Tunable nanostructure and photoluminescence of columnar ZnO films grown by plasma deposition

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Supporting information

S1. Lorentz deconvolution of the (002) diffraction peaks of the films

The XRD patterns have been fitted using up to 4 Lorentz peaks centered at 34.19º, 34.29º, 34.39º and 34. 47º, numbered as nº1, nº2, nº3 and nº4 respectively. Examples of these fits are presented in figures S1a and S1b, corresponding respectively to the "O_2 410K 200nm" and "O_2 410K 1750 nm" films. In the case of the 200 nm-thick film (fig. 4b), two Lorentz functions (nº1 and nº2) have been necessary to fit the (002) peak. A good fit has been performed with the 4 Lorentz peaks in the case of the 1750 nm-thick film (fig. 4c). Similar fits (not presented) show that the (002) peak of the "O_2 410K 450nm", "O_2 410 K 870nm" and "O_2 410K 1270nm" films can be reproduced using 2 (nº1 and nº2), 3 (nº1, nº2 and nº3) and the 4 Lorentz functions respectively. Despite of the crudeness of the fits, qualitative trends can be extracted. The fact that the diffraction peak of the thinnest film can be fitted with 2 Lorentz peaks (nº1 and nº2), both shifted towards low angles when compared to the unstressed value means that this film is, as a whole, under tensile stress. In contrast, fitting the diffraction peak of the thickest film requires to add peaks nº3 and nº4, suggesting that the overall diffraction signal contains contributions of unstressed and stressed regions of the material. The unstressed zones are very likely to be located at the surface of the thick film and not in the first 200 nm, since they are absent in the 200 nm-thick film.

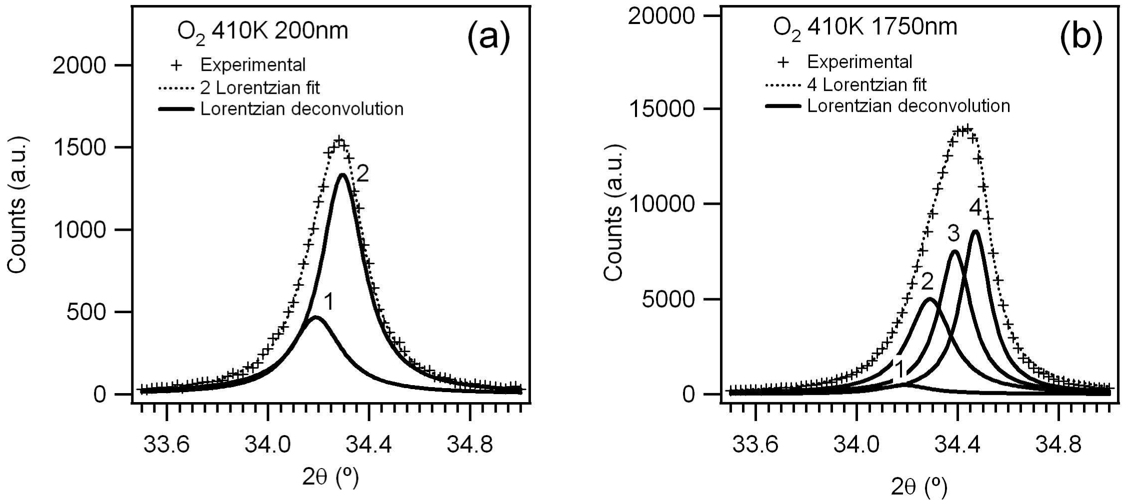

Figure S1. Lorentz deconvolution of the (002) peak of (a) the "O_2 410K 200nm" film (2 Lorentz peaks) and (b) the "O_2 410K 1750nm" film (4 Lorentz peaks).

S2. Composition of the plasma

At first sight it might seem surprising that despite the reducing character of hydrogen O_2/H_2 (80%/20%) plasmas favor the formation of O-rich films. However, the optical emission spectroscopy (OES) analysis of these plasmas have shown that besides H^* and O* intermediate species, the very reactive OH* species are also very abundant (data not shown). We believe that both H* and OH* contribute very actively to the removal (as CO_2, H_2O or CH_4) of the $-CH_3$ groups attached to the Zn in the volatile precursor used for the synthesis, enabling a very effective incorporation of oxygen in the lattice network of the growing oxide.