A Structural Study of Delafossite-type CuInO\textsubscript{2} Thin Films

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Abstract. This contribution reports a study of the preparation of pure and doped delafossite-type material CuInO\textsubscript{2} using pulsed laser deposition. A series of films have been prepared at different oxygen partial pressures. X-ray absorption spectroscopy (XAS) has been used to characterise the microstructure of the films. The results show that the structure of the films is extremely sensitive to the preparation conditions.

1. Introduction
Transparent conducting oxides (TCO) are an important group of materials used in optoelectronics that combine low electrical resistance (typically $<$10$^{-3}$ Ωcm) with high optical transparency (>$>$80%) in the visible range of the electromagnetic spectrum [1]. Optically transparent oxides tend to be electrical insulators as a result of their large electronic band gap of $\geq$3.1eV, corresponding to the energy of a 400nm violet photon. Therefore visible photons with an energy ranging from $\sim$1.8eV (700nm) to 3.1eV (400nm) cannot excite electrons from the valence band into the conduction band and as a result the light is transmitted. However, TCOs are semiconductor materials and the visible photons have enough energy to excite electrons from donor levels to the conduction band (n-type TCO) or holes from the acceptor level into the valence band (p-type TCO). These acceptor or donor levels within the TCO band gap are created by introducing defects through non-stoichiometry and/or doping with appropriate impurity ions in a controlled manner.

The first observation of TCO materials was CdO in 1951 in which it was observed that electrical conductivity and optical transparency could co-exist [2,3]. Similar behaviour was also reported in In$_2$O$_3$ a few years later in 1956 [4] and applications were found for heated windows. A concentrated research effort in the following decade led to the discovery of films of doped SnO$_2$ and In$_2$O$_3$:Sn (In$_{2-x}$Sn$_x$O$_3$; also known as ITO) displaying excellent electrical and optical properties [5,6]. These films were primarily used at the time to reduce heat losses from sodium lamps. At around the same time TCO properties were discovered in ZnO which led to use as part of light emitting diodes (LED) [7,8]. The most common n-type TCOs have remained virtually unchanged over the years with the principal constituents remaining the simple binary oxides SnO$_2$, In$_2$O$_3$, ZnO and CdO. More recent
work has begun to explore new binary oxide combinations, and even ternary oxides such as Cd$_2$SnO$_4$, Zn$_2$SnO$_4$, MgIn$_2$O$_4$, CdSb$_2$O$_6$:Y, ZnSnO$_2$, GaInO$_3$, Zn$_3$In$_2$O$_4$, and In$_4$Sn$_3$O$_{12}$ to name but a few of the prominent examples [9,10].

Although TCOs have many applications as mentioned above, very little work has been done on active device fabrication using TCOs. This is because all of the examples mentioned so far have been n-type semiconductors, and this monopolarity has restricted the use of TCOs to narrow areas such as transparent electrodes within optoelectronic devices. The corresponding p-type TCOs, essential for junction devices were not discovered in thin film form until 1997 when p-type conductivity was reported in highly transparent CuAlO$_{2+x}$ [11]. The discovery of p-type transparent conductive oxides opens up a range of novel applications termed “Transparent Electronics” or “Invisible Electronics” [12] where the combination of the two type of TCO in the form of a p-n junction could lead “functional” window that transmits visible light, yet generates electricity in response to the absorption of ultraviolet photons [11].

Materials with the delafossite-type structure M$^{I}$M$^{III}$O$_2$ ($M^{I}$ = monovalent ions, Cu$^+$ and Ag$^+$; M$^{III}$ = trivalent ions, Al$^{3+}$, Ga$^{3+}$, In$^{3+}$, Cr$^{3+}$, Fe$^{3+}$, Co$^{3+}$ etc.) have been chosen as candidates for p-type TCO materials.

Figure 1 Crystal structure of delafossite-type (M$^{I}$M$^{III}$O$_2$) copper indium oxide

The delafossite structure is shown above in Figure can be seen to have alternate stacking of an O–M$^{I}$–O dumbbell layer and an M$^{III}$O$_6$ edge sharing octahedral layer. The oxide ions form a “pseudo-tetrahedral” coordination (M$^{III}$:M$^{IV}$O) [13] allowing a reduction in the non-bonding nature of the oxide ions and the delocalisation of holes at the valence band edge. The layered structure involving the M$^{IV}$O$_2$ dumbbell effectively reduces the level of cross-linking of M$^{IV}$ ions allowing the enlargement of the band gap [10].

