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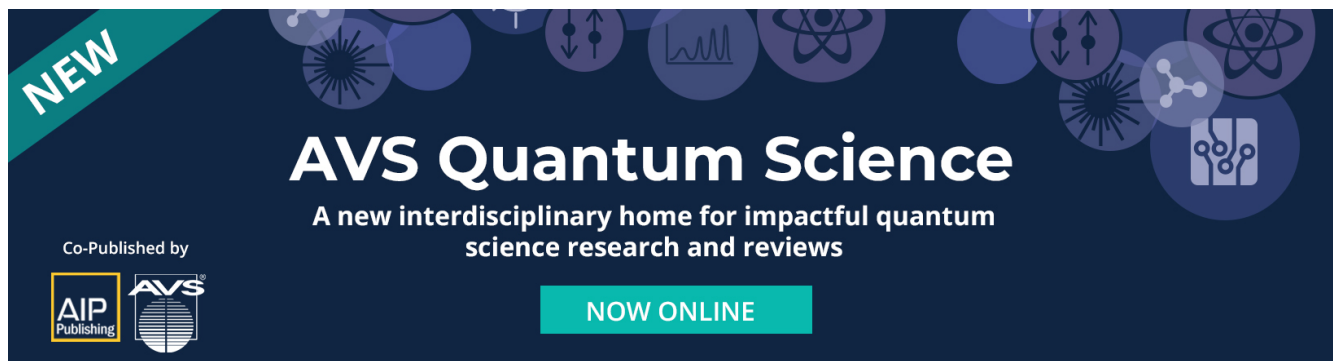
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ABSTRACT

In this communication, fabrication of high aspect ratio $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$ nanotubes is reported and morphological changes at elevated temperatures are investigated. The structures were made by implementing several fabrication methods, such as deep-UV lithography, atomic layer deposition (ALD), and plasma etch methods. During the fabrication, the ALD deposited Al_2O_3 and ZnO conformally passivated the prepared Si-holes template, resulting in the complex coaxial $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$ pillars. By utilizing several scanning and transmission electron microscopy techniques, it is experimentally shown that at elevated temperatures, internal voids form in the nanotube due to diffusion of ZnO into surrounding Al_2O_3 and also ZnAl_2O_4 spinel structure forms. Finally, the porous tubes have been isolated from the surrounding silicon core using a conventional isotropic selective Si plasma etch process. The presented approach opens the opportunity to build complex optical metamaterial compositions, for example, for a new generation of sensors for gas and biomarker detection.

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I. INTRODUCTION

Current progress in optical metamaterials, i.e., artificially engineered materials,¹ has emphasized the significance of developing the fabrication approach that would allow patterning high-quality optical materials at the nanoscale. Far-field imaging with super-resolution,^{2,3} materials with hyperbolic dispersion,^{4–6} and optical cloaking¹ are only a few examples among many different topics that require the realization of highly ordered, periodic metal-dielectric three-dimensional structures with deep subwavelength feature sizes. The topology of metamaterials and metasurfaces typically consists of an array of nanopillars,^{7–9} trenches,^{10,11} and flat multilayers^{12–15} in the simplest forms. The realization of multicoaxial cylindrical structures enables the development of new promising materials with extraordinary and exciting responses to light, which includes hyperbolic¹⁶ and all-dielectric metamaterials.¹⁷ Additionally, such structures are excellent candidates for a new generation of gas and biological sensors, where the response based on the extremely large surface area of active materials can be enhanced further by hyperbolic light

dispersion.^{1,4,7,14,18–20} One method to change the surface area and tune the optical response is to use solid-state interface diffusion and the associated phenomena such as the Kirkendall effect. Different interface reactions have been reported so far, which include ZnO-TiO₂,²¹ ZnO-SiO₂,²² MgO-Al₂O₃,²³ etc. Recent reports pointed out the possible Kirkendall effect in $\text{Al}_2\text{O}_3/\text{ZnO}$ nanolaminates.^{24–26} During annealing, the diffusion of ZnO into Al_2O_3 leads to the formation of crystalline ZnAl_2O_4 spinel. In general, this solid-state reaction is highly sensitive to annealing temperature, annealing time, layer thickness, and other parameters.

This work presents a fabrication approach of freestanding high aspect ratio, hollow coaxial nanotubes, where $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$ coatings exhibit a solid-state diffusion reaction, which transforms ZnO-Al₂O₃ interfaces into porous ZnAl_2O_4 spinel nanocrystals. The Kirkendall effect can be used in the realization of a new class of advanced optical metamaterials, where the porous structure inside the tube can significantly increase the surface area facilitating enhanced sensitivity toward analyzed targets.

II. EXPERIMENT

A. Fabrication details

The nanopillars were fabricated by combining deep-UV lithography, atomic layer deposition (ALD),^{27–29} and advanced deep reactive ion etching (DRIE) techniques.³⁰ A similar approach has been developed recently for the fabrication of high aspect ratio Al-doped ZnO (AZO) pillars,⁹ deep trenches made of Al₂O₃, TiO₂,³¹ TiN,¹⁸ and ZnO.²⁰ The method is based on ALD deposition on high aspect ratio silicon structures (mold) with subsequent selective removal of the silicon template, leaving a negative replica of the template structure in the functional material.

ALD is the only technique that can produce such coatings, all other known methods such as pulsed laser deposition, CVD, or sputtering suffer from poor step coverage and nonuniformity.²⁸ The use of ALD in combination with a sacrificial silicon mold is a novel method to create high aspect ratio metal oxide structures. Figure 1 shows the fabrication steps in the pillars patterning. Starting from the substrate deep-UV lithography and DRIE template preparation [Figs. 1(a)–1(c)], the fabrication continues with ALD deposition, top layer Ar⁺ ion sputtering, and annealing [Figs. 1(d)–1(f)]. The last step is silicon template removal, which was done by an isotropic SF₆ plasma reactive ion etching (RIE) [Fig. 1(g)]. The success of this procedure is heavily dependent on the ability to etch silicon selectively, without affecting the ALD

coatings. It is noteworthy that no distortion of the pillars was observed after template removal in the last step.

