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The effect of sub-oxide phases on the transparency of tin-doped gallium oxide

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There have been a number of studies on the fabrication of Sn-doped gallium oxide (Ga2O3:Sn) films with both conductive and transparent properties using a variety of deposition methods. However, often, synthesis results in films that are not transparent. In this paper, we examine the mechanisms underlying these results in Ga2O3:Sn thin films prepared at various growth temperatures, Sn concentrations, and oxygen partial pressures. With X-ray absorption spectroscopy, transmission electron microscopy and energy dispersive spectroscopy, we find that when films are grown under the oxygen deficient conditions there are Ga sub-oxide and SnOx phases in the Ga2O3:Sn thin film. These Ga sub-oxide phases are only found in non-transparent films, and so we infer that the Ga sub-oxide is responsible for the non-transparency. These observations suggest that to obtain transparent Ga2O3:Sn, films deposition or subsequent annealing must be carefully controlled in both temperature and oxygen partial pressure to avoid the formation of Ga sub-oxide phases. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4964638]

Transparent conducting oxides (TCO) have become essential in a range of applications such as photovoltaics, smart windows, and displays. In the past decade, there have been many studies to improve both the conductivity and transparency of TCOs.1,2 However, there is still demand for TCO materials with low electron affinity and high band gap, which enable a low-loss electron selective contact for solar absorber materials having a small electron affinity. To this end, gallium oxide (Ga2O3) is a promising TCO due to its low electron affinity of 3.7 eV and large band gap of 4.8 eV.3-6 In addition, Ga2O3 has been recently studied for power electronics and solar-blind photodetector applications, which both require control of electrical doping.1,7,8 Extrinsic doping is used in Ga2O3 to achieve high conductivity, similar to other TCOs, including Sn-doped In2O3, Ga-doped ZnO, and F-doped SnO2.9 Among various dopants, Sn has been the most widely investigated and adopted as a promising dopant.10 When Sn substitutes for Ga3+ on the octahedral site in a 4+ oxidation state, it donates an electron to the Ga2O3 lattice, which increases the carrier concentration and thus conductivity.11

To obtain highly conductive and transparent Sn-doped Ga2O3 (Ga2O3:Sn), there have been a number of studies to optimize the fabrication conditions.12,13 It has been reported that the temperature and oxygen pressure during film growth play an important role especially in the transparency.14 Non-transparent Ga2O3:Sn was reported when low temperature and low oxygen pressure are used. However, the mechanism for the non-transparency in such Ga2O3:Sn films has not been clearly identified. Here, we show that various reduced phases can be formed in the Ga2O3:Sn film, including a Ga sub-oxide phase. Based on the optical data, we infer that this is the primary reason for the non-transparency. Understanding the mechanism of the Ga sub-oxide formation will be helpful to guide synthesis to obtain highly transparent Ga2O3:Sn films.

Ga2O3:Sn thin films on glass (SiO2) substrates were prepared using combinatorial pulsed laser deposition (PLD) with orthogonal gradients in chemical composition and substrate temperature, as previously described.15 The films were mapped for chemical composition and thickness (X-ray fluorescence), crystal structure (X-ray diffraction (XRD)), and optical properties (transmittance/reflectance) at 44 individual locations on the combinatorial film library, as described before.16 Further details are provided in the supplementary material.

Thin film microstructures were characterized in cross section using a combination of transmission electron microscopy (TEM) imaging in bright field and dark field modes, electron diffraction, scanning TEM (STEM) imaging, and energy dispersive X-ray spectroscopy (EDS). TEM specimens were extracted at specific locations from the combinatorial film library using standard focused ion beam (FIB) techniques.

X-ray absorption spectroscopy (XAS) is employed to measure the chemical state and local environment of Ga and Sn. We perform Ga K-edge and Sn K-edge X-ray absorption spectroscopy (XAS) at 20-ID-B at the Advanced Photon Source. To determine the crystal structure of the Ga2O3:Sn, high resolution X-ray diffraction (XRD) at beamline 2-1 at
the Stanford Synchrotron Radiation Lightsource (SSRL) was utilized. Experimental details are found in the supplementary material.