Since the first discovery of p-type TCO films in 1997 [11] a number of promising p-type materials have been found, however at present these display conductivity over an order of magnitude less than
n-type materials. One of the classes of material showing the most promise to fulfil the role of a p-type TCO is that of the Cu based delafossite type oxides with examples including CuAlO$_2$ [14], CuGaO$_2$ [15], CuScO$_2$ [16], CuFeO$_2$ [17] and CuInO$_2$ [18,19]. With p-type TCOs now established, more attention has been focussed on the possibility of realising all TCO p-n junctions. However, it has also been shown that in the fabrication of p-n heterojunctions that lattice defects present in the interface or grain boundaries between the different n- and p-type components can degrade the electrical or optical performance of the devices [15]. It was then suggested that improved lattice matching of the p- and n-type TCO components in the form of an all delafossite p-n junction would improve active device fabrication. Until this point these materials had predominantly presented p-type conductivity, and the first delafossite type TCO with n-type conductivity, AgInO$_2$, was discovered in 1998 [20]. It was then suggested that all delafossite p-n heterojunctions could therefore be realised [21] involving a Cu based p-type delafossite TCO, and the n-type AgInO$_2$. Despite the all delafossite TCO p-n heterojunction now being a possibility, a true homojunction with both n- and p-type TCOs formed from the same material would be preferable to give the best lattice matching [22,23]. Although AgInO$_2$ was the first delafossite type TCO to be donor doped to give n-type conductivity, acceptor doping has been unsuccessful in producing p-type conductivity in AgInO$_2$ [24]. Recent work, however, has shown that CuInO$_2$ is unique in that bipolar doping has been reported [14]. Acceptor doping with Ca$^{2+}$ can increase the p-type character, and donor doping with Sn$^{4+}$ can lead to n-type conductivity. The discovery of bipolarity led soon after to the first fabrication of an all CuInO$_2$ based p-n homojunction [25] although it can be noted that improvement is still sought in terms of film quality and conductivity levels.

The discovery of both p-type and n-type conductivity in doped CuInO$_2$ has led to use in TCO p-n homojunctions [25]. However, the levels of conductivity seen in the individual components are still several orders of magnitude lower than in the leading n-type TCOs such as ITO, and improvements must be made if the field of “transparent electronics” is to be fully realised. The defect chemistry of the bipolar doped CuInO$_2$ system (Ca$^{2+}$ for p-type; Sn$^{4+}$ for n-type) is currently not well understood, with very little in the literature regarding point defects such as the doping site preference or any detailed mechanism for the bipolar semiconductivity [26]. The work reported here is an experimental analysis of the local defect structure of thin films of undoped and doped (Sn, Ca or Eu) CuInO$_2$ using x-ray absorption spectroscopy (XAS) at the host Cu K- and In K-edges along with the dopant Ca K-, Sn K- and Eu L$_{III}$-edges. The specific objective of the work was to reveal the role of oxygen partial pressure during film preparation on the average structure of the deposited CuInO$_2$ film. The second objective was to provide experimental evidence for the dopant site preferences for the Ca, Sn and Eu dopants and to observe the effects of increased doping levels (from 2 to 10 atom%) on the bulk structure.

2. Experimental

2.1. Materials
A range of undoped and doped (Ca, Sn or Eu) thin film delafossite-like ‘CuInO$_2$’ samples were studied. These were prepared from a target of Cu$_2$In$_2$O$_5$ (and additional dopant targets) by pulsed laser deposition (PLD) using a KrF excimer laser beam (Lambda Physik Compex 102, $\lambda$ = 248 nm) with a laser fluence of 1–2 J cm$^{-2}$. The substrates were polished sapphire. The base pressure in the chamber was in the order of $1 \times 10^{-6}$ mbar whereas the oxygen pressure varied from $5 \times 10^{-4}$ to $2 \times 10^{-2}$ mbar. The films were characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Rutherford back-scattering (RBS). Further details of the preparation and characterisation of these films can be found in reference [27].
2.2. X-ray absorption measurements
Sn, In and Cu K-edge XAS were recorded on station 9.3, with Ca K, Cu K and Eu L\textsubscript{III} edge XAS being recorded on station 7.1, both utilising double crystal Si(111) monochromators and harmonic rejection set to 50%. The measurements were all made at room temperature and collected in fluorescence mode using a 9-element solid state detector with high count rate electronics.

