# GROWTH OF $SnO_2$ THIN FILMS BY ALD AND CVD: A COMPARATIVE STUDY

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Tin oxide is a transparent conducting oxide, which is prepared on an industrial scale by CVD. The most common precursor combination is $SnCl_4$ and $H_2O$ [1]. Tin oxide films have also been prepared by ALD using the same precursors [2]. In the present study we use the precursor combination $SnI_4$ and $O_2$ to grow thin tin oxide films on $\alpha$-$Al_2O_3$(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 due to the fact that metal iodides have a lower thermal stability 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.

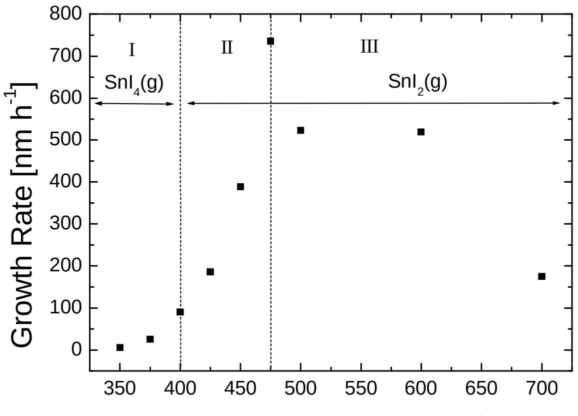

**Figure 1**

In both ALD and CVD of $SnO_2$ using the $SnI_4$–$O_2$ precursor combination, growth was investigated between 350 and 750 °C on $\alpha$-$Al_2O_3$(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. The growth rate in CVD was as expected much higher, and increased exponentially with temperature from 5 nm/h at 350 °C to 735 nm/h at 475 °C (fig. 1). Above 475 °C the growth rate was controlled by the mass flow of the metal precursor. For instance at 500 °C the growth rate could be increased above 1000 nm/h by either increasing the evaporation temperature of $SnI_4$ or by increasing the $N_2$ carrier gas flow. The temperature region below 475 °C, where the growth is controlled by surface kinetics, can be divided into two regions (I and II). In the first region (I) the dominating gas species from the evaporated precursor is $SnI_4$(g) according to thermodynamic calculations, while in the second region (II) the dominating gas species is $SnI_2$(g). These two regions correspond to two different slopes in the Arrhenius plot, one with an apparent activation energy of 220 kJ/mole (I) and one with an apparent activation energy of 140 kJ/mole (II). This suggests that there are different rate-limiting steps, one involving $SnI_4$ at lower temperatures and one involving $SnI_2$ at higher temperatures.

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 202 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.

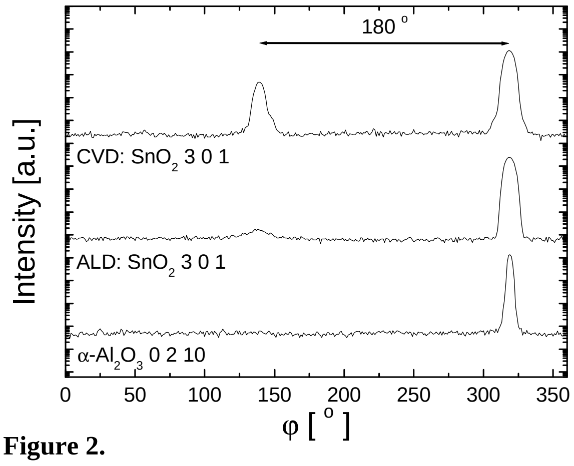

**Figure 2.**

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 $SnO_2$ (3 0 1) plane and the $\alpha$-$Al_2O_3$ (0 2 10) plane for both ALD and CVD films grown at 600 °C. Since the strongest peak of the $SnO_2$ 3 0 1 reflections appear at the same φ-angle as the $\alpha$-$Al_2O_3$ 0 2 10 reflection it can be deduced that the films are grown with the *b* axis of the $SnO_2$ film aligned with the *a* axis of the $\alpha$-$Al_2O_3$ substrate and hence that the in-plane orientational relationships are $[0\,1\,0]_{film} || [1\,0\,0]_{substrate}$ and $[1\,0\text{-}1]_{film} || [\text{-}1\text{-}2\,1]_{substrate}$.

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 $SnI_4$ into the reaction zone. The higher growth rate in CVD affected the crystalline quality of the $SnO_2$ 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 $180^o$ in-plane rotation of the (1 0 1) plane was higher compared to the films grown by ALD.

1. G. Sanon, R. Rup, A. Mansingh, *Thin Solid Films*, **190**, 287 (1990).
2. H. Viirola, L. Niinistö, *Thin Solid Films*, **249**, 144 (1994).