1. Si hole-array template preparation

Homemade silicon-on-insulator (SOI) wafers [Fig. 1(a)] were used for the entire fabrication procedure. First, 150 mm (100) Si wafers were selected, and the wafers were RCA cleaned and later oxidized to achieve 200 nm thick SiO₂ in a conventional quartz tube furnace (from Tempres) using a dry oxidation process based on O₂ at 1100 °C. Afterward, 2 μm polycrystalline silicon was deposited on the SiO₂ surface using a low vapor chemical vapor deposition (LPCVD) technique based on SiH₄, which was carried out at 560 °C (furnace from Tempres). Surface roughness was characterized by atomic force microscopy, which revealed that surface roughness is below 1 nm, validating the use of the SOI wafers as an Si template.

A square lattice of holes [Fig. 1(b)] with a diameter of 300 nm and a lattice constant of 400 nm was patterned using deep-UV lithography on a square chip (1 × 1 cm²) of SOI wafer. The procedure consists of a bottom antireflective coating (BARC), photoresist coating, exposure, postbake, and development. To minimize interference effects and promote adhesion, the substrate surface was coated (Süss MicroTec Gamma 2M spin coater) with a 65 nm thick BARC coating (DUV42S-6, Brewer Science, USA) followed by a

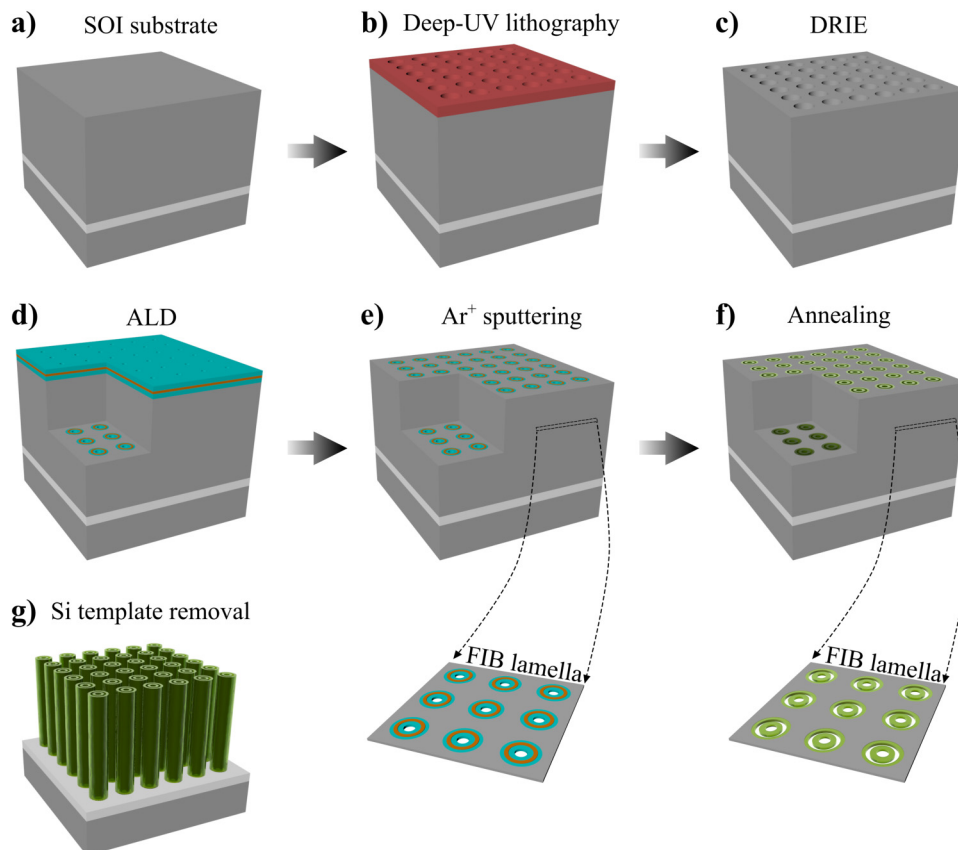


FIG. 1. Fabrication flow. (a) SOI substrates. (b) Deep-UV lithography. (c) Square lattice holes arrays in the silicon substrate as a template prepared by DRIE. (d) Deposition of Al₂O₃/ZnO/Al₂O₃ using ALD. (e) Sputtering of ALD deposited cap layers. (f) Annealing of the structure at 800 °C. (g) Isolation of pillars by etching of the silicon template.

TABLE I. DRIE parameters for template fabrication.

		Passivation (1.5 s)	Etching (2.75 s)
Process gas flow (sccm)	C ₄ F ₈	50	20
	SF ₆	—	60
	O ₂	—	5
Powers (W)	Coil	600	400
	Platen	—	40

bake-out at 175 °C for 60 s. Then, a positive photoresist (KRF M230Y, JSR Micro, NV) was spin-coated to a thickness of 360 nm and baked at 130 °C for 90 s. Next, the SOI wafer with resist coatings was exposed (an exposure dose of 860 J/m²) on field sizes of 1 × 1 cm² (Canon FPA-3000 EX4 DUV stepper). The last lithography step was 90 s postexposure bake at 130 °C followed by developing in 2.38% tetramethylammonium hydroxide solution for 90 s (Süss MicroTec Gamma 2M developer).