Figure 1 shows photographs of the two combinatorial film libraries of the Ga2O3:Sn thin films used in this study. Figure 1(a) shows the film fabricated with no oxygen (GNO) in 1 mTorr of pure Ar, while the film in Figure 1(b) is fabricated with an oxygen (GWO) pressure of 1%–10% O2/Ar. In both films, there is a horizontal gradient in growth temperature, from 260 °C to 520 °C (right to left), and a vertical gradient in Sn concentration gradient from about 2 at. % to 8 at. % of the cationic concentration (bottom to top). These composition and temperature trends in Figure 1(a) are quantified in Figure 1(c), showing the thickness of the GNO films on the color scale. As the temperature increases, the thickness decreases and the composition shifts towards higher Sn content, suggesting that the Ga partially sublimes from the growing film. From Figure 1, the GNO film is transparent for deposition temperatures greater than 500 °C, while the GWO film is transparent for all growth temperatures. Overall, these results are consistent with previous observations reported in literature. Since there is no change in transparency as a function of Sn concentration for both GNO and GWO films, for the rest of this paper we will focus only on the effect of the fabrication temperature and oxygen pressure on transparency by characterizing the film structure and chemical environment at 4 points on each film, which are marked as circles in Figure 1(a) and (b). For the selected films (circles in Figure 1), the Sn concentration is approximately 2–3 at. % of the cationic concentration, except for the 520 °C point where the Sn content is 6–7 at. %, as indicated by arrows in Figure 1(c) for the GNO films. Figure 1(d) shows the transmittance data from the GNO films showing that they are highly transparent (80%–90% transmittance) for deposition temperatures above 500 °C and not transparent (0%–5% transmittance) for lower deposition temperatures. However, the GWO film is highly transparent at all studied substrate temperature, despite being similar in chemical composition to the GNO film. Figure S1 shows the XRD results for the 4 different points on both GNO and GWO films. We find that the diffraction peaks in Figure S1(a), 400 °C, 320 °C, and 280 °C, correspond to the beta phase of Ga2O3. In the GWO film, we find only the beta phase of Ga2O3:Sn at 400 °C. The GWO films are amorphous or nanocrystalline below a deposition temperature of 400 °C. At 520 °C both GWO and GNO films show broad peak around 30.5° and sharp peak at 38.9°, which indicate a mixture of the beta phase and epsilon phase of Ga2O3. The sharp
peak at 38.9° correspond to the (0004) peak from the epsilon phase in the preferentially oriented film.17

Among the 4 points in Figure 1, one point per sample was analyzed by TEM. The 400°C spot was chosen since it is non-transparent in the GNO but transparent in the GWO. Figure 2 illustrates representative high angle annual dark field (HAADF) STEM images and associated EDS elemental hyperspectral images. STEM-HAADF images illustrate both light and dark contrast, corresponding to high and low atomic number regions, respectively. A region corresponding to an area with high concentration of Sn (red) is highlighted with a circle. This region also corresponds to a reduced oxygen concentration, suggesting the presence of a SnO₂ phase in the GNO film. The EDS maps also show that the Ga-rich regions are correlated with the oxygen deficient regions, as marked by squares, indicating the presence of a Ga sub-oxide phase. STEM-EDS analyses from the GWO film in Figure 2(b) illustrate a markedly different and more homogeneous microstructure compared to the GNO film. We can see the composition profile of the STEM-EDS image in the Figure 3. There are Ga sub-oxide regions in the GNO sample near the film surface and at the substrate-film interface in Figure 2(a), whereas no significant change in the composition of the film is observed in the GWO sample in the Figure 2(b). To quantify the amount of oxygen in the EDS spectra, we calculated the composition of the Ga sub-oxide region using the GWO sample as a standard with the assumption that the GWO sample has a stoichiometric composition of Ga₂O₃. The calculated composition of the Ga sub-oxide phase from the surface region, in Figure 3(c) is about GaO₀.₆₃, which is the averaged value through the projected area, which overlaps the Ga₂O₃ region. This is the reason why the Ga concentrations in the Ga sub-oxide are not same in three different regions from Figures 3(c)–3(e), and the Ga concentration in the Ga sub-oxide can be more metallic than GaO₀.₆₃.

