

Interdiffusion and Internal Stress Effects in Closed Geometry

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Abstract

This study examines how cylindrical geometry influences interdiffusion and stress development during the formation of ZnAl_2O_4 in nanoscale $\text{Pt}/\text{Al}_2\text{O}_3/\text{ZnO}$ structures. Double-layered nanopillars with different diameters were annealed to induce reactive diffusion, and STEM imaging was used to measure intermetallic growth. Smaller pillars exhibited thinner ZnAl_2O_4 layers due to stronger diffusion-inhibiting stresses that cannot relax in closed geometries. At longer times parabolic growth behavior was observed. These results show that curvature-dependent stress fields play a key role in regulating diffusion kinetics at the nanoscale.

1. Introduction

Solid state physics has made huge progress in recent decades, which has now made it possible to study and manipulate the properties of materials at the nanoscale. The understanding of the nanoworld has become quite important nowadays, as humanity is trying to reduce dimensions in technology, communication devices, medicine, etc. However, over a certain size range, the properties of matter, such as mechanical, thermal, optical, and magnetic properties change significantly, so it is important to know the physical laws and properties at the nanoscale. One of the key physical phenomena is diffusion, and the development of nanotechnology makes it essential to study this at small scales.

The first goal of this study was to investigate the thickness of the intermediate phase (zinc aluminate (ZnAl_2O_4)) as a function of annealing times in cylindrical geometry and study the influence of curvature radius on the diffusion process. The second goal was to investigate the kinetics of intermetallic phase (IM) growth. In planar diffusion couples, mechanical stresses - generated during interdiffusion experiments- can relax relatively easily (e.g., dislocation motion). In contrast, in closed geometries such as cylindrical or spherical samples, stress relaxation cannot occur through the same mechanisms. In such systems, both the development and relaxation of diffusion-induced stresses strongly depend on the geometry, particularly the shape and size of the sample.

Consider a cylindrical system composed of components A and B, where heat treatment induces reactive diffusion and leads to the formation of a new intermetallic phase at their interface. Under these conditions, the volume change associated with IM-phase formation generates an inhomogeneous stress field. In cylindrical geometry, this stress distribution manifests as tensile stresses near the outer surface and compressive stresses near the inner region, independent of the stacking order of the components. As the IM layer thickens and the local radius of curvature increases, the influence of the initial layer sequence on these effects gradually diminishes. In the limit of planar geometry, internal stresses can relax, so no inhomogeneous stress field persists, no vacancy-concentration gradient develops, and thus no stress-induced diffusion asymmetry arises [1–2]. In this work, we investigate the effect of diffusion-induced stresses in cylindrical geometry using double-layered nanopillars. Specifically, we present an experimental study of reactive diffusion between ALD-grown crystalline ZnO and amorphous Al_2O_3 layers deposited on highly curved solid Pt cores in a $\text{Pt}/\text{Al}_2\text{O}_3/\text{ZnO}$ configuration (double-layered nanopillars, DLNPs). Because this geometry inherently introduces curvature- or radius-dependent effects, we performed experiments on samples with various nominal core diameters to examine how these factors influence the diffusion behavior.

2. Experimental methods

The primary objective of this study was to investigate diffusion processes in cylindrical geometries. To achieve this, nanoscale platinum columns with diameters of 135 nm, 185 nm, and 285 nm were fabricated on cleaned single-crystal silicon substrates using a FIB/SEM system equipped with a gas injection system (GIS). These Pt column arrays were subsequently coated with oxide layers to examine interdiffusion and the growth kinetics of the intermetallic phase formed during annealing as a function of column diameter. The oxide coatings were deposited by thermal atomic layer deposition (ALD), producing 100 nm of amorphous Al_2O_3 followed by 100 nm of hexagonal ZnO [5–6].