DRIE etching (DRIE Pegasus from SPTS) was completed in a switched Bosch process consisting of cyclic steps of etching and passivation [Fig. 1(c)]. During etching, the wafer chuck was held constantly at 0 °C, and the process pressure was fixed at 10 mTorr. Three main steps were implemented for the Si template fabrication: etching of the BARC layer, high anisotropic silicon etching for template preparation (Table I summarizes the Bosch parameters), and remaining resist plasma ashing. The BARC etch proceeds for 45 s using 40 sccm O₂ plasma with coil and platen powers of 400 and 20 W, respectively. In the following Bosch process, the depth of the holes was controlled by correcting the number of cycles (85 cycles correspond approximately to 2 μm deep holes). The strict control is less important in this case since etching basically stops when reaching the SiO₂ layer in the SOI substrates. The depth of the holes is limited to the LPCVD deposited Si, which is, in this case, 2 μm. For deeper profiles that require a thicker Si top layer, a modification of the Bosch process presented in Table I needs to be made as well. Nowadays, the achievable etch depth is comparable to wafer thickness, as more advanced versions of the Bosch process have been developed.^{32,33} The last phase of template fabrication is the removal of the resist leftovers, which was done using an O₂ plasma for 2 min with the flow of 100 sccm. The coil and platen powers were 800 W and 20 W, respectively. The shape and morphology of the produced Si-holes template structures were carefully inspected by scanning electron microscopy (SEM, Supra 60VP from Zeiss) in the cross-sectional mode by sacrificing some of the prepared structures. The achieved diameter of the holes is indeed very close to 300 nm despite imperfections in the etching procedure. Prior to the next step (ALD deposition), the prepared Si template hole-array structures received an additional O₂/N₂ plasma treatment for approximately 20 min in order to eliminate any possible remaining organic residuals from resist coatings and surroundings.

2. Atomic layer deposition

Next, the holes were filled with Al₂O₃/ZnO/Al₂O₃ layers (thicknesses of 50/25/50 nm, respectively) by ALD [Fig. 1(d)]. The deposition was carried out in a commercial hot-wall ALD system

TABLE II. Recipe for one cycle of Al₂O₃.

Precursor	Carrier gas (N ₂) flow (sccm)	Pulse time (s)	N ₂ purge (s)
TMA	150	0.1	0.5
TMA	150	0.1	20
H ₂ O	200	0.1	0.5
H ₂ O	200	0.1	20

(Picosun R-200) using diethyl zinc (DEZ), trimethylaluminum (TMA), and water as precursors at 200 °C. The ALD technique is the ideal choice for precise thickness control and conformal deposition of high aspect ratio structures. The recipes used in this work are presented in Tables II and III. Prior to deposition on the Si hole template, the deposition rates of Al₂O₃ and ZnO were defined by measuring thicknesses of Al₂O₃ and ZnO coatings on flat substrates with spectroscopic ellipsometry (VASE, J. A. Woolam Co.). The deposition rate for Al₂O₃ and ZnO at 200 °C was found to be 0.09 and 0.15 nm/cycle, respectively, which is in good agreement with the previously reported values.^{27,34}

3. Ion beam etching and annealing

The cap of the ALD layers on top of the structures was removed using Ar⁺ ion milling (Ionfab 300 Plus from Oxford Instrument), thereby exposing the silicon matrix between deposited pillars [Fig. 1(e)]. The etching process of ZnO and Al₂O₃ was tuned to approximately 16 and 3.5 nm/min, respectively, which guaranteed well-controlled top layer sputtering. Prepared samples were annealed (furnace PEO-604 from ATV Technology) at 800 °C for 12 h in an N₂ environment at atmospheric pressure in order to induce diffusion [Fig. 1(f)]. SEM images [Figs. 2(a) and 2(b)] reveal surface morphology before and after the annealing from which it is clearly seen [inset in Fig. 3(b)] that ZnO migrated into Al₂O₃ areas resulting in the formation of large voids.

4. Focus ion beam lamella extraction

In order to study structural evolution inside the pillars in detail by transmission electron microscopy (TEM), it was necessary to prepare thin lamellae of the pillars cross section. This was carried out using an *in situ* lift out by focus ion beam (FIB) in an SEM (FEI Helios NanoLab 600 Dual Beam system). To study the evolution, two electron transparent lamellae before and after annealing,

TABLE III. Recipe for one cycle of ZnO.

Precursor	Carrier gas (N ₂) flow (sccm)	Pulse time (s)	N ₂ Purge (s)
DEZ	150	0.1	0.5
DEZ	150	0.1	20
H ₂ O	200	0.1	0.5
H ₂ O	200	0.1	20

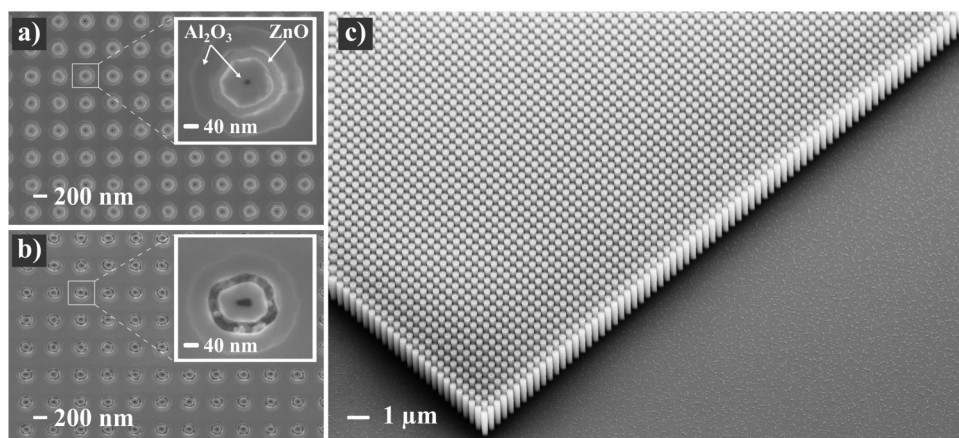


FIG. 2. Fabricated coaxial pillars. (a) Surface directly after ion beam etching. The inset shows the clear boundary between ALD deposited Al_2O_3 and ZnO . (b) Sample surface after annealing at 800°C . The inset shows the magnified image illustrating ZnO migration toward Al_2O_3 . (c) Bird's-eye-view SEM image of isolated tubes standing on Si/SiO_2 platform.

respectively, were extracted in the cross-sectional view [Figs. 1(e) and 1(f)] from the bulk sample, transferred, and attached to a conventional omniprobe TEM grid. Afterward, the samples were additionally thinned to meet high-resolution TEM investigations. SEM images of both high-quality samples are presented in Fig. 3.

