Evaluating the quality of epitaxial In_2O_3 grown by suboxide molecular beam epitaxy

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Abstract:

We present how suboxide molecular beam epitaxy (S-MBE) can be utilized to grow high quality epitaxial In_2O_3 films at rapid growth rates of 0.6 µm/hr at back-end-of-line temperatures below 450ºC. The quality of these films is evaluated by X-ray diffraction and atomic force microscopy. The presence of hybrid reflections and thickness fringes in the 2θ-ω scans and the full-width half maximum of the rocking curve reveal unmatched crystal qualities even at these low deposition temperatures. The surface topography reveals smooth surfaces, if the right deposition pressure is chosen.

Summary of Research:

Indium oxide (In_2O_3) is an commonly used oxide in the electronics industry and shows promise as an active material in transparent thin film transistors (TFTs) which constitute a central element of modern electronics.[1] In_2O_3 has a higher electron mobility than many of the current materials used in transparent TFTs, but growing at back-end-of-line (BEOL) applicable temperatures usually results in polycrystalline In_2O_3; the grain boundaries cause inconsistent electronic properties. Recently, amorphous thin-film In_2O_3 TFTs have been made successfully at BEOL applicable temperatures.[2] However, epitaxial TFTs with similar materials have been shown to exhibit higher drain current and on-off ratios than amorphous TFTs.[3] Therefore, we wanted to develop a method to grow epitaxial In_2O_3 at BEOL temperatures.

For traditional MBE, the oxidation of indium on a substrate surface goes through a two-step reaction consisting of a slow step and a fast step:

$$2\,In + 3\,O \xrightarrow{\text{slow step}} In_2O + 2\,O \xrightarrow{\text{fast step}} In_2O_3$$

However, S-MBE starts with an In_2O source rather than an elemental source by utilizing a mixture of indium metal and indium oxide powder resulting in an In_2O beam. In_2O is volatile, which theoretically allows adsorption controlled growth.[4] Utilizing S-MBE, we are able to grow epitaxial In_2O_3 thin films on YSZ001 with a growth rate of (0.6 µm/hr) at the BEOL applicable temperature of less than 450ºC by bypassing the first slow step. An Empyreon X-ray diffractometer (XRD) with a triple-axis detector was used to evaluate the crystallinity and surface quality of the samples. Hybrid reflections found in 2θ-ω scans and the full-width half maximum (FWHM) of rocking curves are used to evaluate the crystallinity of the film. Thickness fringes in 2θ-ω scans and topography and roughness measurements by atomic force microscopy (AFM) are used to evaluate surface quality.

Results and Conclusions:

Hybrid reflections are a measure of film quality because they can only occur when the bulk film is highly uniform and phase pure.[5] Hybrid reflections occur when an X-ray scattered by the film interferes constructively with an X-ray scattered by the substrate. This results in peaks which appear at angles associated with neither the film nor the substrate. Any defects will cause peak broadening, and the signal becomes unobservable. The hybrid reflection angle 2θ can be calculated using Bragg's law:

$$2\theta = 2\arcsin\left(\frac{\lambda\overrightarrow{|G_u|}}{2}\right), \qquad (1)$$

where λ is the wavelength of incident X-ray and $\overrightarrow{|G_u|}$ is the norm of the hybrid scattering vector, which is:

$$\overrightarrow{|G_u|} = \left|\frac{l_s}{c_s} + \frac{l_f}{c_f}\right|, \qquad (2)$$

where l_s and l_f are the substrate and film out-of-plane Miller indices, respectively, and c_s and c_f are the substrate and film out-of-plane lattice parameters, respectively. Combining Equations (1) and (2) yields:

$$2\theta = 2\arcsin\left(\frac{\lambda}{2}\left|\frac{l_s}{c_s} + \frac{l_f}{c_f}\right|\right). \qquad (3)$$

Using the parameters $l_s = 3$ and $l_f = -2$ along with the lattice parameters of the unit cell as calculated by the location of the substrate (002) plane (*) and film (004) plane, the hybrid reflection should occur at 2θ = 34.69º.

Figure 1a, shows a ϕ scan at the angle of the hybrid reflection (2θ=34.69º) of a representative In_2O_3 film. The diffraction pattern shows repeating sets of two peaks approximately every 90º, which corresponds to the symmetry of the cubic unit cell of the film and substrate. We chose 113.43º and 50º as ϕ angles with and without a hybrid reflection maxima, respectively. In Figure 1b, a 2θ-ω scan reveals the presence of the hybrid reflection (the (003) substrate plane interacting with the (002) film plane) at 2θ= 34.58º. At ϕ=113.43º, the hybrid reflection is present; however, at ϕ=50.00º, the peak is not visible. This confirms that this peak is a hybrid reflection. A small shift of the hybrid and film peak from the expected 2θ value can be ascribed to the presence of oxygen vacancies.

