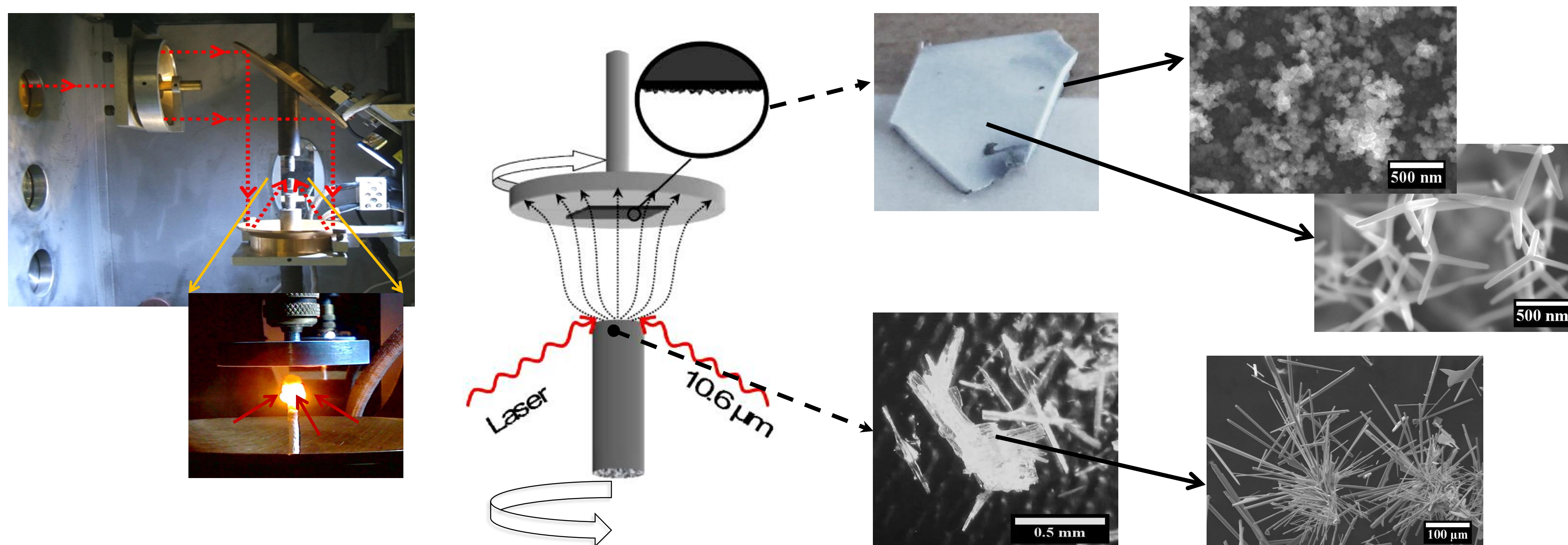


ZnO MICRO/NANOCRYSTALS GROWN BY LASER ASSISTED FLOW DEPOSITION



Joana Rodrigues
PhD. Student

Supervisor: Prof. F. M. Costa
Co-supervisor: Prof. T. Monteiro



Objectives

ZnO is one of the most widely studied materials due to its high potential for applications in several fields, such as optoelectronics, energy conversion or biomedicine. The high vapour pressure of ZnO and the fact that the material decomposes into its atomic components at the melting temperature (1977 °C) at atmospheric pressure, makes ZnO a suitable candidate for the Laser Assisted Flow Deposition (LAFD) growth. This method is a high yield technique that takes advantage of the mentioned properties combined with the local heating generated by a high power laser. The LAFD can be used in the growth of different morphologies. The crystals grown by this process usually reveal high structural and optical quality.

Methods and techniques

The LAFD was performed on a modified laser floating zone (LFZ) growth chamber which comprises a 200 W CO₂ laser coupled to a reflective optical set-up producing a circular crown-shaped laser beam. The beam is focused on the tip of the extruded cylindrical rods. The substrates are placed on a sample holder attached to the upper spindle of the LFZ system.

The samples morphology was characterized by SEM and the microstructure was analyzed by TEM. Furthermore, the crystal structure of the ZnO microstructures was investigated by measuring θ -2 θ scans of XRD and by Raman spectroscopy. Steady state PL was generated using the 325 nm light from a cw He-Cd.

