

Template-based synthesis of AlN hollow nanofibers via plasma-enhanced atomic layer deposition

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ABSTRACT

Aluminum nitride (AlN) hollow nanofibers were synthesized by depositing conformal thin films via plasma-enhanced atomic layer deposition on sacrificial electrospun nylon 66 nanofiber templates having different average fiber diameters. Scanning electron microscopy studies have shown that there is a critical wall thickness-to-inner diameter ratio for these nanostructures to preserve their shapes after the polymeric template has been removed by calcination. Best morphologies were observed for AlN hollow nanofibers prepared by depositing 800 cycles on templates having ~330 nm average fiber diameter. Al 2p high resolution XPS subpeaks located at 73.5 ± 0.2 eV confirmed the presence of AlN for coated and calcinated samples. Transmission electron microscopy (TEM) images indicated uniform wall thicknesses along the fiber axes. Synthesized AlN hollow nanofibers were polycrystalline with a hexagonal crystal structure as determined by high resolution TEM and selected area electron diffraction.

Keywords: aluminum nitride, hollow nanofiber, template-based synthesis, electrospinning, atomic layer deposition

1 INTRODUCTION

Aluminum nitride (AlN) exhibits attractive material properties such as wide and direct band gap of 6.2 eV (hexagonal AlN), small (even negative) electron affinity, piezoelectric response, good dielectric properties, chemical stability, high thermal conductivity, and low thermal expansion. Owing to this unique set of properties, nanostructures of AlN have recently attracted much attention as potential candidates for future applications.

Template-free or template-based approaches may be adopted for the syntheses of tubular AlN nanostructures. Although template-free methods were reported in most cases [1-7], they generally require high temperatures ($> 1000^\circ\text{C}$) and in some cases there exist additional morphologies such as nanoparticles or nanowires in the final product. The most obvious constraint of template-free synthesis is probably the limited control over the properties of resulting structure (e.g. crystal structure, dimensions, etc.). Template-based synthesis, on the other hand, is a straightforward way of producing nanostructures with controlled properties, which in general requires a suitable

deposition method and a sacrificial substrate having the desired geometry. Selected template should be resistant to the conditions at deposition, but also be able to disappear with a simple post-deposition treatment unless it has a function in the final structure. Template-based synthesis of coaxial C-AlN-C composite and epitaxial hexagonal AlN nanotubes at temperatures $> 1000^\circ\text{C}$ have been reported [8,9].

Temperatures used for the synthesis of AlN nanostructures can be lowered considerably by using atomic layer deposition (ALD), a special type of low temperature chemical vapor deposition in which the substrate is exposed to two or more precursors in a sequential manner. Besides being a low temperature process, ALD also offers precise thickness control as well as excellent uniformity and conformality with its self-limiting growth mechanism [10].

Variety of templates increases as the deposition temperature decreases. Polymers are promising materials as sacrificial templates due to their availability and low cost. Polymeric fibers having diameters in the range of few microns to few hundred nanometers can be obtained via electrospinning, a versatile and cost-effective technique in which a polymer solution or melt pumped from syringe is subjected to high voltages [11]. In literature, electrospinning and ALD processes have been combined for synthesizing tubular nanostructures. Peng et al. [12] used an electrospun template for fabricating long and uniform metal-oxide microtubes with precise wall thickness control. In their study, Al_2O_3 was deposited by ALD on polyvinyl alcohol microfibers, which were then selectively removed by calcination. Their approach was followed by others, who synthesized hollow nanofibers (or nanotubes) of various sizes, materials (Al_2O_3 [13], SnO_2 [14], TiO_2 [15-17], ZnO [13,18-20]), and structures (e.g. core-shell nanofibers) using different electrospun polymers (polyvinyl acetate [17-20], polyvinyl alcohol [13], polyacrylonitrile [14], polyvinyl pyrrolidone [15,16]) as templates.

In this study, we report on the template-based synthesis and characterization of AlN hollow nanofibers. The process has three-steps (Figure 1): (i) preparation of the nylon 66 (PA66) nanofiber template by electrospinning, (ii) conformal deposition of AlN on the electrospun polymer template via plasma-enhanced ALD (PEALD), and (iii) removal of the organic template by calcination.

