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Two-Step Reaction in Oxides: Nucleation and Growth Kinetics of $ZnAl_2O_4$ Spinel in ZnO/Al_2O_3 Bilayers

Zoltan Erdélyi[1]*, János J. Tomán[1], Gergő Vecsei[1], Peter Petrik[2,3], Csaba Cserháti[1]

[1] Department of Solid State Physics, Faculty of Sciences and Technology, University of Debrecen, P.O. Box 400, H- 4002, Debrecen, Hungary
[2]HUN-REN Centre for Energy Research, Konkoly-Thege út 29-33, Budapest, H-1121, Hungary
[3]Department of Electrical Engineering, Institute of Physics, Faculty of Science and Technology, University of Debrecen, Bem tér 18, Debrecen, 4026, Hungary
*Presenting author: zoltan.erdelyi@science.unideb.hu

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This work summarizes our recent findings on the nucleation and growth kinetics of $ZnAl_2O_4$ spinel in crystalline ZnO–amorphous Al_2O_3 bilayers prepared by ALD, highlighting the two-step reaction pathway identified in Ref. [1].

Spinel materials, with the formula AB_2O_4, where A is divalent and B trivalent, are of interest for their optical, electronic, and catalytic properties. Zinc-aluminate ($ZnAl_2O_4$ or gahnite) is noted for its optical and catalytic features, with diverse applications. [2–4] It acts as a catalyst for NOx reduction by hydrocarbons, degrades toxic compounds like toluene, and catalyzes CO hydrogenation to methanol/dimethyl ether. Its luminescence spectrum varies with thermal history, making it a potential sensor. With doping, its photoluminescence color is adjustable for phosphor use. Its nonlinear optical properties suggest it could be an optical limiter. It's also suitable as an antireflective coating to enhance silicon solar cells' efficiency.

$ZnAl_2O_4$'s diverse production methods, including sol-gel, hydrothermal, solid-gas, molten salts, and solid-state reactions, enhance its industrial applicability by optimizing costs. Our research focuses on the solid-state reaction between ZnO and Al_2O_3. Limited studies exist on the reaction kinetics in this binary system. An earlier study identified linear phase growth between crystalline layers, suggesting an interface-controlled reaction [5].

The solid-state reaction of ZnO and Al_2O_3 to form zinc-aluminate spinel gained attention for producing hollow $ZnAl_2O_4$ or laminated composite nanotubes. [6–8]. This requires multilayered cylindrical structures with crystalline ZnO and amorphous Al_2O_3 layers, typically made using atomic layer deposition (ALD), which uniformly coats cylindrical templates like nanowiresor holes.

Here, we investigate nucleation and growth of $ZnAl_2O_4$ in planar crystalline ZnO – amorphous Al_2O_3 bilayers grown by thermal ALD at 100 °C [1]. ZnO (~163 nm) was deposited from DEZ/H_2O, while amorphous Al_2O_3 (~88 nm) was deposited from TMA/H_2O. (see Fig. 1a)

Lamellae suitable for transmission-mode imaging were prepared using a focused ion beam in a scanning electron microscope (FIB-SEM), and the corresponding transmission-mode images were acquired in the same instrument.

After pretreatment up to 550 °C, no reaction was observed (Fig. 1b). Annealing at 700 °C in air yielded formation of a new crystalline phase confirmed by Grazing incidence X-ray diffraction (GIXRD) as $ZnAl_2O_4$ (Fig. 2), while alumina remained amorphous. The spinel product formed exclusively on the Al_2O_3 side of the interface, consistent with dominant diffusion of Zn/O species from ZnO into Al_2O_3, as also found in ALD-based nanostructures [6–8]. Kirkendall voids at the reaction front (Fig. 1c–d) also indicate strong diffusional asymmetry and vacancy transport [9].

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Fig. 1. Spinel formation sequence in planar crystalline ZnO/amorphous Al_2O_3 bilayer.