During these experiments problems were encountered due to diffraction peak contamination. These can arise where the incident photon wavelength satisfies a Bragg condition for a set of planes in the film or its substrate. The dominant effect in this case occurs when the Bragg reflected beam enters the fluorescence detector and \( I_0 \) is increased. In this case the apparent absorption coefficient appears bigger than it actually is. When the diffracted beam enters the \( I_0 \) chamber the effect is the opposite and a decrease in absorption coefficient is observed. Several methods have been employed to work around this problem, including spinning or wobbling the sample, using energy discriminating detectors, multiple detector arrays, masking and dodging [28-31]. The method chosen was to rotate the samples during data collection. When the sample is spinning, the diffraction condition is met for only a brief time compared to the overall data averaging time. Hence, the amplitude of the diffraction feature in the XAS is significantly reduced, often to a level below visual detection. Although the contaminating peak has not been completely removed, the amplitude is reduced such that the fitting and removal of a cubic-spline curve is adequate in eliminating any residual non-oscillatory contribution. The spinner was mounted onto the beam line between the ion chambers \( I_0 \) and \( I_t \) and set to an angle of 45\(^\circ\) with respect to both the direction of the incident beam and the fluorescence detector. The rotation speed was a few hundred rpm.

Samples of Cu\(_2\)O, CuO, In\(_2\)O\(_3\), SnO\(_2\), EuO\(_2\) and CaCO\(_3\) were mixed with PVP and pressed into pellets with a 13mm IR press for use as standards. The amount of material used in each pellet was adjusted to give an absorption of about \( \mu d = 1 \).

The raw data were converted to an energy scale with the Daresbury programme EXCALIB. Background subtraction for both X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (EXAFS) work was carried out using VIPER [32,33]. EXAFS analysis was performed using EXCURV98 [34,35]. The phase shifts were calculated \textit{ab initio} from Hedin-Lundqvist exchange potentials and Von Barth ground state potentials. Theoretical fits to the \( k^2 \)-weighted EXAFS were produced by least-squares refining \( E_f \) (an energy offset), and for each shell RD (absorber-scatter distance) and \( 2\sigma^2 \) (Debye-Waller factor representing both static and thermal disorder). The coordination number can also be refined, but this option was not utilised in this work. The quality of the fit is measured by an R-factor [35] and the errors in RD are approximately ±0.02Å and approximately ±20% in \( 2\sigma^2 \) and CN.

3. Results and discussion
XRD peaks that indexed to delafossite-type CuInO\(_2\) were seen in all samples, with preferential orientation mostly for the (012) plane. The presence of In\(_2\)O\(_3\) is also seen in the sample prepared at the low partial pressure of 5x10\(^{-4}\) mbar. The TEM micrographs showed that the films also contained some amorphous material.

As mentioned in experimental section 2.2, it was found that the fluorescence XAS signal detected was contaminated with Bragg peaks in the higher \( K \) region, which may be caused by either the films being epitaxial, or more likely as a result of diffraction from the Al\(_2\)O\(_3\) substrate. Unfortunately, with the films being relatively thin, simply changing the angle away from the preferred 45\(^\circ\) angle relative to the beam and detector also results in a large reduction in fluorescence intensity observed for the sample therefore making this method largely unsuitable for removing the interference. However, as seen in Figure 2 the effect of spinning the sample was very effective in removing the interference at high \( k \) values.

