SPATIAL-ALD OF TRANSPARENT AND CONDUCTIVE OXIDES
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ABSTRACT
The rapid growth of the electronics and solar industry has guided the investigation of Zn-based transparent and conductive materials. The industrial needs for low-cost deposition processes with high throughput has driven the development of atmospheric pressure Spatial-ALD, which combines the advantages of conventional ALD with high growth rates (up to nm/s). We have used the Spatial-ALD technique to grow polycrystalline i-ZnO, Al:ZnO, In:ZnO and amorphous InZnO, InGaZnO. ZnO films have been deposited by sequentially exposing a substrate to water and the metal precursors (i.e. diethylzinc together with trimethylaluminum or trimethylindium and/or triethylgallium) vapor, spatially separated in the spatial ALD injector, so that a purge step is no longer needed. The electrical properties of transparent (85% in Vis) i-ZnO films have been controlled, ranging from n-type conductive ($n = 7 \cdot 10^{19}$ cm$^{-3}$ and $\mu = 30$ cm$^2$/V·s) to insulating, by varying the DEZ partial pressure and the deposition temperature (150 - 250 °C). The carrier density increases with Al or In content, ranging from $7 \cdot 10^{18}$ cm$^{-3}$ (i-ZnO) to a maximum value of $5 \cdot 10^{20}$ cm$^{-3}$ (Al/Zn $\approx 0.09$) and $6 \cdot 10^{20}$ cm$^{-3}$ (In/Zn $\approx 0.02$), as shown in Fig. 1. A transition from polycrystalline In:ZnO to transparent (90% in the Vis) and conductive (4 mOhm·cm, 180 nm thickness) amorphous InZnO and InGaZnO occurs with increasing In and Ga content (up to In/Zn $\approx 0.3$ and Ga/Zn $\approx 0.06$), as revealed by XRD analysis (inset in Fig. 1).

A nucleation phase of about 300 ALD-cycles is found for InGaZnO films by measuring the film thickness with Spectropic Ellipsometry, before the onset of the bulk growth at a rate of about 0.03 nm/cycle. The early stages of the nucleation phase (from 5 to 100 ALD-cycles) have been investigated by Low Energy Ion Scattering (LEIS), a non-destructive surface analysis technique. The surface coverage of the Si-substrate by the different metal elements (Zn, In and Ga) is resolved and the composition of the nucleating film is measured by the LEIS technique (Fig. 2). An initial In-rich phase (Zn/In $\approx 0.06$) is found after 5 cycles, followed by a film closure (no Si detected) at 100 cycles with Zn/In $\approx 1.3$. The amorphous structure of the film bulk is confirmed by XRD-diffraction. The electrical properties of the bulk can be controlled by varying its metal composition: carrier density and mobility range from $7 \cdot 10^{18}$ to $6 \cdot 10^{20}$ cm$^{-3}$ and from 1 to 20 cm$^2$/Vs, respectively, when varying the Ga/Zn from 0 to 0.06 and In/Zn from 0 to 0.32, as measured by EDX analysis. The use of Spatial-ALD GIZO films as an active channel in Thin Film Transistors has been tested after a post-deposition annealing, resulting in a device mobility of 3.5 cm$^2$/Vs and on-off ratio of $10^4$.

Fig. 1 Carrier density of In:ZnO and Al:ZnO versus In/Zn and Al/Zn content. Inset: XRD spectra of polycrystalline In:ZnO and amorphous InZnO

Fig. 2 Elemental composition of S-ALD GIZO films after 5 (red line) and 100 (blue line) cycles.