Electronic supplementary information

AlN Nanostructures: Tunable Architectures and Optical Properties

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Experimental section.

The AlN nanostructures were synthesized in an improved arc plasma setup (Fig. S1). Differing from previous setup, we designed a Mo plate as an upper substrate which located near the tip of W cathode, a small circulation of reactive vapors (circulation II in Fig. S1) between the Mo substrate and Al anode is formed, which results in high flux Al and N vapors knocking against the Al anode. As a result, AlN nanostructures grew on Al anode. In a typical run, pure N_2 gas (99.999%) and NH_3 gas purity (99.999%) were used as the working media. Before the direct current arc was ignited, the chamber pressure was evacuated to less than 1 Pa, and then working gas was introduced into the chamber. The total pressure is 20 kPa, the mixture ratio of N_2–NH_3 was controlled by the flow rate of the gas. When the direct current arc was ignited, the input current was maintained at 150 A and the voltage was a little higher than 35 V. After reaction, the products were passivated for about 24 h in pure Ar gas at 80 kPa. Finally the products in the form of nanostructures and nanoparticles were collected from the Al anode and Mo substrate, respectively.

The mechanism related with a thermodynamic process.

The proposed growth mechanism is further analyzed with thermodynamic arguments. In our case, NH_3 has active chemical properties in the plasma. It can dissociate as follows:

$$NH_3 \rightarrow NH_2 + H$$

$$NH_2 \rightarrow NH + H$$

$$NH \rightarrow N + H$$

$$H + H \rightarrow H_2$$

Here, Hydrogen, nitrogen and aluminum were reactive atoms or ion states. Consequently, the formation of AlN could be conducted easily. The reaction scheme from Al to AlN at high temperature may be expressed as follows:

$$2Al + 2NH_3 \rightarrow 2AlN + 3H_2,$$

$$Al + NH_2 \rightarrow 2AlN + 3H_2,$$

$$2Al + 2NH \rightarrow 2AlN + H_2,$$

$$2Al + N_2 \rightarrow 2AlN$$

$$Al + N \rightarrow AlN$$

In the initial stages, as the AlN (0001) faces are the highest-energy low-index planes, a fast growth in [0001] is thermodynamically favored. This leads to the formation of AlN sixfold symmetric microboxes along the [0001] direction on the Al anode, which is a thermodynamic equilibrium process. With the increase of the reaction time, the degree of supersaturation of AlN vapor decreases due to the consumption of Al vapor and N_2 gas. Thus, the AlN molecules are not enough to provide the growth of AlN sixfold symmetric microboxes along all the directions. Under this condition, the surface diffusion becomes more pronounced, and then the AlN molecules diffuse to the positions where the surface energies are higher. For AlN sixfold symmetric microboxes, the AlN molecules prefer to be absorbed on the (0001) surface which are the highest-energy plane. When the adsorption of AlN molecules on the (0001) surface of microboxes reaches equilibrium, the AlN molecules tend to form the thermodynamically stable shape of hexagonal pyramids. As the AlN hexagonal pyramids continue to grow, the surface energy at the edge of hexagonal pyramids and grain boundary regions of the (0001) surface of microboxes increase. At a critical saturation point, the AlN nanowalls begin to grow along the edge of hexagonal pyramids and grain boundary regions of the (0001) surface, which are the most thermodynamically active sites for saturation and precipitation. As a result, the nanowalls covered the (0001) surface of microboxes.

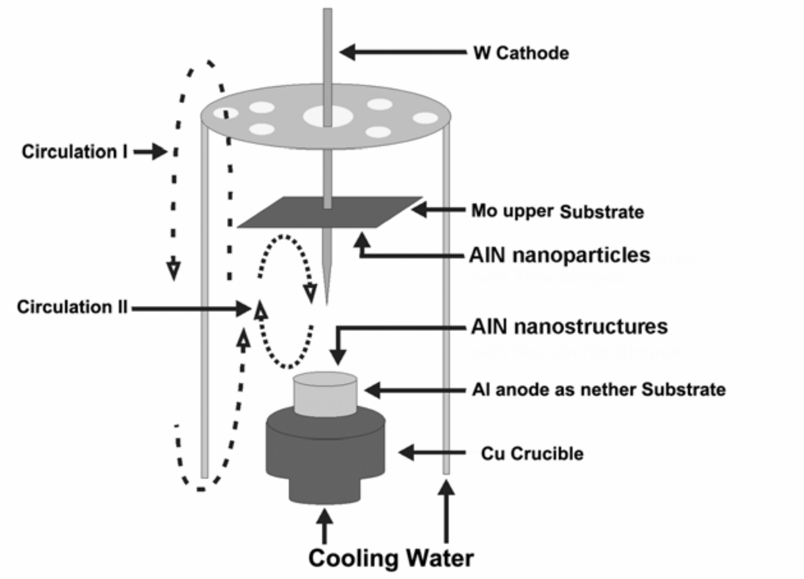

Fig. S1 Schematic setup of the improved arc plasma system.