The Cu K-edge XANES spectra for undoped delafossite-type CuInO\(_2\) films prepared under varying oxygen partial pressures is shown below in Figure 3. The average oxidation state of the Cu site is difficult to quantify by XANES with the shift for Cu\(^0\) and Cu\(^+\) being very similar. An added
complication is that the change in environment can also have an effect on the edge position. The films prepared at $5 \times 10^4$ and $2 \times 10^3$ mbar appear to have an oxidation state of around $+1$, with the $1 \times 10^2$ mbar film appearing to be very slightly above $+1$. The $2 \times 10^2$ mbar film appears to be further oxidised to around $\text{Cu}^{II}$, although again the exact oxidation state cannot be quantified. The delafossite type CuInO$_2$ has oxidation states of $\text{Cu}^I$ and $\text{In}^{III}$ [19], and therefore the only films that are likely to present the delafossite phase are the $5 \times 10^4$ to $1 \times 10^2$ mbar prepared samples, although it has been suggested that the material can be oxidised to CuInO$_{2.5}$ with copper present as $\text{Cu}^{2+}$ [36]. The Cu K-edge XANES spectra for the 10% Ca doped samples appeared very similar to those of the undoped ‘CuInO$_2$’ films, suggesting that the oxygen pressure of the film preparation is very important to the deposited sample, and that the presence of the dopant has little effect on the overall structure. This was supported by the Cu K-edge XANES spectra for the 10% Sn doped ‘CuInO$_2$’ films. Again the samples prepared between $5 \times 10^4$ and $1 \times 10^2$ mbar appear to have copper oxidation states of roughly $\text{Cu}^+$ and are very similar to the equivalent undoped films.

The In K-edge XANES spectra for the undoped ‘CuInO$_2$’ films showed that in all cases there appeared to be no deviation away from the expected $\text{In}^{III}$ oxidation state, showing that any additional oxidation taking place is compensated by increasing the oxidation state of the copper from $\text{Cu}^+$ towards $\text{Cu}^{2+}$ as expected [36,37]. The Eu L$_{III}$-edge XANES spectra showed that the Eu appears to be present as $\text{Eu}^{3+}$ at all doping concentrations from 2 to 10% with the Eu L$_{III}$-edge position appearing in an identical position to that of Eu$_2$O$_3$. Sn K- and Ca K-edge data were also recorded, however the poor quality data did not allow for quantitative or qualitative XANES information to be extracted. This is the result mostly from the weak/noisy signal leading to large data collection times, which when coupled with the lack of a monitor spectrum meant the spectra could not be accurately calibrated.

The Cu K-edge EXAFS and Fourier transform of the ‘CuInO$_2$’ film deposited with an oxygen pressure of $2 \times 10^2$ mbar is shown in Figure 4 with the best fit parameters displayed in Table 1. The data has only been fitted to three shells as there is very little contribution visible in the EXAFS and
Fourier transforms above 3.5 to 4 Å. The first point to note is the high level of disorder seen in the sample. Through the high Debye-Waller factors for the Cu-Cu and Cu-In correlations. These values could be expected to be higher than normally seen in other compounds due to the Cu movement perpendicular to the O-Cu-O bond as in Cu$_2$O. Similarly high values of ~0.04Å$^2$ have been reported [38] for the 2σ$^2$ values for the Cu-Cu correlation in CuGaO$_2$. The data does not fit well to the delafossite-type CuInO$_2$ model, with the Cu-Cu correlation unable to settle at a distance close to the 3.292Å expected. The Cu-O distance of 1.938Å would also suggest an increased oxidation state from Cu$^+$ towards Cu$^{2+}$ as seen in the XANES and similar to the Cu$^{3+}$O distance of 1.956Å in CuO. The low Debye-Waller factor for the Cu-O shell would also suggest an increase in coordination number (CN and 2σ$^2$ are highly correlated) as would be expected in comparison to the Cu$^{3+}$ standards CuO and Cu$_2$In$_2$O$_5$, which show a first shell coordination number of four compared to two for the linear CuO$_2$ geometry expected in Cu$_2$O and CuInO$_2$. The structure of CuInO$_{2+δ}$ appears to be mistakenly reported in the literature, with the delafossite type CuInO$_{2.66}$ structure [36] reported in the ICSD [39] claiming an additional 18 O

Figure 3 Cu K edge XANES (top) and derivative (bottom) for delafossite-type CuInO$_2$ films prepared under different pO$_2$, through the high Debye-Waller factors for the Cu-Cu and Cu-In correlations.
atoms surround each Cu atom at a distance of 1.936Å which would not provide the correct stoichiometry. The possibility of the 2×10⁻² mbar film displaying the CuInO₂⁺ structure has therefore not been modelled due to the uncertainty in structure, and the apparent high level of disorder in the sample.