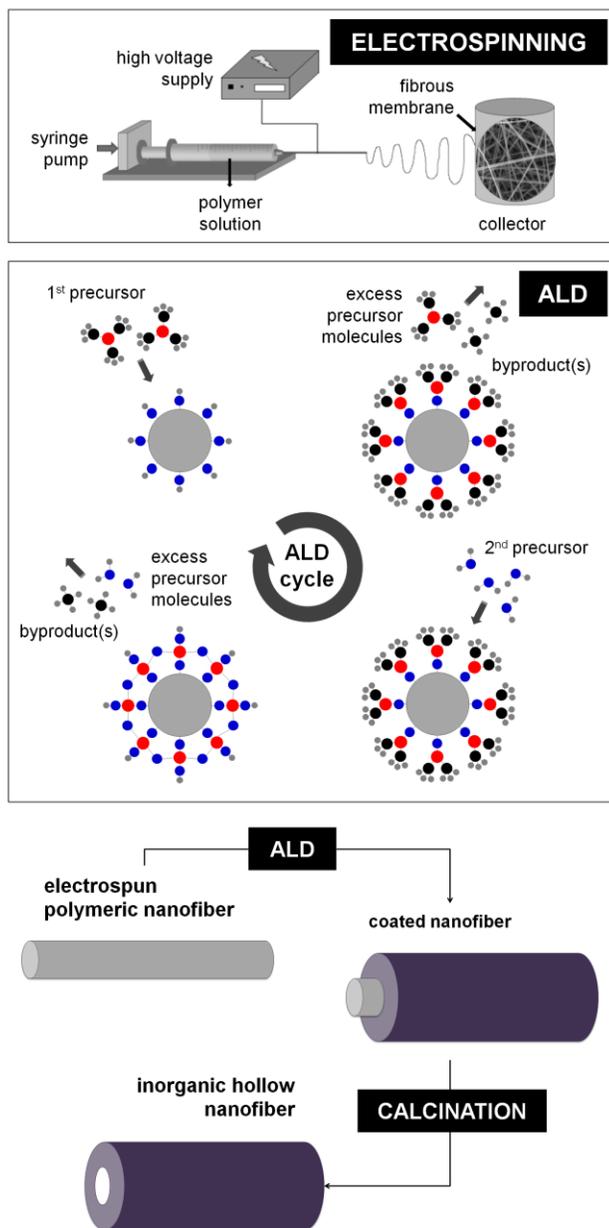


Figure 1: Template-based synthesis of inorganic hollow nanofibers; preparation of the nanofiber template by electrospinning, conformal deposition on electrospun nanofibers via atomic layer deposition, and removal of the organic template by calcination.

2 EXPERIMENTAL DETAILS

PA66 nanofiber templates were prepared by electrospinning of formic acid and hexafluoroisopropanol (HFIP) solutions. Different polymer concentrations and solvent systems were used in order to obtain nanofibers having different diameters (Table 1). For all the polymer solutions studied; feed rate, applied voltage and tip-to-collector distance were 1 ml/h, 15 kV and 10 cm,

respectively. Morphology, uniformity, and dimensions of electrospun nanofibers were analyzed by using scanning electron microscopy (SEM).

Depositions were carried out at 200°C in Fiji F200-LL ALD reactor (Cambridge Nanotech) with a base pressure of 0.25 torr. 400 and 800 cycles of AlN were deposited via PEALD using trimethylaluminum (TMA) and ammonia (NH₃), where one cycle consisted of 0.1 s TMA/10 s Ar purge/40 s NH₃ plasma (50 sccm, 300 W)/10 s Ar purge [21]. Ar was used as the carrier and purge gas. Precursor and plasma carrier gas flow rates were 60 and 200 sccm, respectively. *In-situ* calcination of the AlN-coated nanofibers was carried out at 500°C for 2 h under continuous Ar flow. AlN hollow nanofibers were also prepared by *ex-situ* calcination at air ambient.

Chemical composition and bonding states of the AlN nanostructures were investigated by X-ray photoelectron spectroscopy (XPS) using Thermo Scientific K-Alpha spectrometer with a monochromatized Al K α X-ray source. Electron microscopy and selected area electron diffraction (SAED) studies were carried out by using FEI Quanta 200 FEG scanning electron and FEI Tecnai G2 F30 transmission electron microscopes.