5. Isolation of pillars by selective template back etch

The last step in tubes fabrication was silicon back etch between structures. This was done by RIE using conventional equipment (RIE, from SPTS) with SF_6 process gas [Fig. 1(g)], where the flow was kept constant at 35 sccm at a substrate temperature of 20°C . The coil power and process pressure were 30 W and 80 mTorr, respectively. This process proceeds with extreme selectivity toward the deposited ALD layer without any observable damage brought on the coaxial structure. It takes around 3 min to remove the Si core entirely. This etch time is not critical since the process basically stops at the 200 nm thin SiO_2 interlayer of the SOI substrate. Further details regarding the sustainability of the structures in SF_6 plasma environment are given elsewhere,⁹ where the fabrication of Al-doped ZnO nanotubes with 20 nm thick walls is described and provided detailed TEM images of side walls. The result of freestanding annealed tubes on the Si/SiO_2 surface is presented in Fig. 2(c), where the bird's-eye-view SEM image shows a well-preserved corner of the tube arrays.

B. Characterization details

The fabricated isolated coaxial tubes were thoroughly inspected using SEM. Figure 2(a) shows SEM images of the fabricated structure at the intermediate stage shown in Fig. 1(e). The top layer of $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$ has been sputtered away, revealing a silicon matrix between coaxial nanotubes. After annealing at 800°C for 12 h, the morphology of the nanotubes was changed [Fig. 2(b)]. Next, by applying reactive ion etching based on an SF_6 continuous plasma etch, the Si core was removed, thus leaving porous freestanding coaxial structures in a periodic pattern on Si/SiO_2 platform [Fig. 2(c)].

Microstructural evolution inside the tubes was studied using several electron microscopy characterization techniques. The methods that have been applied for sample investigation inside a TEM

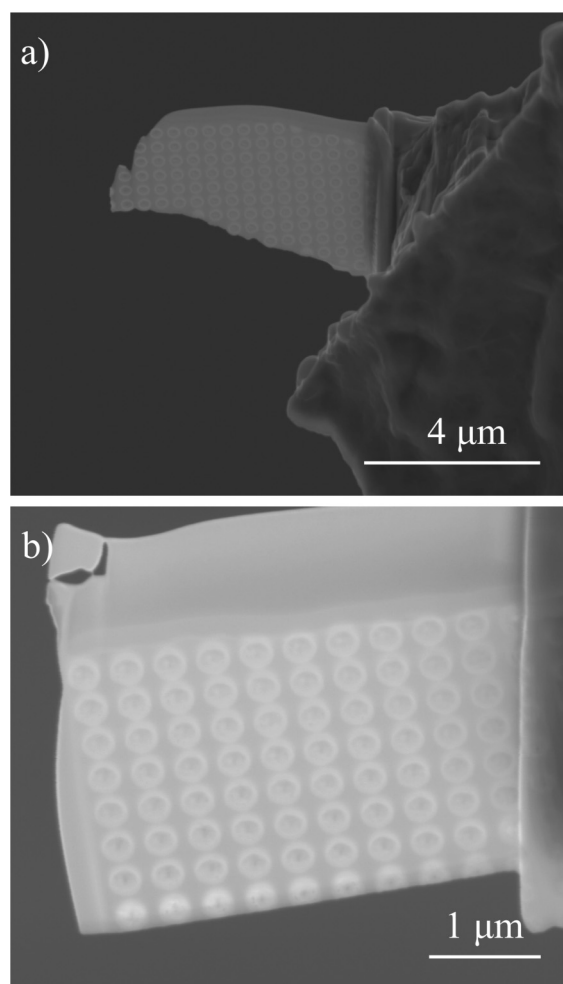


FIG. 3. FIB lamella extracted from the surfaces and attached to the TEM grid. (a) From sample before annealing. (b) From sample after annealing.

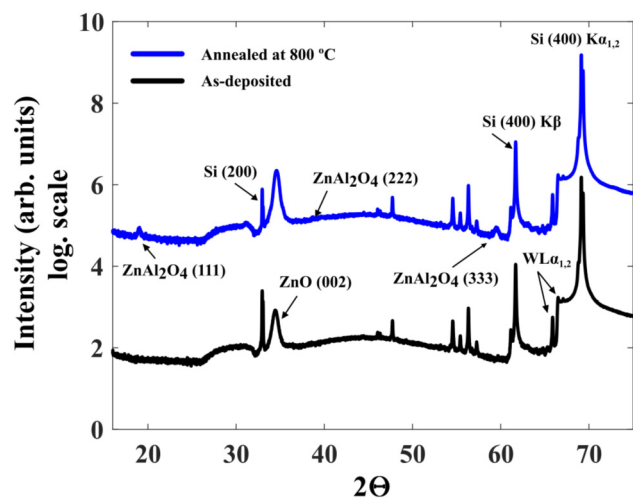


FIG. 4. XRD profiles of the flat films containing $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$ layers deposited on Si substrates with thicknesses 50, 25, and 50 nm, respectively, before and after annealing. The scan of the sample after annealing indicates the formation of a ZnAl_2O_4 spinel phase as well as a shrinkage of the ZnO crystal lattice in the c-axis direction as a result of heat treatment.

instrument (FEI, Titan 80-300ST, 120 keV) include high-resolution transmission electron microscopy (HRTEM) and high angular annular dark-field and annular dark-field scanning transmission electron microscopy, abbreviated as HAADF-STEM and ADF-STEM, respectively. Elemental mapping was performed with energy-dispersive x-ray spectroscopy (EDS) analysis (x-ray spectrometer from

Oxford Instrument integrated with the TEM equipment). Selected area electron diffraction (SAED) was carried out on tube samples, and conventional x-ray diffraction (XRD) was performed to study the crystal orientations of the ALD deposited materials on planar Si (100) surfaces in the Bragg-Brentano geometry by a Rigaku SmartLab 3 kW diffractometer equipped with Cu $\text{K}\alpha$ x-ray source. The XRD profiles were scanned in steps of $0.002^\circ 2\theta/\text{s}$.

