Experiment title: Site configuration of Ga in $Zn_{1-x}Mg_xO$:Ga transparent conducting thin films: electrically active versus non-active configurations.	**Experiment number**: 25-01/652

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Report:

The principal aim of this experiment was to identify the configuration of electrically active and inactive Ga centres in heavily doped wurtzite ZnO by means of XAS measurements. To this end thin films of Ga doped ZnO with a typical thickness of 0.5 μm were prepared by pulsed laser deposition on sapphire substrates. Targets were made from high purity (99.999%) ZnO and Ga_2O_3 powders with a Ga atomic proportion (with respect to the total cation content) from 0.25 to 5%. Films were previously characterised by optical, transport, microanalysis and XPS/UPS measurements.

We have shown in [1] that an increase in deposition temperature in the range 200 – 600ºC strongly reduces the proportion of electrically active Ga, despite an increase in the overall Ga concentration. Post-deposition thermal annealing in air produces a similar decrease in carrier concentration, so samples with a range of deposition temperatures and post-deposition annealing were investigated. XANES and EXAFS spectra were taken in the fluorescence detected mode at the Ga K-edge (10.367 keV) using ionisation chambers to optimise the energy of the incident beam. The lowest areal concentration of Ga atoms (in films with 0.25% Ga) was 5×10^{15} cm^{-2}, well above the detection limit of the energy resolving Ge detector used in the experiments.

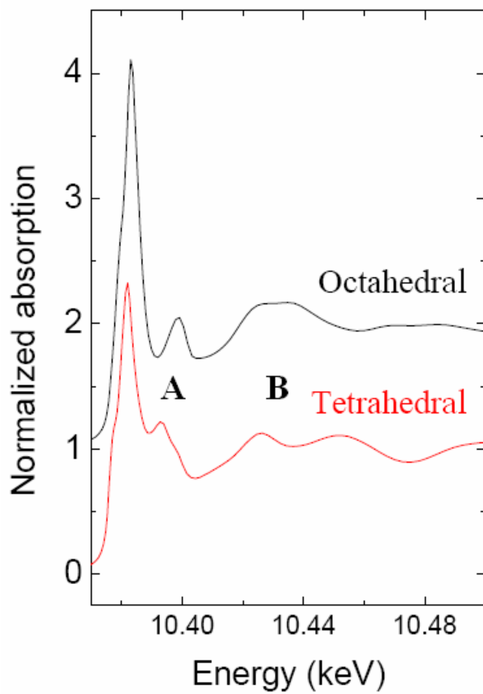

Fig. 1: XANES simulation of Ga site configurations.

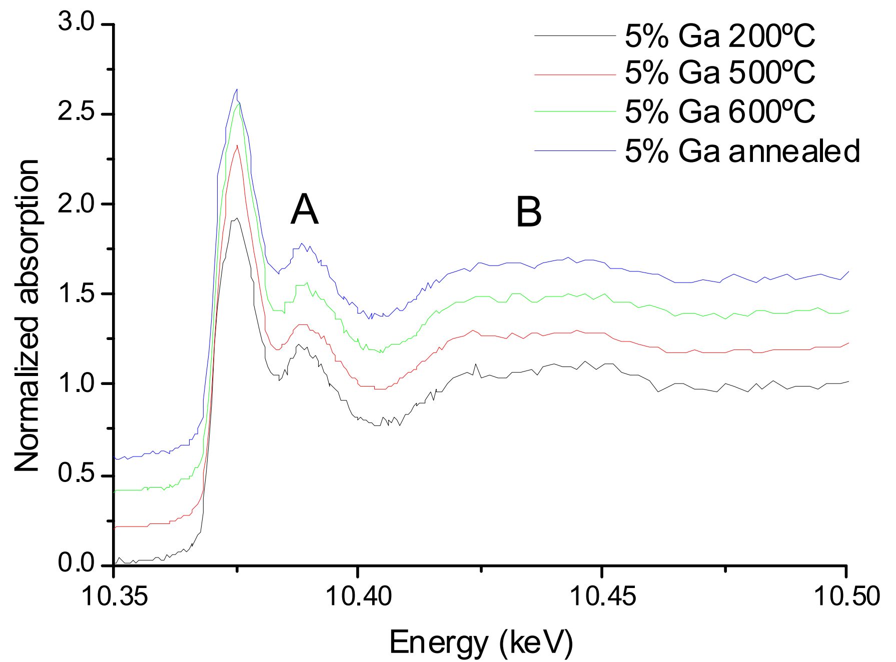

Fig. 2: Normalised XANES of 5% Ga doped ZnO with a variety of deposition temperatures and post-deposition annealing.

As expected, the spectra with the clearest features came from the films deposited using the target with the highest Ga concentration (5%). Therefore, XANES simulations corresponding to Ga with tetrahedral and octahedral coordination shown in fig. 1 shall be compared to the spectra in fig. 2. We note that a mixture of the two phases exists and that changes between spectra are relatively small. However, the peak labelled "A" appears to broaden as the deposition temperature increases and the absorption in the region of "B" becomes somewhat flatter. Annealing the sample deposited at 200º in air at a temperature of 580º for several hours also produces these changes. Referring to the simulations it is clear to see that these features are both characteristics of a transition from tetrahedral to octahedral coordination. Tetrahedral coordination corresponds to the wurtzite phase where Ga occupies the substitutional position of Zn. In this case the Ga centre is electrically active, as a conduction electron is released. Octahedral coordination corresponds to the spinel ($ZnGa_2O_4$) phase, which has a much larger bandgap than ZnO (4.7 eV [2]) and is not electrically active. Therefore, the XAS results provide a good explanation for the decrease in the proportion of electrically active Ga centres, shown by the decrease in conductivity, on increasing the deposition temperature and annealing in the previously described manner.

Due to the speed of measurement and relative lack of complications, there was also time to take preliminary XAS measurements on $Zn_{1-x}M_xO$ (M = Mn, Fe, Cu, Ni) films, which were prepared in a similar way to the Ga doped samples.

[1] J.A. Sans, A. Segura, J.F. Sánchez-Royo, V. Barber, M.A. Hernández-Fenollosa and B. Martí. Superlattices and Microstructures **39**, 282 (2006).
[2] G.B. Palmer and K.R. Poeppelmeier. Solid State Sci. **4**, 317 (2002).