The full width half maximum (FWHM) of the rocking curves for the film and substrate is compared to evaluate the bulk film quality. The ideal film will only have a FWHM as small as the substrate, so close agreement between the FWHM of the film and substrate indicate a good film.[6] In Figure 1c, the substrate (FWHM=0.0197º) is very close to the film (FWHM=0.0189º), indicating good film quality.

Thickness fringes are another measure of film quality because they can only occur when the surface of the film is smooth. Thickness fringes occur when X-rays which are reflected from the surface of the film constructively interfere with the reflections from the film-substrate interface. Typically, this phenomenon occurs at very low angles, where 2θ is in the range of 0º to 8º; however, when a film has exceptional surface quality, these fringes can appear at higher 2θ angles.[7] AFM was used to verify the relationship between smooth film surface and the presence of thickness fringes. Figure 1d shows the surface of an In_2O_3 film which was deliberately grown with excess In_2O, which cannot desorb at BEOL temperatures.[4] This results in the formation of what are likely In_2O islands, resulting in a rough surface with a root mean squared (RMS) of 11.50 nm. On the other hand in Figure 1e, the surface of a sample grown in ideal conditions is shown, resulting in a smooth surface with few protrusions and an RMS of 2.327 nm. The respective 2θ-ω scans in Figure 1f reveal that the smooth sample (in red) has thickness fringes whereas the rough sample (in blue) does not. However, the excess In_2O only affects the surface; both samples have a highly uniform and phase-pure bulk film, as exhibited by the hybrid reflection at around 34.6º.

We have shown the exceptional crystal quality achieved by S-MBE for epitaxial (001) In_2O_3 films. Compared to literature, S-MBE grows higher quality films than any other method, even epitaxial methods at higher temperatures, e.g. Bierwagen *et al.* achieved a FWHM of 0.11 at 650ºC.[8] Additionally, hybrid reflections and thickness fringes have never been observed for (001) In_2O_3 films. The quality of the epitaxial films grown by S-MBE is, thus, unparalleled.

Future Work:

The next step is the fabrication of BEOL In_2O_3 TFTs using our films. This work will need to consider if the superior crystal quality correlates to superior electronic transport properties and address eventual challenges such as the active control of electronic properties and possible downsizing effects.

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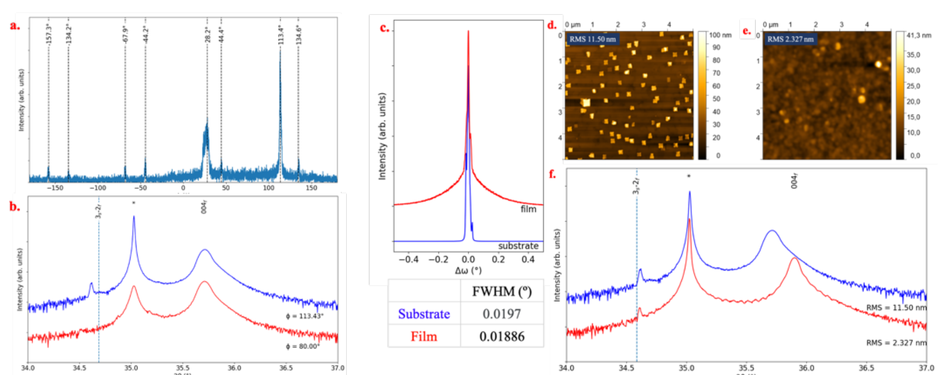

Figure 1. In (a), a ϕ scan at the angle of the hybrid reflections (2θ = 34.6º) of In_2O_3 shows a repeating set of two peaks (black vertical dashed lines) occur approximately every 90º. This behavior is characteristic of a hybrid reflection for a cubic unit cell. 2θ-ω scans in (b) at the maximum intensity at 113.4° (blue) and no intensity at 50.00° (red) show how the visibility of a hybrid reflection depends on ϕ, proving it is a hybrid reflection. Part (d) shows the rocking curves of substrate and a film grown under ideal conditions. The FWHM of the film rocking curve is almost equal to the FWHM of the substrate rocking curve, also indicating good bulk crystal quality. The surface topography of two samples, one grown in an oxygen-deficient environment (d) and one grown at ideal conditions (e), imaged by AFM. In (f), the 2θ-ω scans taken by XRD show thickness fringes are present in the sample with a very smooth surface (grown in ideal conditions, red), whereas the sample with a rough surface (grown in oxygen-deficient conditions, blue) does not. However, the bulk of both samples is highly phase-pure and uniform, which causes the hybrid reflection to be visible.