Scientific Paper

AZO (Al-doped ZnO) thin films fabricated by DALP®: a combinatorial approach

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Introduction

The ability to precisely engineer complex materials with tailored functional properties is a critical enabler for next-generation electronic, optical, and energy devices.[1], [2] Al-doped ZnO (AZO) is a representative transparent conductive oxide that combines high optical transparency with tunable electrical conductivity, making it attractive for applications ranging from transparent electronics and photovoltaics to sensors and optoelectronic systems.[1], [2] However, conventional thin-film deposition techniques face significant limitations in achieving atomic-scale control over composition, uniformity, and microstructure, particularly for ternary and doped oxide systems.[3]

In this work, we demonstrate preliminary results on the fabrication of AZO thin films using ATLANT 3D's Direct Atomic Layer Processing (DALP®) technology. By leveraging digitally defined, spatially resolved atomic layer deposition and automated materials printing, we allow rapid and highly controlled growth of Al_2O_3:ZnO multilayer structures, enabling the exploration of composition–structure relationships in AZO.

Methodology

AZO films were fabricated by printing defined multilayer structures composed of alternating ZnO and Al_2O_3 layers. Horizontal ZnO lines and vertical Al_2O_3 lines of systematically varied thickness were deposited at 200 °C using optimized ALD chemistries. By repeating this programmed sequence over multiple

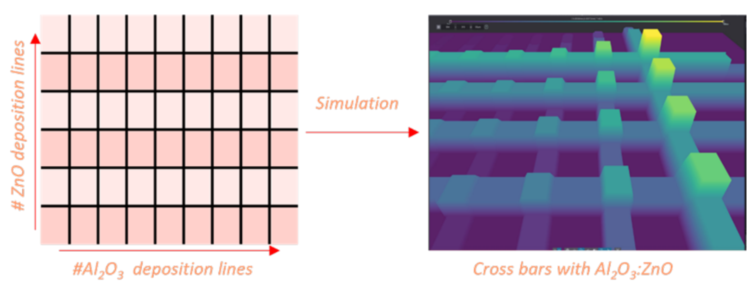

Figure 1. (Left) Al2O3:ZnO deposition patterns (Right) and the corresponding simulated thickness profiles of deposition lines

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supercycles, we created a matrix in which the intersection of orthogonal ZnO and Al_2O_3 lines forms discrete nodes, each corresponding to a unique Zn/Al cycle ratio (Figure 1).

Results

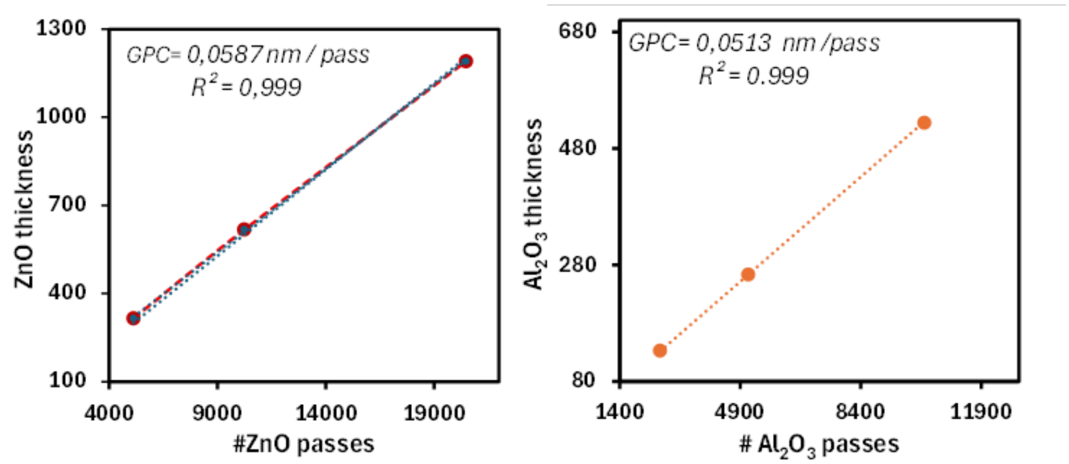

Figure 2 Growth profiles of individual ZnO (left) and Al2O3 (right) across the cross bars.

Figure 2 shows the individual thickness profiles of ZnO (left panel) and Al2O3 (right panel) with the corresponding growth rates. Thickness increases linearly with the number of passes, indicating constant growth-per-cycle (GPC) values of 0.0587 nm/cycle for ZnO and 0.0513 Ånmcycle for Al_2O_3.

The printed design produced a combinatorial matrix of 81 distinct AZO compositions on a single substrate. Depending on individual layer thicknesses, the resulting structures span from alloy regimes, where ultrathin layers intermix at the atomic scale, to nanolaminate regimes, where sharp interfaces dominate material behavior.

