ESRF	**Experiment title:** XRD and GID study of semiconductor nanocrystals-based floating gate flash memory structures	**Experiment number:** **SI 1780**
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Report:

Semiconductor nanocrystals (NCs) have emerged as an excellent candidate for potential applications in non volatiles memory (NVM) devices. Among the various semiconductors, ZnO, being a wide band gap semiconductor, presents a large exciton binding energy (60 meV) and therefore a better confinement effect, which makes it a good material for carrier storage and memory applications. Moreover, theoretical calculations predicted that ZnFO doped with transition metals (F: Mn, Co, Fe, and Ni) could show ferromagnetism at room temperature (RT) and even above. This makes ZnFO NCs to be good candidates for spin storage with an increased storage capability with respect to available spin based-NVM.

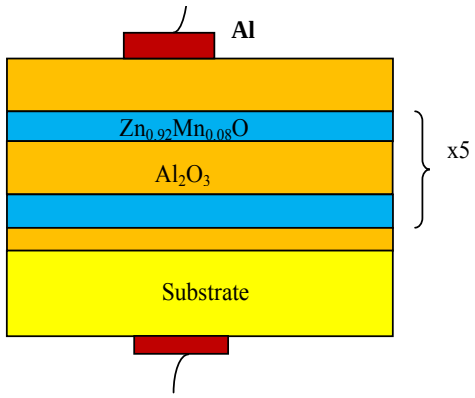

Fig. 1. Schematic of the studied samples.

During this experiment the multilayer $Zn_{0.92}Mn_{0.08}O$ (NC)/Al_2O_3 samples produced by pulsed laser deposition (PLD) in our laboratory at University of Minho, schematically shown on the Fig.1, were characterized by Grazing Incidence Small Angle X-ray Scattering (GISAXS) and Grazing Incidence X-ray Diffraction (GIXRD). Fig. 2a shows a 2D GISAXS pattern representing the map of scattering intensities in reciprocal space of an as-grown multilayer sample. Intensity is colour-scaled and plotted as a function of the in-plane and out-of-plane components of the momentum wave-vector transfer $Q_{\|}=(Q_x^2+Q_y^2)^{1/2}$ and Q_z, respectively. In the reciprocal space map (Fig 2a) the several sheets of enhanced intensity elongated along the horizontal axis are clearly seen. These, so-called Bragg sheets, arise from the coherent superposition of X-rays scattered on

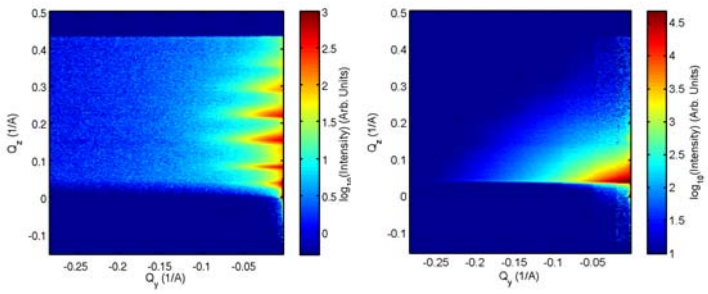

Fig. 2. Typical GISAXS map of the (a) as-grown and (b) annealed at 600 ºC $Mn_{0.08}Zn_{0.92}O/Al_2O_3$ multilayered nanostructures.

different rough interfaces of the multilayer. Their presence evidences for high correlation of the roughness profile of the neighbouring surfaces, i.e. the interface profile is inherited from bottom to top interfaces during the multilayer growth.The distance ΔQz of the neighbouring Bragg sheets along the Q_z direction is related to the average width of the bi-layers D in the periodic multilayer structure as $D = \frac{2\pi}{\Delta Q_z}$. The bi-layer determined from positions of the Bragg sheets in sections along the Q_z axis of the reciprocal space map was calculated to be about (9±0.3) nm that is in a good agreement with the value of 9.5 nm obtained from a simulation of Rutherford Backscattering Spectrometry (RBS) measurements (not shown here).

The effective number of bi-layers, for which interface roughness is correlated, can be estimated from the full width at half maxima (FWHM) of the Bragg sheets δQ_z^{BS} along the Qz direction as $N_{eff} = \frac{2\pi m}{D\delta Q_z^{BS}}$ [2]. Here, m is the order of the Bragg sheet. For lateral spatial frequencies $Q\|$<0.3 nm^{-1} the FWHM of the Bragg sheet was constant δQ_z^{BS}=(0.08±0.005) nm^{-1}, which corresponds to N_{eff} = 9. It means that low lateral frequencies of the interfaces undulations are well replicated from bottom to up throughout the entire multilayer structure.

GIXRD study shows that all the as-grown structures were amorphous (Fig. 3). The annealing at 600 °C leads to the crystallization of the structures with highly textured ZnMnO layers. All the grown ZnMnO nanostructures were found to be *c*-axis oriented, exhibiting only *(l00)* XRD lines of ZnMnO (*a*-axes lying in in-plane of substrate). The estimation of the *a* lattice parameter from GIXRD data gives a value of 0.326 nm, what indicates an increase of ZnO cell parameter (a=3.2498 nm) due to the Mn doping because of higher ionic radius of Mn^{2+} (0.66Å) in compare with 0.60 Å of Zn^{2+}. Both, as grown and annealed samples showed no peaks relative to Mn oxide secondary phases, indicating a good substitution of Zn with Mn. According to Debye-Sherrer formula we deduce the NCs mean size to be about 12 nm.

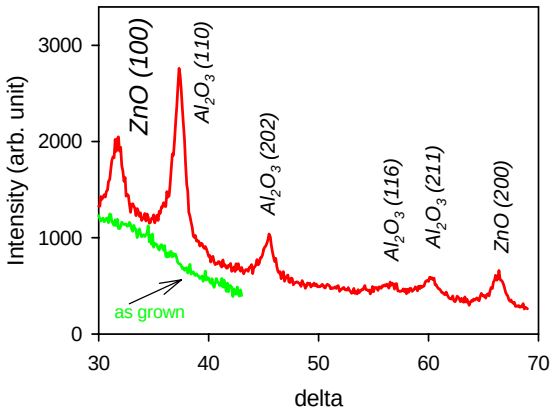

Fig. 3. GIXRD data for as grown and annealed samples.

In contrast to the as-grown sample, reciprocal space map measured on the annealed structures (see Fig. 2b) does not demonstrate any Bragg sheets. Thus the multilayer structure was destroyed by the annealing process. Instead, a strong diffuse scattering appears close to the origin of the reciprocal space, which indicates formation of NCs. Applying Guinier plot to the 1D GISAXS profile of the annealed sample and suggesting spherical shape of NCs the diameter of NCs was estimated to be about 9 nm.

Capacitance voltage (C - V) characteristics were investigated to study the memory effects on theese structures and a memory window up to 2.25 V has been obtained for C-V loops between -10 V and +10 V, which is higher than reported before for similar systems.