III. RESULTS AND DISCUSSION

A. XRD analysis of planar coatings

To investigate crystallinity of the samples before and after annealing, the ALD coatings were deposited not only on the Si template [Fig. 1(c)] but also on flat silicon (100) surfaces. These samples have been annealed simultaneously with the tube structures. Figure 4 shows the XRD pattern of flat films before and after heat treatment. The annealed samples show the presence of (111) family peaks of ZnAl_2O_4 , indicating the formation of the cubic spinel structure.^{35,36} Furthermore, the characteristic peak of the ZnO (002) reflection shifts to a higher 2θ angle, which indicates a reduction of the ZnO lattice constant. This can be attributed to the replacement of the larger Zn^{2+} ions by the smaller Al^{3+} ions in the lattice.^{9,37}

B. STEM analysis

Figures 5(a)–5(c) show the initial nanotubes (ca. 300 nm diameter) surrounded by crystalline Si before annealing. The single pillars consist of a polycrystalline ZnO layer between amorphous Al_2O_3 oxide layers, with an empty core [Fig. 5(a)]. A higher magnification image [Fig. 5(b)] reveals that the ZnO layer is assembled from crystals of approximately $25 \times 10 \text{ nm}^2$ oriented in the radial

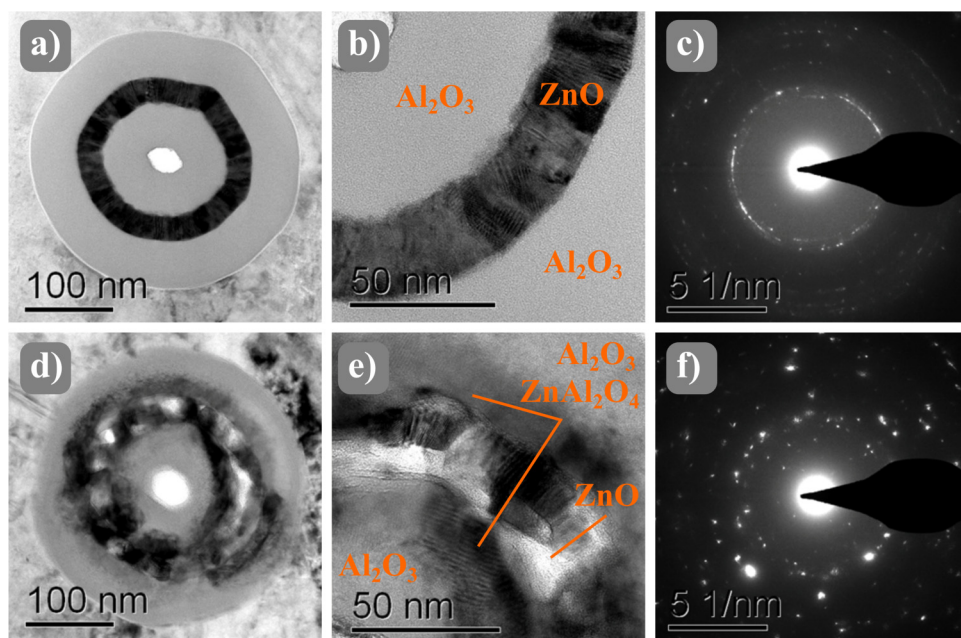


FIG. 5. (a) TEM image of cross-sectional lamella sample showing one individual tube. (b) The corresponding HRTEM image of ZnO interlayer. (c) SAED pattern. (d)–(f) present the corresponding results for the annealed sample.

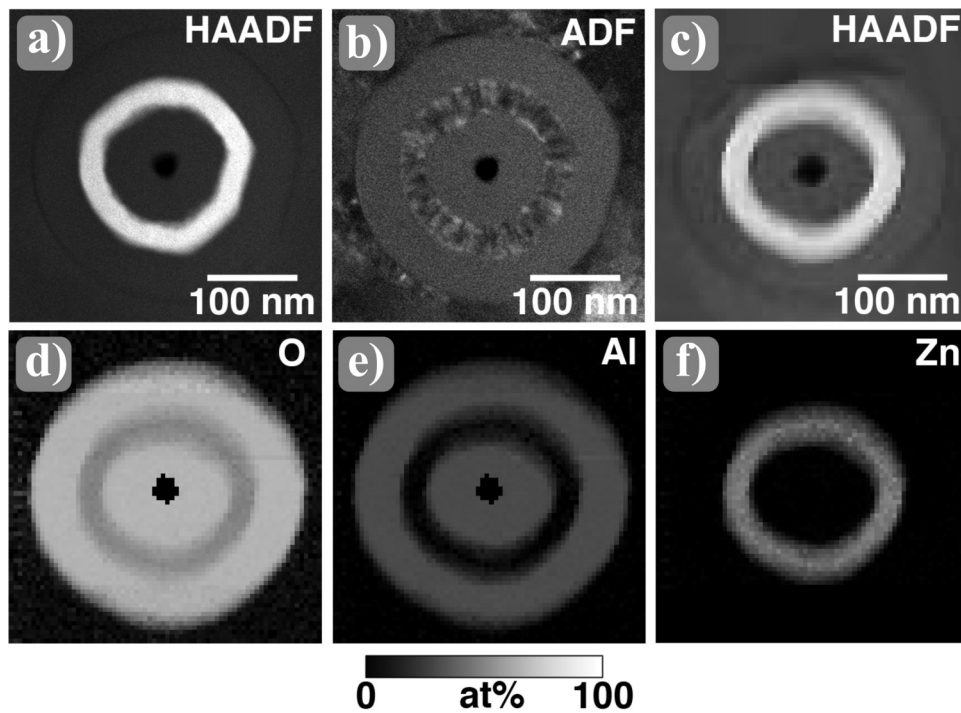


FIG. 6. STEM HAADF, ADF, and EDS quantitative maps of the initial sample. (a) HAADF image. (b) ADF image. (c) STEM HAADF image of the measured area and (d)–(f) oxygen, aluminum, and zinc elemental maps.