Solvent system	% PA66	Viscosity (PA.s)	Fiber diameter (nm)	Fiber morphology
	(w/v)			
Formic acid	8	0.0493	67 ± 35	bead-free
HFIP	5	0.0413	330 ± 83	bead-free
HFIP	8	0.2300	737 ± 266	bead-free

Table 1: Properties of PA66 solutions and the resulting electrospun nanofibers.

3 RESULTS AND DISCUSSION

400 cycles AlN were deposited on an electrospun template (average fiber diameter ~740 nm) at 200°C by PEALD. Recently, we have reported the deposition rate of AlN at this temperature as 0.86 Å/cycle for planar substrates [21], which corresponds to a ~34 nm thick film for a 400 cycle deposition. As expected, the characteristic self-limiting growth mechanism resulted with highly uniform and conformal AlN layers on electrospun PA66 nanofibers. However, integrity of these conformal layers could not be retained after *ex-situ* calcination at air ambient (Figure 2). Although wall thickness of the resulting inorganic hollow nanofibers could easily be controlled by the number of ALD cycles, there seems to be a critical wall thickness-to-inner diameter ratio for ALD-grown layers to preserve their shapes after the sacrificial templates have been removed by calcination.

800 cycles (~69 nm) AlN were deposited on a polymeric template having ~740 nm average fiber diameter, followed by an *in-situ* heat treatment under continuous Ar flow. Resulting structures were hollow, although they have

been calcinated at an oxygen-free ambient. The critical wall thickness-to-inner diameter ratio could not be reached despite the doubled number of ALD cycles. Figure 3 is the SEM image of hollow nanofibers synthesized by depositing 800 cycles AlN on a template having ~330 nm average fiber diameter. For this combination, the resulting structure was a perfect replicate of the electrospun nanofiber template. For the hollow nanofibers synthesized by depositing 800 cycles AlN on a template having ~70 nm average fiber diameter, the individuality of the fibers has been lost due to the coalescence of AlN layers deposited on different fibers. Wall thickness-to-inner diameter ratio for this combination was too high.

Chemical compositions of the synthesized hollow nanofibers were investigated by XPS. Survey scans detected peaks of Al, N, O, and C for all samples. XPS results of bare polymeric template, as well as coated and calcinated samples are summarized in Table 2 for 800 cycles AlN deposited on a template having ~330 nm average fiber diameter. Results indicated oxidation of AlN layer in the case of *ex-situ* calcination and ineffectiveness of *in-situ* calcination in terms of removing the organic template. High resolution XPS scans were also obtained in order to reveal bonding states of AlN hollow nanofibers. Al 2p scans of coated and calcinated (both *in-situ* and *ex-situ*) samples prepared by using polymeric templates having ~70 nm average fiber diameter were fitted by two subpeaks located at 73.5 ± 0.2 and 74.5 ± 0.3 eV, corresponding to Al-N [22] and Al-O [23] bonds, respectively. N 1s data obtained from the *in-situ* calcinated sample prepared by using ~740 nm average fiber diameter template was at the same location with that obtained from sample prepared by using ~740 nm average fiber diameter template, and fitted by two subpeaks. The peak located at 396.57 eV was attributed to the N-Al bond [22]; whereas the one located at 399.06 eV was assigned as the N-O bond [24]. The presence of N-O bond, which was also observed for the bare PA66 template, is a direct proof of the existence of organic component in the sample prepared by *in-situ* calcination.

Figure 4(a) and (b) are the TEM image of the samples prepared by using templates having average fiber diameters of ~70 and ~330 nm, respectively. Wall thicknesses of these samples were found to be highly uniform along the fiber axes. Wall thickness of the sample shown in Figure 4(a) was measured as ~64 nm, which is consistent with the deposition rate of AlN PEALD process at 200°C. The sample shown in Figure 4(b) was seen to be composed of two different layers. The thickness of the outer layer was measured as ~65 nm, which is in good agreement with the expected film thickness. The inner layer, which is believed to be related to the remaining organic content, had a thickness of ~10-11 nm. Crystal structure of the AlN film deposited on PA66 nanofiber templates was studied by high resolution TEM (HR-TEM) and SAED. HR-TEM images revealed a polycrystalline structure with nanometer sized grains, which was further confirmed by SAED. SAED

pattern of the sample prepared by depositing 800 cycles AlN on a template having ~330 nm average fiber diameter was consisted of seven polycrystalline diffraction rings, which correspond to the hexagonal AlN phase.