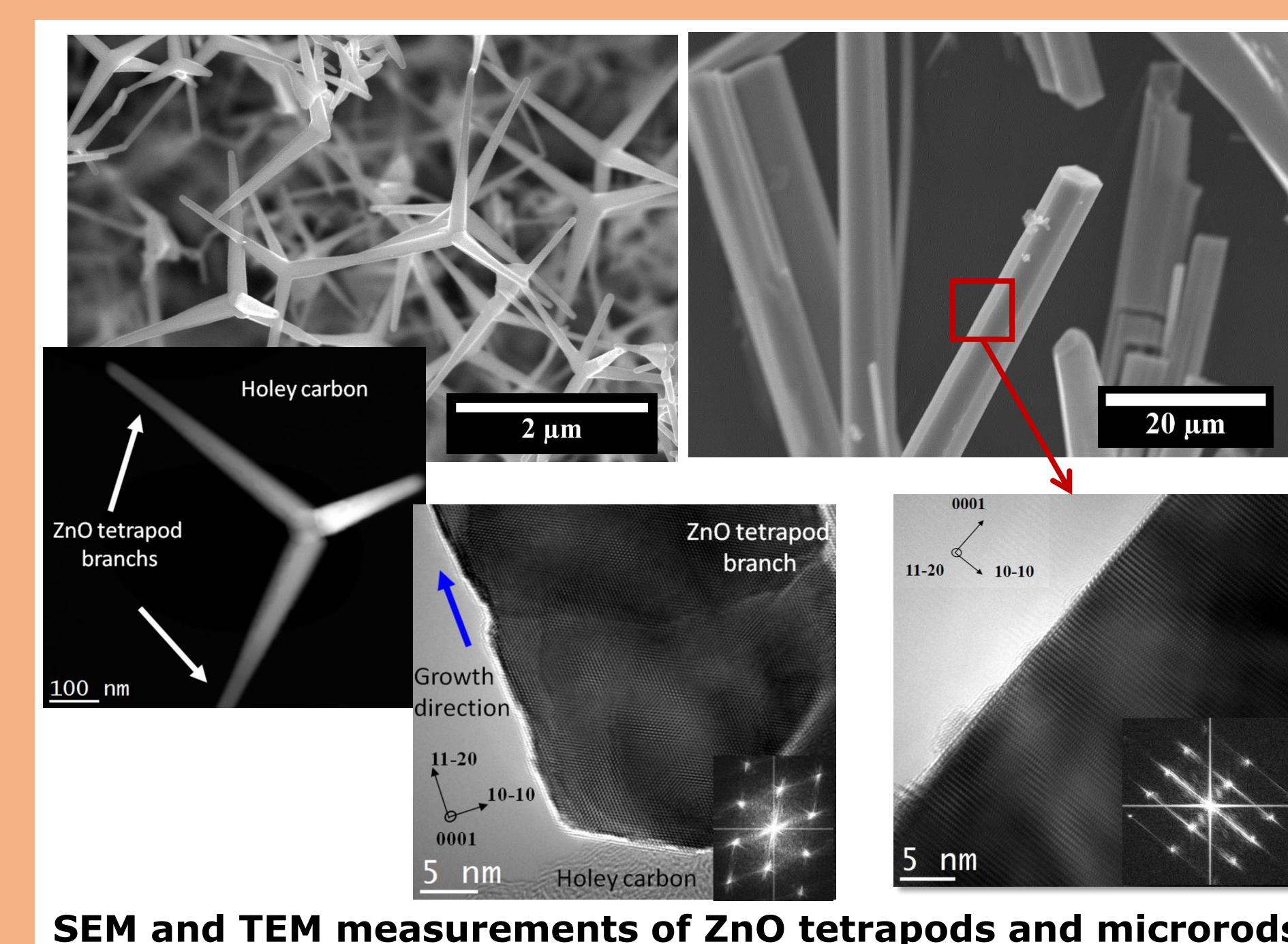
Results

The LAFD technique leads to different ZnO morphologies depending on the region of the growth chamber where the products are formed (mainly nanoparticles, tetrapods and microrods). These morphologies are formed during the same run of growth. Nonetheless, with an appropriate choice of the growth conditions, namely the laser power and the growth atmosphere, it is possible to control the growth of some of the morphologies.