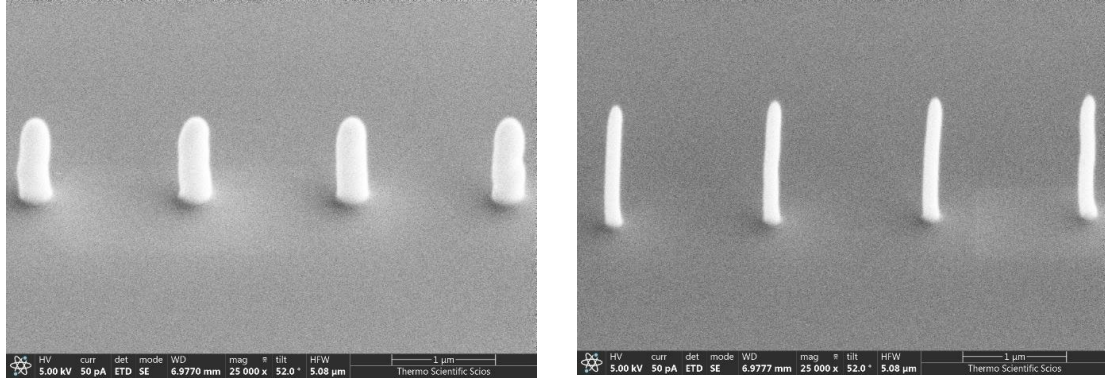


Fig. 1. Platinum columns with diameters of 285 nm and 135 nm

Because blistering of ALD-grown oxide layers is known to cause detachment of the film from the substrate [5–6], a pre-annealing “burn-out” treatment [7] was applied to minimize this effect. During burn-out, the temperature was ramped from room temperature to 230 °C at 10 °C/min, then further increased to 550 °C at 2 °C/min to remove residual gases. Afterward, the coated nanopillars were annealed at 700 °C for various durations (4, 8, 12, and 32 h).

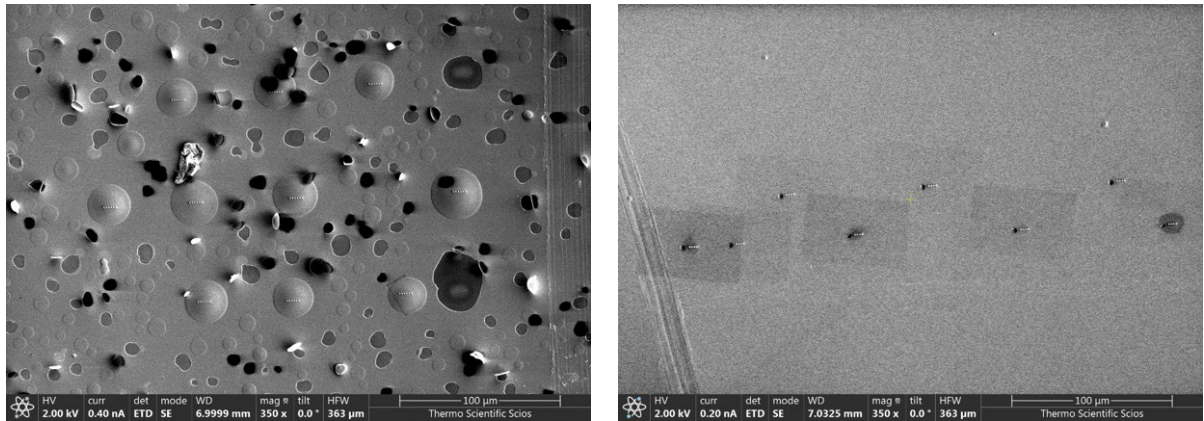


Fig. 2. Sample surface without “burn-out” and with “burn-out”

Plan-view TEM lamellae were prepared using a combined FIB–SEM system, and scanning transmission electron microscopy (STEM) images were acquired to measure the thickness of the newly formed intermetallic (IM) layer. The reaction product formed during diffusion was identified as zinc aluminate (ZnAl_2O_4) [3–4].

3. Results

When comparing column groups subjected to identical heat-treatment times but with different diameters, we observed that the extent of IM-phase growth varied significantly. The smallest-diameter columns (135 nm) produced the thinnest IM layers, whereas the largest columns (285 nm) developed the thickest layers. This behavior can be attributed to the stronger mechanical stresses generated in smaller-diameter pillars, which more effectively hinder diffusion; in such confined geometries, these stresses cannot relax as they do in planar samples. As the pillar diameter increases, the magnitude of stress decreases, reducing its inhibitory effect on diffusion and enabling the formation of a thicker IM phase.