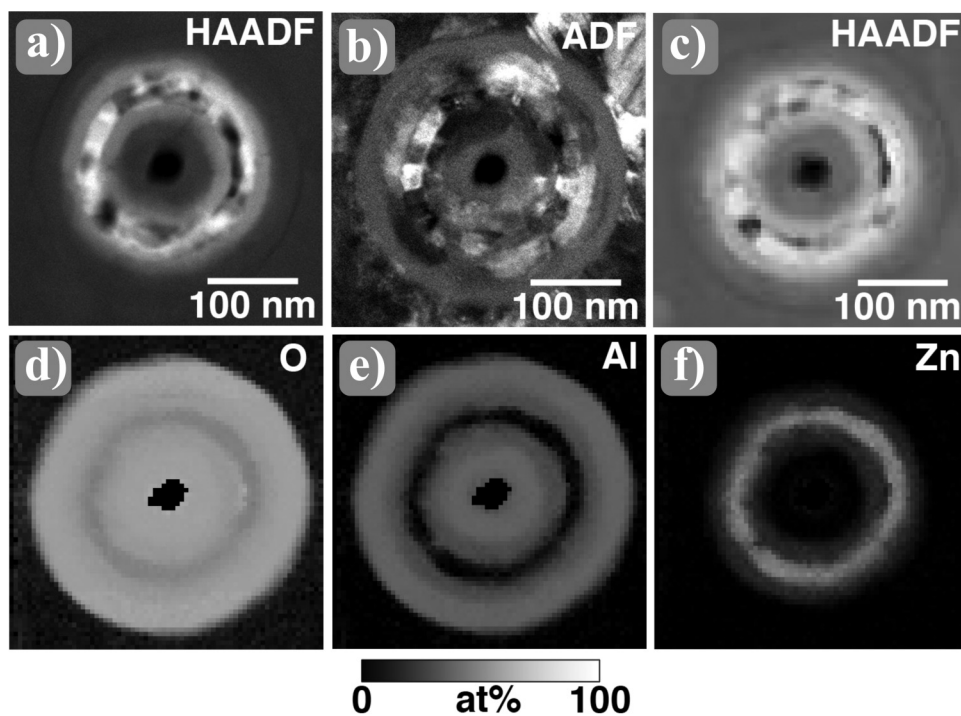


FIG. 7. STEM HAADF, ADF, and EDS quantitative maps of the annealed sample. (a) HAADF image. (b) ADF image. (c) STEM HAADF image of the measured area and (d)–(f) oxygen, aluminum, and zinc elemental maps.

direction. SAED from a single pillar confirms that ZnO is hexagonal, which is consistent with the XRD result.

Annealed pillars surrounded by crystalline Si exhibit different morphology and microstructure as summarized in Figs. 5(d)–5(f). The single nanowires consist of a porous ZnO layer sandwiched by (Zn-diffused) crystalline ZnAl_2O_4 layers next onto an Al_2O_3 layer [Fig. 5(d)]. The magnified TEM image [Fig. 5(e)] shows the structural evolution as a result of the annealing. The presence of voids in the ZnO region indicates diffusion of ZnO toward the initially amorphous Al_2O_3 layers. Diffraction patterns in SAED [Figs. 5(c) and 5(f)] reveal a big difference between the initial and annealed tubes. The continuous rings of the initial sample, which represent polycrystalline ZnO, are transformed into individual spots pattern, which can be interpreted as an increase in grain sizes of remaining ZnO and transformation to a new crystalline ZnAl_2O_4 spinel oxide.

For acquiring further elemental and microstructural information, STEM-HAADF (inner detector diameter, 87.7 mrad), STEM-ADF (inner and outer detector diameter, 9.7 and 41.7 mrad), and STEM-EDS were used. The HAADF and ADF were acquired from the same pillar at the same time. In the HAADF mode, the image contrast is sensitive to the mean atomic number and the specimen thickness so that higher mean atomic numbers or thicker regions appear brighter. In fact, the brightest contrast in the initial sample [Fig. 6(a)] corresponds to ZnO, which has a heavier element than Al_2O_3 does. In the annealed sample [Fig. 7(a)], the ZnO layer has considerable contrast variation, originating from the presence of voids. The additional two layers of ZnAl_2O_4 that are located on both sides of the ZnO layer appear more clearly in Fig. 7(a). The ZnAl_2O_4 layers have continuous circular shapes with approximately 20 nm in height and lose image contrast gradually in the outer direction from the ZnO layer. This gradual change and vague phase boundary are also observed in the TEM image [Fig. 5(e)].

The ADF signal [Figs. 6(b) and 7(b)] has a more predominant contribution of diffracted electron beams over specimen thickness or composition. Therefore, the domainlike contrast suggests a polycrystalline structure, where each domain has the same diffracting condition. A uniform contrast would indicate either single crystalline or an amorphous phase. This supports the previous conclusion that the inner and outer shells of Al_2O_3 coatings remain amorphous after annealing, which was also supported by the conventional TEM [Fig. 5(e)]. Nevertheless, apparently, some crystals are extended to the Al_2O_3 region since the ZnAl_2O_4 thickness is almost constant and locally ZnO is missing [Fig. 7(b)]. This means that the diffusion may occur at an earlier stage due to gradual warm-up of the annealing furnace and low temperature (below 800 °C) or that a quick reaction with a narrow temperature window may take place.