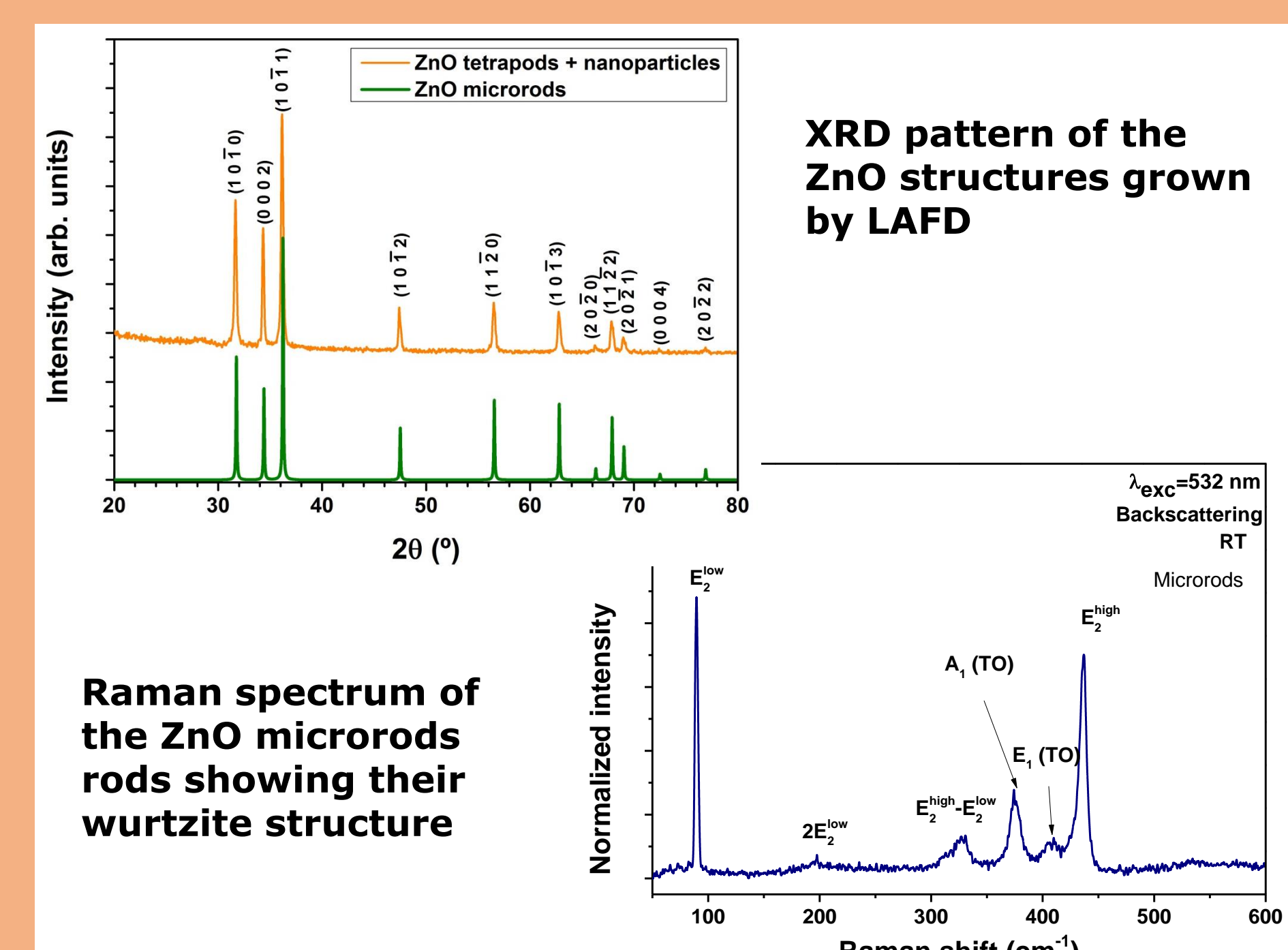
The structural measurements results put in evidence the high crystallinity of the samples. While the tetrapods PL emission is dominated by the donor-bound excitons (D⁰X) in the ultra-violet region and almost no visible luminescence is observed, in the case of the ZnO microrods besides the near band edge recombination also the green broad band related to deep level defects is identified. Noteworthy, in addition to the free exciton (FX) and D⁰X recombination lines, the luminescence of these samples is dominated by a line peaked at 3.31 eV followed by its longitudinal optical (LO) phonon replicas.

Publications

- J. Rodrigues *et al.*, Thin Solid Films 520 (2012), pp 4717–4721;
- J. Rodrigues *et al.*, Acta Materialia 60 (2012), pp 5143–5150;
- J. Rodrigues *et al.*, Journal of Nano Research 18-19 (2012), pp 129-137;
- J. Rodrigues *et al.*, Microscopy and Microanalysis 18, S5 (2012), pp 87-88;
- J. Rodrigues *et al.*, Proc. SPIE, SPIE OPTO (International Society for Optics and Photonics, 2014), pp. 89871F.

