Nucleation and growth kinetics of $ZnAl_2O_4$ spinel in crystalline ZnO - amorphous Al_2O_3 bilayers prepared by atomic layer deposition

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Spinel type materials have attracted considerable interest recently due to their excellent optical, electronic and catalytic properties. Zinc-aluminate ($ZnAl_2O_4$) is particularly interesting both as a catalyst and as an optical material. One finely tunable way to produce this material in practically any shape of a 3D nanostructure is using a removable template and coating it with crystalline ZnO and amorphous Al_2O_3 by atomic layer deposition (ALD). During the proper heat-treatments, the two layers go through solid-state reaction and form $ZnAl_2O_4$. We have experimentally investigated this process in planar geometry to observe the phase-formation and to determine the growth kinetics for the thickness of product phase.

Using low-temperature (100°C) thermal atomic layer deposition (LT-ALD) Al_2O_3/ZnO planar thin film samples were prepared on native oxide covered Si(111) substrates. Heat-treatments at 700°C were performed in air atmosphere using a tube furnace. In every stage of the experiment grazing incidence X-ray diffractograms (GIXRD) were collected. Also, transmission electron microscope (TEM) lamellae were prepared from the samples using focused ion beam and scanning electron microscope (FIB-SEM) and scanning transmission electron microscope (STEM) images were taken using a retractable STEM detector. On the prepared STEM images image analysis was applied.

Based on the obtained diffractograms, it is clear that the deposited Al_2O_3 layer is amorphous, while the ZnO is crystalline. After annealing, the appearing new phase was identified as the crystalline $ZnAl_2O_4$ product phase. On the prepared STEM images, a two-stage phase-formation can be observed, which can be familiar from the literature of metallic materials but counts as a novelty in the literature of spinel forming oxide materials. The first stage is the nucleation of the reaction product in the form of flat, "pancake-like" islands, which then grow mainly laterally and coalesce into a continuous layer. [1] In the second stage, planar growth of the product layer takes place (see the schematic illustration in Figure 1). Contrary to the case of crystalline parent phases, the product layer forms and grows strictly in the Al_2O_3 which indicates that interdiffusion is asymmetric in the amorphous - crystalline system. The growth kinetics for the thickness of the product phase has only been determined for crystalline parent phases before, with the time-exponent of 1.0, indicating interface-controlled reaction. But for the first time, we determined this exponent between ALD-layers, and it appeared to be even lower than 0.5, which indicates a reaction controlled by grain-boundary diffusion and grain-coarsening.

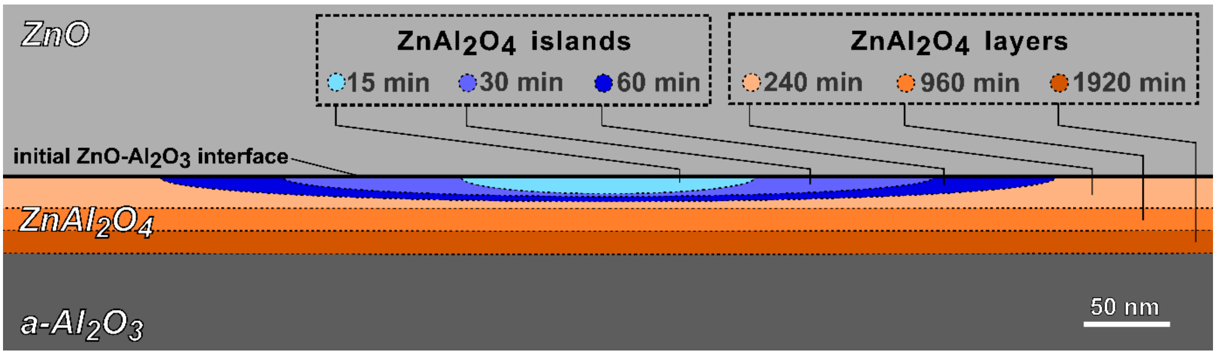

Figure 1: Schematic figure to demonstrate the two-stage growth of the $ZnAl_2O_4$ spinel product phase.

References

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