Figure 4 Cu K edge EXAFS (left) and Fourier transform (right) for ‘CuInO₂’ film prepared at pO₂ 2×10⁻² mbar

| CuInO₂ crystallographic data [19] | EXAFS |
|-------------------------------|-------|
| Atom | CN | RD (Å) | Atom | CN | RD (Å) | 2σ² (Å²) | E_f (eV) | R (%) |
| O    | 2  | 1.845  | O    | 2  | 1.938  | 0.001     |          |       |
| Cu   | 6  | 3.292  | Cu   | 6  | 3.351  | 0.048     | 0.18     | 50.77 |
| In   | 6  | 3.466  | In   | 6  | 3.501  | 0.045     |          |       |

Table 1 Best-fit parameters for Cu K edge EXAFS of ‘CuInO₂’ made at pO₂ 2×10⁻² mbar

The Cu K-edge EXAFS and best-fit parameters for the pO₂ 1×10⁻² mbar film are displayed in Figure 5 and Table 2, respectively.
Figure 5 Cu K edge EXAFS (left) and Fourier transform (right) for ‘CuInO$_2$’ film prepared at $p\text{O}_2$ $1\times 10^{-2}$ mbar

| CuInO$_2$ crystallographic data [19] | EXAFS |
|--------------------------------------|-------|
| Atom | CN | RD (Å) | Atom | CN | RD (Å) | 2σ$^2$(Å$^2$) | $E_f$(eV) | R (%) |
| O     | 2  | 1.845  | O     | 2  | 1.861  | 0.010         | -6.63     | 39.08 |
| Cu    | 6  | 3.292  | Cu    | 6  | 3.287  | 0.046         |           |       |
| In    | 6  | 3.466  | In    | 6  | 3.479  | 0.045         |           |       |

Table 2 Best fit parameters for Cu K edge EXAFS of ‘CuInO$_2$’ film prepared at $p\text{O}_2$ $1\times 10^{-2}$ mbar

The EXAFS refinement fits much better to the delafossite-type CuInO$_2$ model (R=39%) with excellent agreement in the radial distances well within the expected ±0.02Å. The Debye-Waller factors for the Cu-Cu and Cu-In shells remain high however, which may be as a result of the expected disorder in the sample due to the movement around the O-Cu-O linear bond, or a suggestion that the sample is fairly disordered overall.

The Cu K-edge EXAFS for the films prepared at oxygen pressures of $2\times 10^{-3}$ mbar and $5\times 10^{-4}$ mbar gave very poor fits to the delafossite structure. The Cu-Cu distances did not settle close to the 3.29Å distance expected, and falling a large distance outside the expected ±0.02Å error. Additionally the Debye-Waller factors were very large suggesting that the Cu environment in this sample is not correctly modelled by a Cu site in delafossite type CuInO$_2$. The most striking observation, however, was the presence of the peaks at around 2.5Å and 4.5-5Å in the sample prepared at $5\times 10^{-4}$ mbar which shows that there is Cu metal present in the sample. It would appear that the low oxygen pressure is not high enough to allow all of the copper to form in an oxidised form, resulting in a mixed structure with both Cu$^0$ and Cu$^+$ present.

The Cu K-edge EXAFS for the various doped films confirmed the picture that emerged from the XANES data. The spectra were not affected by the doping and reflected the spectra of the undoped films prepared at the same oxygen partial pressures.

The In K-edge EXAFS of the undoped ‘CuInO$_2$’ film prepared at the oxygen pressure of $2\times 10^{-2}$ mbar confirmed the picture that emerged from the Cu K-edge EXAFS for this film; i.e. the local environment is not the delafossite-type CuInO$_2$ structure. The difference is again the copper sites, with the In-Cu shell unable to refine to the distance expected of 3.466Å and the excessively large 2σ$^2$ value suggesting that the correlation does not really exist.