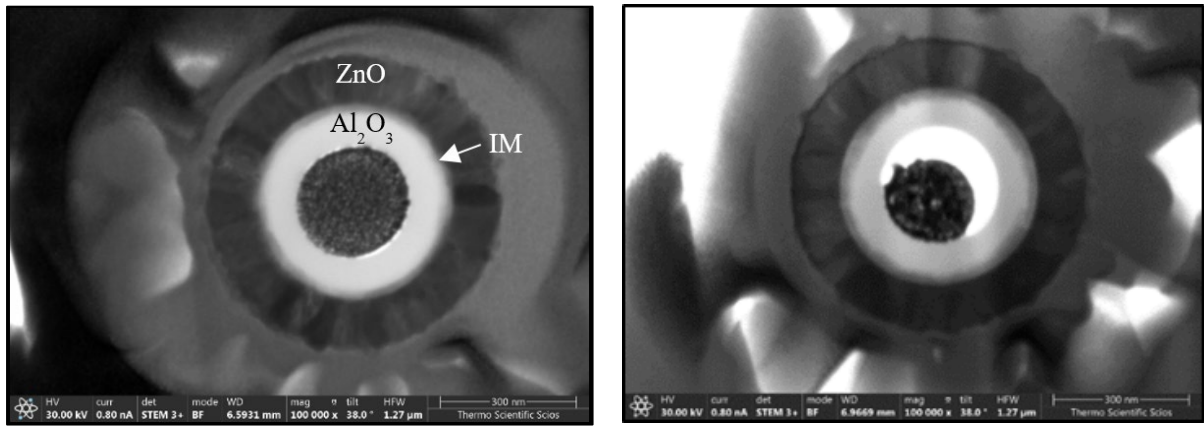


Fig. 3. STEM images of lamellae formed from 285 nm diameter columns annealed for 4 and 32 hours at 700 °C.

By incorporating data from previous work [8], we obtained a more complete understanding of diffusion behavior in closed geometries. The IM-phase growth kinetics were found to change noticeably between 8 and 12 hours of annealing due to detachment of the oxide bilayer from the platinum core. This detachment reduces the accumulated mechanical stress, which in turn accelerates IM-phase growth.

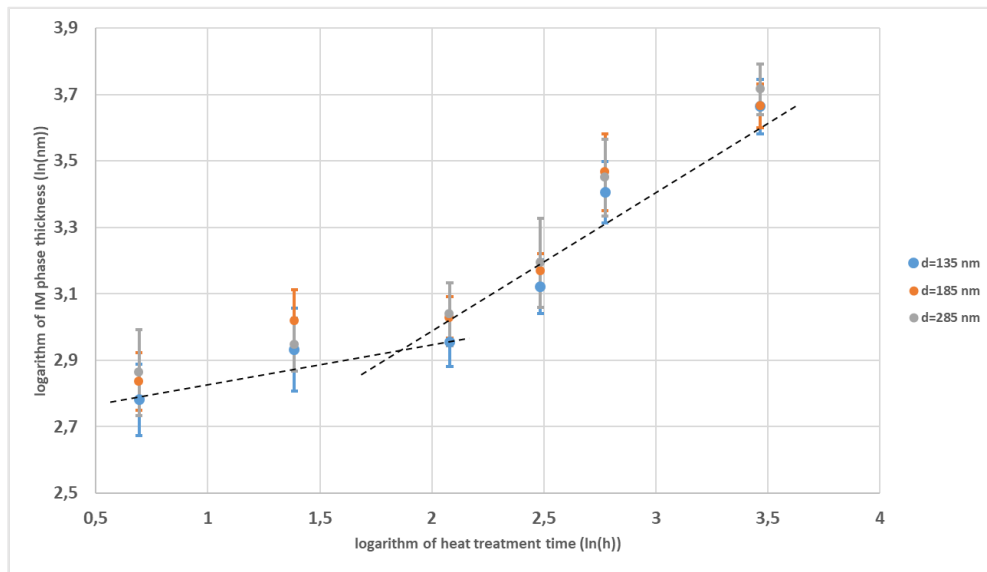


Fig. 4. Curve of IM phase growth.

Our results show that the growth kinetics of the intermediate oxide phase follow a parabolic time dependence at long annealing durations, while at shorter times (< 8 h) the growth is significantly slower. We attribute this behavior to competing vacancy fluxes generated by the stress fields that develop during the reaction–diffusion process.

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