C. STEM-EDS investigations

For STEM-EDS analysis, the specimens were tilted to 20° about the horizontal axis for optimal geometry of the spectroscopy and the measured area presented in the tilted HAADF images [Figs. 6(c) and 7(c)]. The quantitative maps of the initial and annealed specimens are presented in Figs. 6(d)–6(f) and 7(d)–7(f), respectively. The annealed tubes show more a homogeneous oxygen distribution and apparent Zn and Al concentration variations (at. %) from the ZnO into the inner and outer directions due to diffusion. In addition to

elemental maps presented in Figs. 6 and 7, the carbon signal was detected, which is conventional microscopy contamination and FIB lamella preparation.

Figure 8 shows the EDS quantitative line profile, which gives additional information on chemical distribution and diffusion. The annealing also affects the amorphous outer regions of alumina. Although the majority of the coatings appear to be preserved as the amorphous phase, the composition (Al at. %/O at. % = 40/60) is different from that in the initial tubes (Al at. %/O at. % = 30/70). This outcome is quite interesting since the ALD reaction based on water-TMA thermal interaction is expected to provide a stoichiometric Al_2O_3 film. Nevertheless, such high initial content of oxygen in the deposited alumina can be explained by the absorption of water inside the Si template during the ALD process. Postannealing removes this water, leaving the alumina with the predicted ratio (2:3). Moreover, Fig. 8(b) shows characteristic shoulders on Zn, Al,

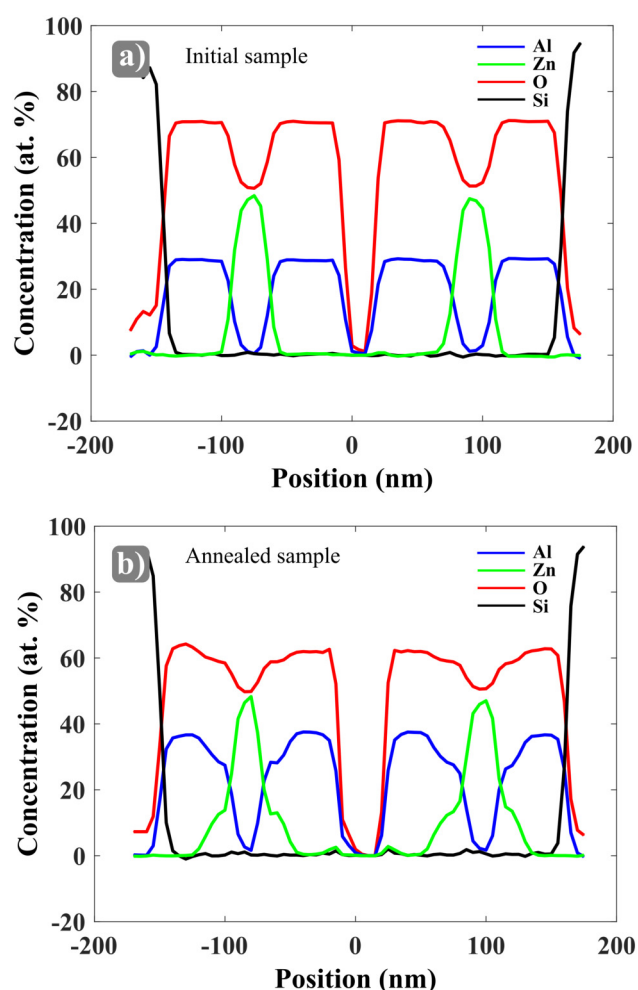


FIG. 8. EDS quantitative line profiles. (a) Initial sample and (b) annealed sample.

and O elemental line profiles of the annealed sample, which is a consequence of the diffusion process (the Kirkendall effect). Composition stoichiometry extracted from Fig. 8(b) highly suggests the formation of ZnAl_2O_4 spinel. The thickness of the spinel layer can be estimated from the HAADF image of the annealed sample [Fig. 7(a)], and the chemical composition is provided by EDS [Fig. 8(b)]. Despite the excess of initial Al_2O_3 and ZnO and prolonged annealing, it does not exceed 20 nm. This limitation needs to be addressed in future fabrication designs.

IV. SUMMARY AND CONCLUSIONS

To summarize, high aspect ratio arrays of isolated nanotubes were fabricated by combining deep-UV lithography, ALD, and DRIE techniques. The diffusion of ZnO into amorphous alumina was studied by various TEM techniques using FIB extracted lamellae. The work demonstrates a new and generic fabrication method to create and thermally manipulate the inner composition of all-dielectric multilayered nanotubes. Realized annealed structures clearly show the diffusion of ZnO into surrounding amorphous alumina and partial transformation to the crystalline ZnAl_2O_4 spinel structure. It demonstrates that a complex material multilayer can undergo multidirectional diffusion and formation of the prescribed periodic spinel. The total thickness of the ZnAl_2O_4 region is approximately 20 nm.

As for the outlook, further work is needed for understanding the details of the diffusion kinetics. Improved annealing conditions and posttreatment methods need to be developed if fully separated, continuous, and pin-hole free multilayers are required. Additionally, in the ALD deposition step, other precursors such as O_3 need to be considered to eliminate the presence of absorbed water in the structures and reduce analysis complexity. Further studies on the applications of these transformed nanotubes are in progress.

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REFERENCES

- ¹W. Cai and V. Shalae, *Optical Metamaterials: Fundamentals and Applications* (Springer, New York, NY, 2010).
- ²D. Lu and Z. Liu, *Nat. Commun.* **3**, 1205 (2012).
- ³T. Repän, A. V. Lavrinenko, and S. V. Zhukovsky, *Opt. Express* **23**, 25350 (2015).
- ⁴A. Poddubny, I. Iorsh, P. Belov, and Y. Kivshar, *Nat. Photonics* **8**, 78 (2013).
- ⁵L. Ferrari, C. Wu, D. Lepage, X. Zhang, and Z. Liu, *Prog. Quantum Electron.* **40**, 1 (2015).
- ⁶O. Takayama and A. V. Lavrinenko, *J. Opt. Soc. Am. B* **36**, F38 (2019).