The In K-edge EXAFS and Fourier transforms for the undoped film prepared with a $p\text{O}_2$ of $1\times 10^{-2}$ mbar is displayed in Figure 6 with the best-fit parameters shown in Table 3. The displayed results show an excellent agreement (R=39.78%) to the expected In environment in delafossite CuInO$_2$, and also to the Cu-In distances provided by the Cu K-edge EXAFS of the same sample within the expected ±0.02Å error. The Debye-Waller factors are also reasonable and show the expected increase for the outer shells. They also appear to show that there is a significantly lower level of disorder presented in the average In environment compared to Cu environment. This would be consistent with the Cu K- and In K-edge XANES which showed variation in valency and geometry around the Cu with changing $p\text{O}_2$, whilst the In site remained consistent.

The refinement of the In K-edge EXAFS results for the undoped ‘CuInO$_2$’ film prepared at $p\text{O}_2$ $2\times 10^{-3}$ mbar appears to show the local structure of the indium fits well to the delafossite-type CuInO$_2$ model (R=30.74%) with good agreement in radial distances and reasonable 2σ$^2$ values suggesting the local structure displays relatively low value of disorder compared to the Cu site. This however, is in stark contrast to the Cu K-edge EXAFS for the same sample which suggests the average Cu environment is not representative of the CuInO$_2$ structure. The combination of the results for the two absorption edges would suggest that the film may not present a single phase of CuInO$_2$, with perhaps
an additional Cu containing phase a possibility to explain the disorder seen in the average local structure of the copper. To confirm this other techniques would need to be employed such as high resolution XRD to provide a model for further EXAFS refinement.

Figure 6 In K edge EXAFS (left) and Fourier transform (right) for ‘CuInO$_2$’ film prepared at $p_{O_2}$ 1×10$^{-2}$ mbar

### Table 3 Best fit parameters for In K edge EXAFS of ‘CuInO$_2$’ film prepared at $p_{O_2}$ 1×10$^{-2}$ mbar

| CuInO$_2$ crystallographic data [19] | EXAFS |
|--------------------------------------|-------|
| Atom | CN | RD (Å) | Atom | CN | RD (Å) | 2σ$^2$ (Å$^2$) | $E_f$(eV) | R (%) |
| O    | 6  | 2.173  | O    | 6  | 2.153  | 0.013         |         |       |
| In   | 6  | 3.292  | In   | 6  | 3.302  | 0.015         | -5.36   | 39.78 |
| Cu   | 6  | 3.466  | Cu   | 6  | 3.466  | 0.032         |         |       |

The results of the In K-edge EXAFS of the undoped ‘CuInO$_2$’ film prepared under an oxygen partial pressure of 5×10$^{-4}$ mbar did not fit well to the CuInO$_2$ model, with variation in the In-In and the In-Cu distances in particular well outside of the ±0.02Å error, with the Cu shell refining to 3.734Å – a value around 0.27Å higher than expected. The average local environment of the indium here actually appears to be In$_2$O$_3$ which is supported by XRD data. The sample appears therefore to be a mixed structure containing In$_2$O$_3$, Cu metal and some oxidised Cu component, although only very weak signals are seen in the XRD pattern for the other components suggesting there may be a large amount of amorphous material or very small nanocrystalline regions present.

It has been assumed experimentally and suggested by computer simulation studies in the literature [26] that for doping of Sn$^{4+}$ and Ca$^{2+}$ into the CuInO$_2$ structure, the dopant is incorporated by substitution onto an In$^{3+}$ site. In a similar fashion, it is expected that the Eu$^{3+}$ will be incorporated onto an In$^{3+}$ site. The Eu L$_{III}$-edge EXAFS data gave a poor fit for the substitution onto a Cu site in all samples (2 to 10% Eu doping levels), with poor agreement to the radial distances expected for the CuInO$_2$ model and unrealistic and unacceptable values of −37 to −40eV for the Fermi energy ($E_f$). In comparison, the data fitted much better with a model of Eu on an In site, with much more sensible values for $E_f$. There also appears to be a local expansion around the Eu compared to undoped model which would be expected from the relative ionic radii (In$^{3+}$ = 0.94Å, Eu$^{3+}$ = 1.09Å [40]). Unfortunately the Ca and Sn data were not of sufficient quality to identify the dopant site.
4. Conclusions
The combination of Cu K- and In K-edge EXAFS and XANES spectra show that the structure of films deposited by PLD is very sensitive to the partial pressure of oxygen used during deposition as suggested in the literature [18,26,27,36]. This is also seen to a lesser extent in our preliminary XRD data in which the main effect seen in the longer range order is a change in the preferential orientation. Below a pressure of $5 \times 10^{-4}$ mbar, no CuInO$_2$ is seen with a mixture of copper and indium oxides formed.