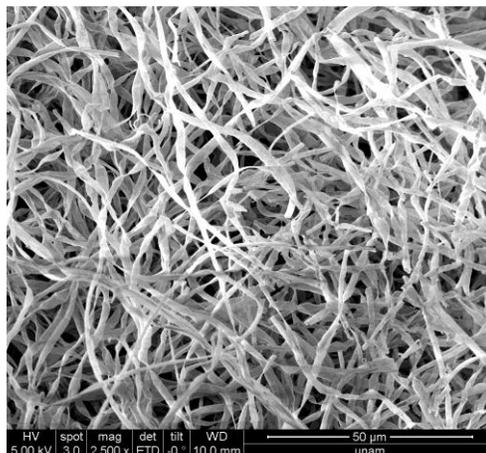


Figure 2: SEM image of inorganic hollow nanofibers synthesized by depositing 400 cycles AlN on a template having ~740 nm average fiber diameter. AlN-coated fibers were calcinated *ex-situ* at air ambient.

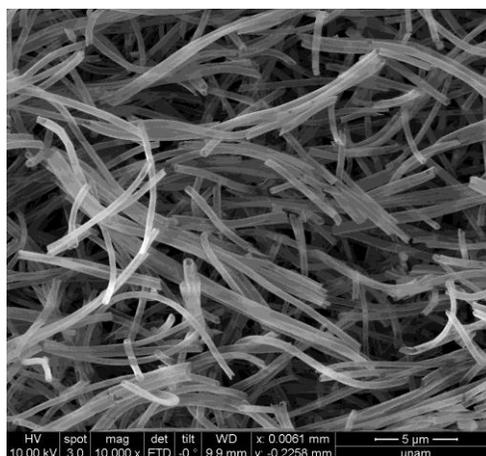


Figure 3: SEM image of hollow nanofibers synthesized by depositing 800 cycles AlN on a template having ~330 nm average fiber diameter. AlN-coated fibers were calcinated *in-situ*.

	at. %	Al	N	O	C
bare template		-	9.79	11.71	78.5
coated		20.69	8.33	33.74	37.24
calcinated <i>ex-situ</i>		33.02	5.78	42.02	19.18
calcinated <i>in-situ</i>		21.87	7.51	37.14	33.49

Table 2: XPS survey scan results. 800 cycles AlN were deposited on a template having ~330 nm average fiber diameter.

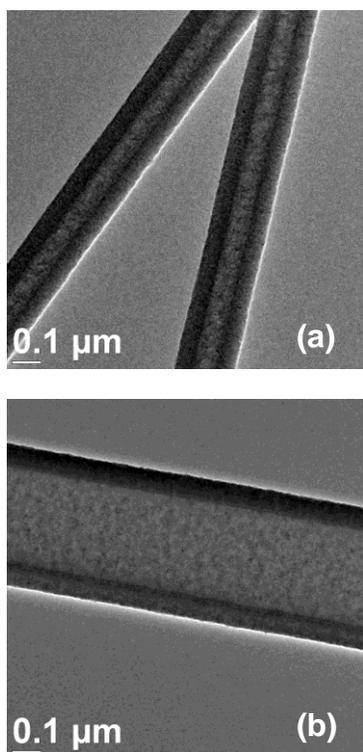


Figure 4: TEM images of hollow nanofibers synthesized by depositing 800 cycles AlN on templates having average fiber diameters of (a) ~70, and (b) ~330 nm, followed by *in-situ* calcination.

4 CONCLUSION

Template-based synthesis of AlN hollow nanofibers was demonstrated by combining electrospinning and PEALD processes. Conformal AlN films were deposited at 200°C on sacrificial electrospun PA66 nanofiber templates, using TMA and NH₃ plasma. AlN-coated nanofibers were then calcinated *in-situ* or *ex-situ* at 500°C for 2 h in order to remove organic components. SEM studies showed that there is a critical wall thickness-to-inner diameter ratio for AlN hollow nanofibers to preserve their shapes after the polymeric template has been removed by calcination. TEM images indicated uniform wall thicknesses along the fiber axes. Synthesized AlN hollow nanofibers were polycrystalline with a hexagonal crystal structure as determined by HR-TEM and SAED.

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