GROWTH OF SnO₂ THIN FILMS BY ALD AND CVD: A COMPARATIVE STUDY

Jonas Sundqvist and Anders Härsta

Department of Materials Chemistry
The Ångström Laboratory, Uppsala University,
Box 538, SE-751 21 UPPSALA, Sweden

Tin oxide is a transparent conducting oxide, which is prepared on an industrial scale by CVD. The most common precursor combination is SnCl₄ and H₂O [1]. Tin oxide films have also been prepared by ALD using the same precursors [2]. In the present study we use the precursor combination SnI₂ and O₂ to grow thin tin oxide films on α-Al₂O₃(0 1 2) substrates by both CVD and ALD. The main advantages of employing this precursor combination is that the resulting films will most probably have a lower halide contamination level compared to the corresponding metal chlorides and also that no residual hydrogen will be present in the films since a hydrogen free oxygen precursor is used.

In both ALD and CVD of SnO₂ using the SnI₂-O₂ precursor combination, growth was investigated between 350 and 750 °C on α-Al₂O₃(0 1 2) substrates. In the case of ALD no film growth was detected at 350 °C. However from 400 °C the growth rate increased linearly up to 500 °C and was found to saturate at around 0.10-0.12 nm/cycle (18-22 nm/h) at 500-750 °C and was found to saturate at around 0.10-0.12 nm/cycle (18-22 nm/h) at 500-750 °C. In CVD much higher growth rates can be obtained. Furthermore, the growth is governed by surface kinetics up to 475 °C, while above 475 °C, the growth rate depends on the feed rate of SnI₂ into the reaction zone. The higher growth rate in CVD affected the crystalline quality of the SnO₂ films in two ways. First, a growth rate above 1000 nm/h resulted in film growth with other orientations than [101]. Since the relatively low rocking curve FWHM values (< 1.0°) of the 1 0 1 reflection suggest epitaxial growth, ϕ-scans were made to investigate the in-plane orientational relationship between the film and the substrate. Figure 2 shows examples of ϕ-scans from the SnO₂ (3 0 1) plane and the α-Al₂O₃ (0 2 10) plane for both ALD and CVD films grown at 600 °C. Since the strongest peak of the SnO₂ 3 0 1 reflections appear at the same ϕ-angle as the α-Al₂O₃ 0 2 10 reflection it can be deduced that the films are grown with the b axis of the SnO₂ film aligned with the a axis of the α-Al₂O₃ substrate and hence that the in-plane orientational relationships are [0 1 0]film || [1 0 0]substrate and [1 0 -1]film || [-1 2 1]substrate.

No iodine could be detected by XRFS in any of the grown films. This is true for films deposited by both CVD and ALD. The detection limit for iodine by XRFS is estimated to be less than 0.2 at%. Finally, it is worth mentioning that the films are relatively smooth, both with respect to the film surface and the film/substrate interface, since XRR curves (not shown here) with an extensive number of thickness fringes were possible to measure.

The main difference between the two deposition techniques revealed in this study is the growth rate dependence on deposition temperature. In ALD the growth rate is independent of substrate temperature in a temperature window from 500 to 750 °C. In CVD much higher growth rates can be obtained. Furthermore, the growth is governed by surface kinetics up to 475 °C, while above 475 °C, the growth rate depends on the feed rate of SnI₂ into the reaction zone. The higher growth rate in CVD affected the crystalline quality of the SnO₂ films in two ways. First, a growth rate above 1000 nm/h resulted in film growth with other orientations than [101]. Secondly, the probability of 180° in-plane rotation of the (1 0 1) plane was higher compared to the films grown by ALD.

Films deposited by both ALD and CVD were grown with a pronounced [101]-orientation in the examined temperature range, since only the 1 0 1 and 2 0 2 reflections were visible in the XRD patterns. However, it should be mentioned that for the highest deposition rates (>1000 nm/h) in the CVD process, a weak 2 0 0 reflection could also be detected.

Since the relatively low rocking curve FWHM values (< 1.0°) of the 1 0 1 reflection suggest epitaxial growth, ϕ-scans were made to investigate the in-plane orientational relationship between the film and the substrate. Figure 2 shows examples of ϕ-scans from the SnO₂ (3 0 1) plane and the α-Al₂O₃ (0 2 10) plane for both ALD and CVD films grown at 600 °C. Since the strongest peak of the SnO₂ 3 0 1 reflections appear at the same ϕ-angle as the α-Al₂O₃ 0 2 10 reflection it can be deduced that the films are grown with the b axis of the SnO₂ film aligned with the a axis of the α-Al₂O₃ substrate and hence that the in-plane orientational relationships are [0 1 0]film || [1 0 0]substrate and [1 0 -1]film || [-1 2 1]substrate.

No iodine could be detected by XRFS in any of the grown films. This is true for films deposited by both CVD and ALD. The detection limit for iodine by XRFS is estimated to be less than 0.2 at%. Finally, it is worth mentioning that the films are relatively smooth, both with respect to the film surface and the film/substrate interface, since XRR curves (not shown here) with an extensive number of thickness fringes were possible to measure.

The main difference between the two deposition techniques revealed in this study is the growth rate dependence on deposition temperature. In ALD the growth rate is independent of substrate temperature in a temperature window from 500 to 750 °C. In CVD much higher growth rates can be obtained. Furthermore, the growth is governed by surface kinetics up to 475 °C, while above 475 °C, the growth rate depends on the feed rate of SnI₂ into the reaction zone. The higher growth rate in CVD affected the crystalline quality of the SnO₂ films in two ways. First, a growth rate above 1000 nm/h resulted in film growth with other orientations than [101]. Secondly, the probability of 180° in-plane rotation of the (1 0 1) plane was higher compared to the films grown by ALD.