To further study the secondary phases observed by TEM, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements of the two films series were acquired. Figures 4(a) and 4(b) show the Ga K-edge XANES from GNO and GWO, respectively. The XANES spectrum is sensitive to the oxidation state and local chemical environment of the element being measured. Figures 4(a) and 4(b) show the normalized absorption spectra and derivative of the absorption spectra. The Ga K-edge absorption is 10 367 eV as shown as the maximum peak of Ga metal foil in the derivative plot. In the Figure 4(a), the derivative absorption spectra of the 520°C, 400°C, 320°C, and 280°C points show strong peaks near 10372.5 eV, which correspond to Ga³⁺. Remarkably, there are weaker peaks near 10367 eV in the derivative absorption spectra of the 400°C, 320°C, and 280°C, which are similar to those seen for Ga metal. From this, we confirm that there are Ga sub-oxide phases with a reduced oxidation state of Ga from Ga³⁺ in the GNO film for growth at 400°C and below. On the other hand, the XANES of the transparent 520°C point shows no Ga sub-oxide peak. The intensity of Ga sub-oxide peak in the derivative XANES plot of the 280°C and 300°C films are same, and decreased for the 400°C film. Therefore, this indicates that the Ga sub-oxide starts to oxidize after 300°C, and finally disappears above 400°C.

FIG. 3. Composition profiles through the lines in STEM-EDS images of (a) GNO and (b) GWO films, fabricated at 400°C. All scale bars are 90 nm. (c), (d), and (e) show specific composition profiles in different regions.

FIG. 4. Ga K-edge XANES spectra for (a) GNO film, and (b) GWO film. The left graphs show normalized absorption, and the right graphs are the derivative plots of the left graphs. The dashed line represents the Ga metal reference foil.
Figure 4(b) shows that the XANES results from all 4 growth temperatures in the transparent GWO do not have the Ga sub-oxide peaks near 10 367 eV. Therefore, we conclude that there are no Ga sub-oxide regions in the GWO films. These XANES results implicate the Ga sub-oxide phase with reduced oxidation state of Ga as a cause of the lack of transparency in the low temperature growth in non-oxidizing environments and may be commonplace for low temperature Ga$_2$O$_3$ growth in low oxygen environment.

Figures 5(a) and 5(b) show the absorption results for the Sn K-edge absorption for both the GNO and GWO films, and we find the normalized absorption results and the derivative absorption results. In the XANES results, we can see that all of the spectra from 4 points overlap each other in the Figures 5(a) and 5(b), and they are located between the references of Sn, SnO, and SnO$_2$. The XANES signal can originate from Sn$^{2+}$ and Sn$^{4+}$ substituting for Ga$^{3+}$ in the Ga$_2$O$_3$ lattice, or from Sn$^{0}$, Sn$^{2+}$, and Sn$^{4+}$ in the SnO$_x$ phases. From the derivative XANES results, we find that three different oxidation states of the Sn, Sn$^{0}$, Sn$^{2+}$, and Sn$^{4+}$, can be all present in the films. Through the EXAFS analysis in Figure S2, we can get information of local structure near the Sn atom, and we identify that most of the Sn exist in the amorphous or nanocrystalline SnO and SnO$_2$. Details of analysis on Sn-K edge EXAFS are described in the Table S1. As the mixed state of SnO$_x$ does not appear to be dependent on the fabrication conditions, we can identify that SnO$_x$ species do not affect the transparency.

In summary, we prepare Ga$_2$O$_3$:Sn thin films via PLD method with different fabrication temperatures, Sn concentrations, and oxygen partial pressures. We find that the oxygen pressure and the fabrication temperature affect the transparency. We observe both Ga sub-oxide and SnO$_x$ phases in TEM analysis. Together with TEM and XAS analysis, we confirm that there are Ga sub-oxide phases in the non-transparent regions of the GNO film (fabrication below 400°C), but we do not find evidence of the Ga sub-oxide phases in the transparent GWO film. The SnO$_x$ phases are observed in every measured point of the film regardless of transparency. Therefore, we conclude that the Ga sub-oxide phase is the origin of non-transparency, and SnO$_x$ phase do not seem to affect the overall transparency in the Ga$_2$O$_3$:Sn. These results can help avoid Ga sub-oxide phase formation in order to fabricate highly transparent Ga$_2$O$_3$:Sn films.

See supplementary material for experimental details, XRD results, Fourier-transformed EXAFS spectra, and fitting parameters of Sn-K edge data.

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\[ \text{Normalized } \chi(E) \text{ (A.U.)} \]

\[ \text{Energy (eV)} \]

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\[ \text{Energy (eV)} \]

\[ \text{Normalized } \chi(E) \text{ (A.U.)} \]

\[ \text{Energy (eV)} \]

FIG. 5. Sn K-edge XANES spectra for (a) GNO film, and (b) GWO film. The left graphs show normalized absorptions, and the right graphs show derivative plots of the left graphs. The black solid line, dashed line, and dotted line represent Sn$^0$ metal, Sn$^{2+}$, O, and Sn$^{4+}$O$_2$ references, respectively.

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