite ZnO is observed, indicating the absence of any other crystalline phase.

S3: examples of oriented attachment of doped ZnO nanocrystals as observed by High Resolution TEM



Two AZO (3%) nanocrystals (labelled 1 and 2) in oriented attachment. The dotted line highlights the continuity of the crystalline planes from particle 1 to particle 2. The facet where the OA takes places is pointed by the arrows.



Four AZO (3%) nanocrystals in OA. Right: FFT of the high resolution TEM image. The OA is distinguishable by the intense diffractrion spot made of several individual diffracting spots. The fact that the OA is not perfect can be observed since the highlighted spot is spread.



Illustration of the OA attachment of AZO (3%) nanocrystals: particles 1 and 2 are in OA. The dotted line highlights the continuity of the common crystalline planes. Identically, particles 3 and 4 are in OA as evidenced by the common planes (dotted line). Particle 5 is in imperfect OA with particle 4. To accommodate the small mismatch, dislocations are created.



S4: Reflectance spectra of AZO (3%) nanocrystals annealed by RTA in Ar. Upper panel: AZO nanocrystals synthesized in a O-rich environment; lower panel: AZO nanocrystals synthesized in a O-poor environment

Whatever the sample, the plasmon resonance is red-shifted, indicating a reduction of the electron gas concentration. Since the Ar atmosphere is neutral (non oxidizing), the reduction of the electron gas concentration reveals the metastability of the Al dopants rather than the introduction of compensating defects



S5: Reflectance spectra of O-Rich AZO (3%) nanocrystals annealed in H2 during 30 min at 400°C. Even though the annealing is carried out in reducing atmosphere, the LSPR disappears.