Fig. 2. GIXRD patterns after two heat treatments: the black dashed curve shows the sample after pre-treatment, while the red solid curve corresponds to an additional 1920 min anneal at 700 °C. Vertical dashed lines mark the strongest $ZnAl_2O_4$ reflections. [1]

Two growth regimes were identified (Fig. 3):

1. **Pancake-like nucleation and lateral island growth:** After 15–60 min, thin, laterally extended $ZnAl_2O_4$ islands appeared on the alumina side (Fig. 1c–d). Their lateral dimension follows a power-law exponent of ~0.8, whereas vertical thickness follows ~0.28. This behavior aligns with theoretical predictions for 2D growth governed by interfacial and grain-boundary diffusion, with volume diffusion suppressed [9–11].

2. **Coalescence and slow planar thickening**: After ~240 min, islands coalesced to form a continuous $ZnAl_2O_4$ layer (Fig. 1e–f). Further growth was dominated by thickness increase following $t^{0.37}$ scaling (Fig. 4). This exponent is significantly below the value of 1.0 reported for crystalline/crystalline interfaces [5], and below $t^{0.5}$ expected from volume diffusion, indicating a grain-boundary-diffusion-controlled process accompanied by grain coarsening [10–11].

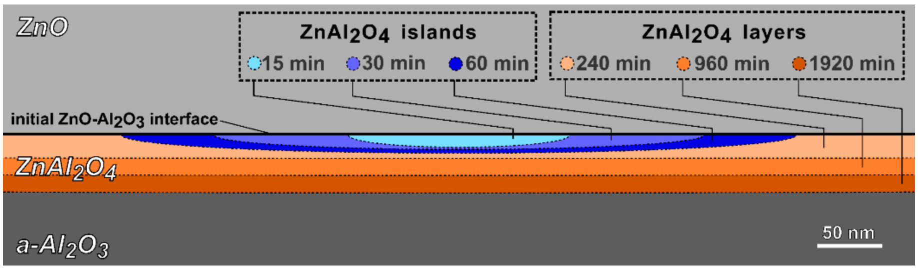

Fig. 3. Schematic illustration of the two-stage formation of the $ZnAl_2O_4$ spinel layer: initially, discrete islands grow and later coalesce into a continuous film. The relative lateral dimensions and thicknesses reflect the experimentally observed scale. [1]

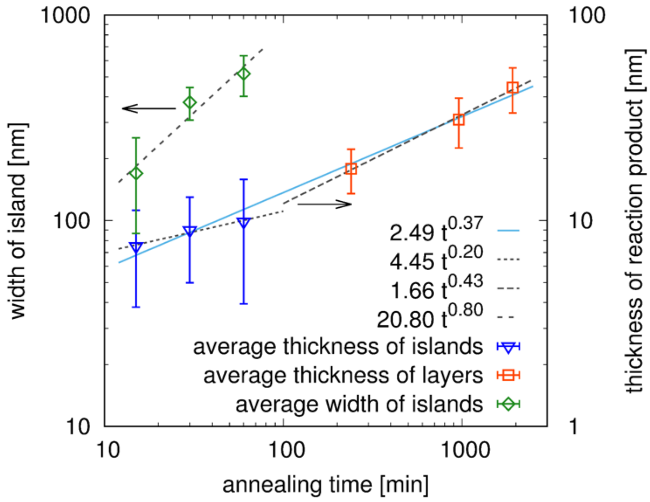

Fig. 4. Evolution of island width and average product-layer thickness over time. The thickness follows a power-law exponent of 0.37, with lower growth for individual islands (0.20) and higher for the continuous layer (0.43). Island width increases with a power-law exponent of 0.80. (Note the two y-axes.) [1]

These results demonstrate that the solid-state reaction is driven by diffusion along grain boundaries and interfaces, rather than the interface reaction control seen between crystalline parent phases. As far as we know, this is the first time this process has been observed between two oxides. We are currently extending this work using non-destructive, in-situ characterization techniques.

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