- ⁷A. V. Kabashin, P. Evans, S. Pastkovsky, W. Hendren, G. A. Wurtz, R. Atkinson, R. Pollard, V. A. Podolskiy, and A. V. Zayats, *Nat. Mater.* **8**, 867 (2009).
- ⁸C. T. Riley, J. S. T. Smalley, K. W. Post, D. N. Basov, Y. Fainman, D. Wang, Z. Liu, and D. J. Sirbully, *Small* **12**, 892 (2016).
- ⁹E. Shkondin, O. Takayama, M. E. Aryae Panah, P. Liu, P. V. Larsen, M. D. Mar, F. Jensen, and A. V. Lavrinenko, *Opt. Mater. Express* **7**, 1606 (2017).
- ¹⁰O. Takayama *et al.*, *ACS Photonics* **4**, 2899 (2017).
- ¹¹A. A. High, R. C. Devlin, A. Dibos, M. Polking, D. S. Wild, J. Perczel, N. P. De Leon, M. D. Lukin, and H. Park, *Nature* **522**, 192 (2015).
- ¹²G. V. Naik, B. Saha, J. Liu, S. M. Saber, E. A. Stach, J. M. K. Irudayaraj, T. D. Sands, V. M. Shalae, and A. Boltasseva, *Proc. Natl. Acad. Sci. U.S.A.* **111**, 7546 (2014).
- ¹³S. V. Zhukovsky, A. Andryeuskii, O. Takayama, E. Shkondin, R. Malureanu, F. Jensen, and A. V. Lavrinenko, *Phys. Rev. Lett.* **115**, 177402 (2015).
- ¹⁴K. V. Sreekanth, Y. Alapan, M. El Kabbash, E. Ilker, M. Hinczewski, U. A. Gurkan, A. De Luca, and G. Strangi, *Nat. Mater.* **15**, 621 (2016).
- ¹⁵J. Sukham, O. Takayama, A. V. Lavrinenko, and R. Malureanu, *ACS Appl. Mater. Interfaces* **9**, 25049 (2017).
- ¹⁶K.-H. Kim, Y.-S. No, S. Chang, J.-H. Choi, and H.-G. Park, *Sci. Rep.* **5**, 16027 (2015).
- ¹⁷P. Moitra, Y. Yang, Z. Anderson, I. I. Kravchenko, D. P. Briggs, and J. Valentine, *Nat. Photonics* **7**, 791 (2013).
- ¹⁸E. Shkondin, T. Repän, O. Takayama, and A. V. Lavrinenko, *Opt. Mater. Express* **7**, 4171 (2017).
- ¹⁹M. A. Baqir, A. Farmani, T. Fatima, M. R. Raza, S. F. Shaukat, and A. Mir, *Appl. Opt.* **57**, 9447 (2018).
- ²⁰E. Shkondin, T. Repän, M. E. Aryae Panah, A. V. Lavrinenko, and O. Takayama, *ACS Appl. Nano Mater.* **1**, 1212 (2018).
- ²¹Y. Yang, R. Scholz, H. J. Fan, D. Hesse, U. Gösele, and M. Zacharias, *ACS Nano* **3**, 555 (2009).
- ²²Y. Yang, R. Bin Yang, H. J. Fan, R. Scholz, Z. Huang, A. Berger, Y. Qin, M. Knez, and U. Gösele, *Angew. Chem. Int. Ed.* **49**, 1442 (2010).
- ²³H. Fan, M. Knez, R. Scholz, K. Nielsch, E. Pippel, D. Hesse, U. Gösele, and M. Zacharias, *Nanotechnology* **17**, 5157 (2006).
- ²⁴F. Güder, Y. Yang, S. Goetze, A. Berger, N. Ramgir, D. Hesse, and M. Zacharias, *Small* **6**, 1603 (2010).
- ²⁵F. Güder, Y. Yang, S. Goetze, A. Berger, R. Scholz, D. Hiller, D. Hesse, and M. Zacharias, *Chem. Mater.* **23**, 4445 (2011).
- ²⁶A. A. El Mel, R. Nakamura, and C. Bittencourt, *Beilstein J. Nanotechnol.* **6**, 1348 (2015).
- ²⁷R. L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005).
- ²⁸S. M. George, *Chem. Rev.* **110**, 111 (2010).
- ²⁹V. Cremers, R. L. Puurunen, and J. Dendooven, *Appl. Phys. Rev.* **6**, 021302 (2019).
- ³⁰B. Wu, A. Kumar, and S. Pamorthy, *J. Appl. Phys.* **108**, 051101 (2010).
- ³¹E. Shkondin, O. Takayama, J. M. Lindhard, P. V. Larsen, M. D. Mar, F. Jensen, and A. V. Lavrinenko, *J. Vac. Sci. Technol. A* **34**, 031605 (2016).
- ³²B. Chang, P. Leussink, F. Jensen, J. Hübner, and H. Jansen, *Microelectron. Eng.* **191**, 77 (2018).
- ³³B. Chang, F. Jensen, J. Hübner, and H. Jansen, *J. Micromech. Microeng.* **28**, 105012 (2018).
- ³⁴V. Miikkulainen, M. Leskela, M. Ritala, and R. L. Puurunen, *J. Appl. Phys.* **113**, 021301 (2013).
- ³⁵Q. Hou, F. Meng, and J. Sun, *Nanoscale Res. Lett.* **8**, 144 (2013).
- ³⁶Z. Bi, R. Zhang, X. Wang, S. Gu, B. Shen, Y. Shi, Z. Liu, and Y. Zheng, *J. Am. Ceram. Soc.* **86**, 2059 (2003).
- ³⁷A. Crovetto, T. S. Ottsen, E. Stamate, D. Kjær, J. Schou, and O. Hansen, *J. Phys. D Appl. Phys.* **49**, 295101 (2016).