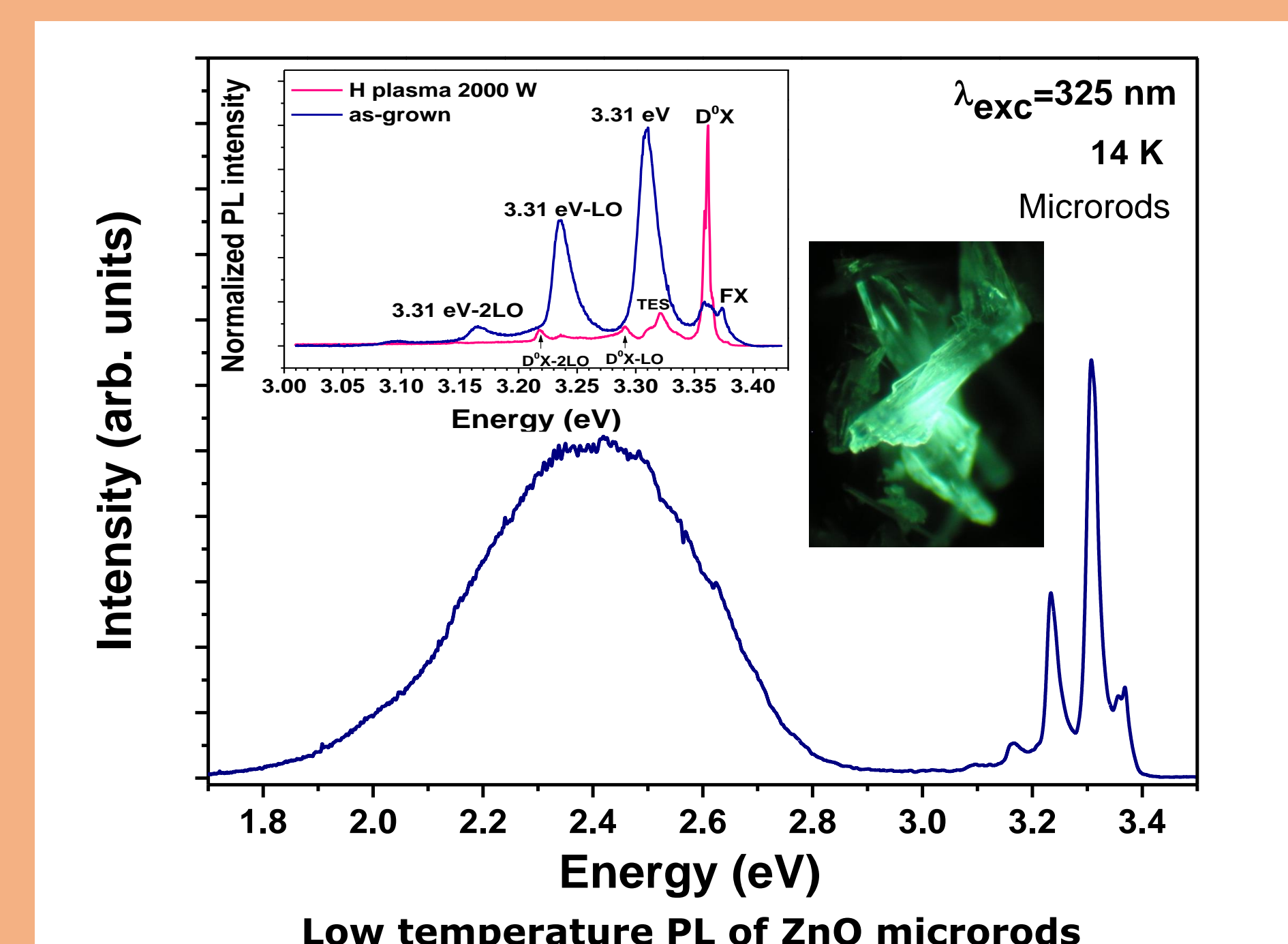


SEM and TEM measurements of ZnO tetrapods and microrods



XRD pattern of the ZnO structures grown by LAFD

Raman spectrum of the ZnO microrods showing their wurtzite structure



Low temperature PL of ZnO microrods