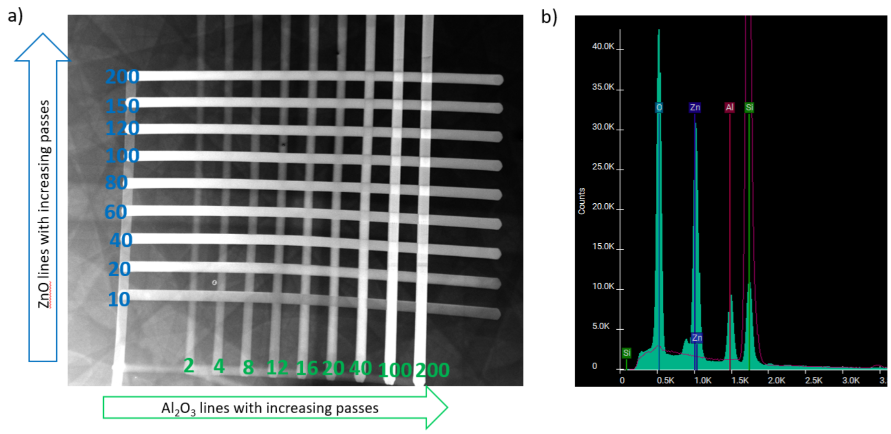

Figure 3: Left: SEM picture of AZO matrix. In green, the number of deposition cycles for each line of Al2O3 is indicated. In blue, the ZnO cycles. Each node has a different Zn/Al ratio, ranging from 0.05 to 100. Right: EDS spectrum confirming Zn and Al signals for one node of the matrix.

SEM imaging confirms the integrity of the printed AZO matrix, as can be seen in Figure 3. Energy-dispersive X-ray spectroscopy (EDS) performed across all nodes reveals a wide compositional window, with Zn/Al atomic ratios spanning from Al-rich (~0.05) to Zn-rich (>40) regimes, which are summarized in Figure 4.

	46.59	45.30	38.10	28.99	26.46	21.90	8.67	2.63	1.32
	39.02	34.22	29.52	24.97	19.15	16.12	6.55	2.03	0.99
	29.11	27.39	25.48	19.94	16.82	14.16	5.72	1.64	0.79
	24.23	23.02	20.02	18.71	16.20	12.84	4.85	1.38	0.66
Zn/Al atm%	20.51	18.26	15.48	14.14	10.60	8.81	3.93	1.07	0.52
	13.17	13.35	11.09	9.45	6.85	5.76	2.42	0.73	0.37
	6.24	5.97	6.53	5.13	4.46	3.69	1.45	0.45	0.23
	1.82	1.97	1.88	1.78	1.88	1.69	0.86	0.26	0.13
	1.16	1.06	1.09	1.07	1.11	1.08	0.59	0.18	0.09

Figure 4: Zn/Al at% for each node according to EDS.

Figure 5 (left) graphically renanopresents the fraction of Al detected by EDS in the AZO cation amount. An asymmetry is present as a higher Zn signal is observed even at equal Zn and Al cycle counts, likely due to differences in growth rate, density, or EDS sensitivity.

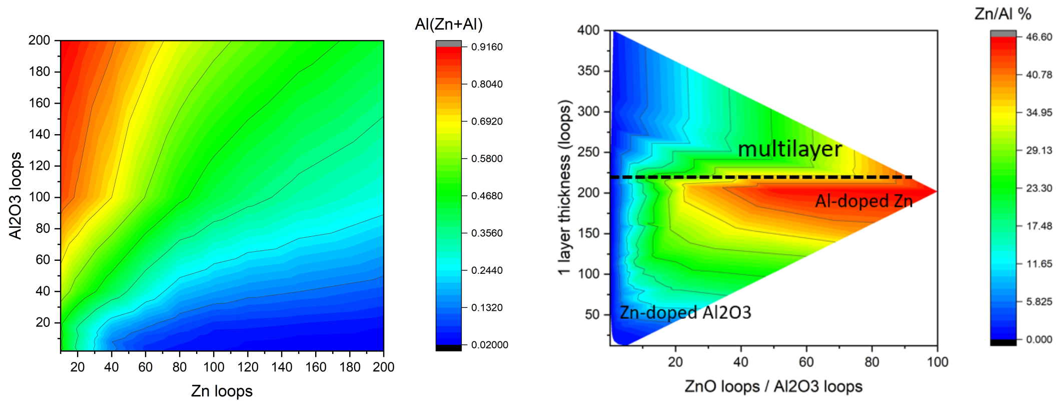

Figure 5: Left: Al/(Zn+Al) amount (in at%) depending on the amount of loops of Zn and Al precursors. Right: Zn/Al atm% ratio at different Zn/Al cycles (or loops) and different thicknesses of 1 supercycle

Figure 5 (right) correlates the Zn/Al atomic ratio with both the nominal Zn/Al cycle ratio and the thickness of a single supercycle layer (Al2O3 + ZnO). Above a critical supercycle layer thickness around 225 nm, the detected Zn content drops sharply, consistent with the formation of thick, unmixed layers, demonstrating an insight not only into chemical composition but also into microstructural evolution within complex oxide stacks.

4. Conclusions & Plans

This study indicates that DALP® can significantly accelerate ternary materials development, enabling the fabrication and screening of 81 distinct compositions and microstructures within a single deposition run. Beyond AZO, this digitally programmable approach is directly extensible to more complex ternary and quaternary oxide systems.

Future work will focus on functional characterization of each node, including electrical conductivity, optical transparency, and electromechanical response, to identify optimal AZO compositions for transparent conductive applications.

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[1] G. Luka *et al.*, “Aluminum-doped zinc oxide films grown by atomic layer deposition for transparent electrode applications,” *J Mater Sci: Mater Electron*, vol. 22, no. 12, pp. 1810–1815, Dec. 2011, doi: 10.1007/s10854-011-0367-0.
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