The only undoped sample that fits well to the delafossite-type CuInO$_2$ EXAFS model for both Cu and In sites is that prepared at $1 \times 10^{-2}$ mbar. This is a similar value suggested for the optimal growth of CuInO$_2$ by several other groups using PLD [18,41,42]. The XRD patterns for the $2 \times 10^{-3}$ and $1 \times 10^{-2}$ mbar oxygen films appear to be very similar, but the EXAFS reveals that although the average indium environment is delafossite CuInO$_2$ that the average copper environment deviates from CuInO$_2$ in the $2 \times 10^{-3}$ mbar film. As seen in previous studies [18,42] this could be evidence of partial decomposition of the ternary CuInO$_2$ structure into binary oxides (e.g. Cu$_2$O or In$_2$O$_3$) when the films are prepared under lower oxygen pressure. This pattern is further highlighted at the lowest oxygen pressure of $5 \times 10^{-4}$ mbar in which the average indium environment is now mostly In$_2$O$_3$ and the average Cu environment displays a mixture of both metallic and oxidised Cu species.

HRTEM measurements on these films reveal that regions of both crystalline and amorphous material are visible within the grains [27] with region sizes as small as ~5nm. This could go some way to explaining the higher than expected Debye-Waller factor values observed for the Cu-Cu and Cu-In correlations in EXAFS, in which the average local structure of all Cu atoms in the sample is observed. A mixture of amorphous and crystalline material would create an increase in disorder in the average structure in the sample visible by an attenuation in the outer shell correlations in the EXAFS. An additional factor could be the minor decreases in coordination number/increases in Debye-Waller factor expected for small nano-particles [43] although it can be stressed that the size-effect will be minor compared to the effect of an amorphous/crystalline mixture.

For the doped (Ca, Sn or Eu) ‘CuInO$_2$’ films, the bulk structure is very similar to that of the undoped films, only demonstrating the delafossite-type CuInO$_2$ structure when prepared under a partial oxygen pressure of $1 \times 10^{-2}$ mbar. The dopant site identification was less successful with large background interference from the In L-edges rendering the Ca K edge data unreliable, and the energy range of the solid state fluorescence detector reducing the efficiency of the Sn K-edge data. However, the Eu was successfully identified as being incorporated as Eu$^{3+}$ on an In$^{3+}$ site in agreement with the expected site preference for both Ca$^{2+}$ and Sn$^{4+}$ [26]. The CuInO$_2$ matrix appears to become less ordered with increasing dopant concentration in agreement with the long range order seen by XRD. This pattern is also observed in the dopant site in the Eu L$_{III}$-edge EXAFS in which a clear attenuation in the outer shell intensities can be seen.

In summary, the conclusions for the study are:

- Delafossite-type CuInO$_2$ formed at pO$_2$ $1 \times 10^{-2}$ mbar
- Films prepared at pO$_2 \leq 2 \times 10^{-3}$ mbar do not form phase-pure delafossite CuInO$_2$, decomposing into a mixture including CuInO$_2$, binary oxides such as Cu$_2$O and In$_2$O$_3$ as well as some Cu metal formation at pO$_2$ $5 \times 10^{-4}$ mbar
- At pO$_2$ $2 \times 10^{-2}$ mbar the copper is oxidised to Cu$^{2+}$ and the film has become less ordered, no longer appearing to display the delafossite-type structure
- All films display a mixture of crystalline and amorphous material
- Eu is doped as Eu$^{3+}$ on an In$^{3+}$ site in delafossite type CuInO$_2$ at pO$_2$ $1 \times 10^{-2}$ mbar
- Higher doping concentration leads to a loss of film crystallinity observed by both EXAFS and XRD

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