The crystal structure of the products was examined by X-ray diffraction (XRD) measurements using Cu Ka radiation (Fig. S2). All observed peaks can be indexed to a pure hexagonal phase [space group: P63mc (186)] of AlN (JCPDS file No. 08-0262).

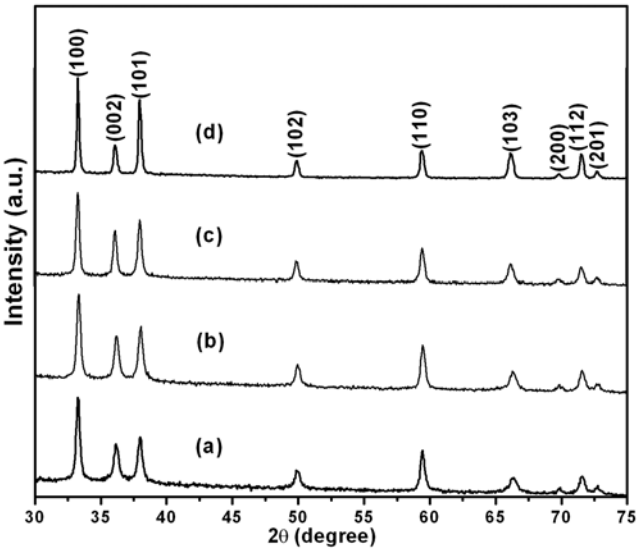

Fig. S2 The corresponding X-ray powder diffraction patterns of the as-synthesized AlN architectures: (a) Sample 1, AlN sixfold symmetric microboxes, (b) Sample 2, hexagonal pyramids on the top surface of microboxes, (c) Sample 3, nanowalls among the hexagonal pyramids on the top surface of microboxes, (d) Sample 4, nanowalls covered on the top surface of microboxes.

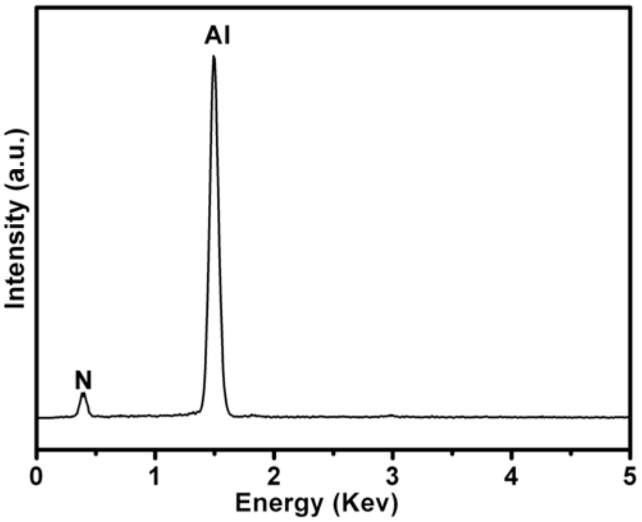

Fig. S3 The corresponding EDS spectrum of AlN architectures.

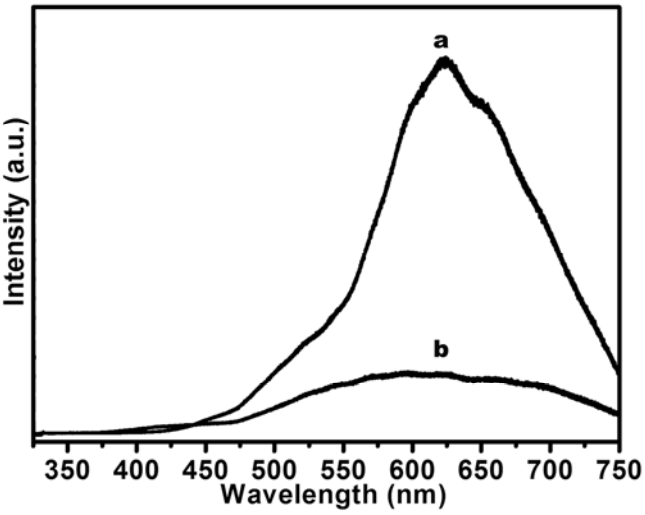

Fig. S4 Room-temperature PL spectra of the AlN nanowalls (a) and nanowalls annealed in nitrogen ambient (b).

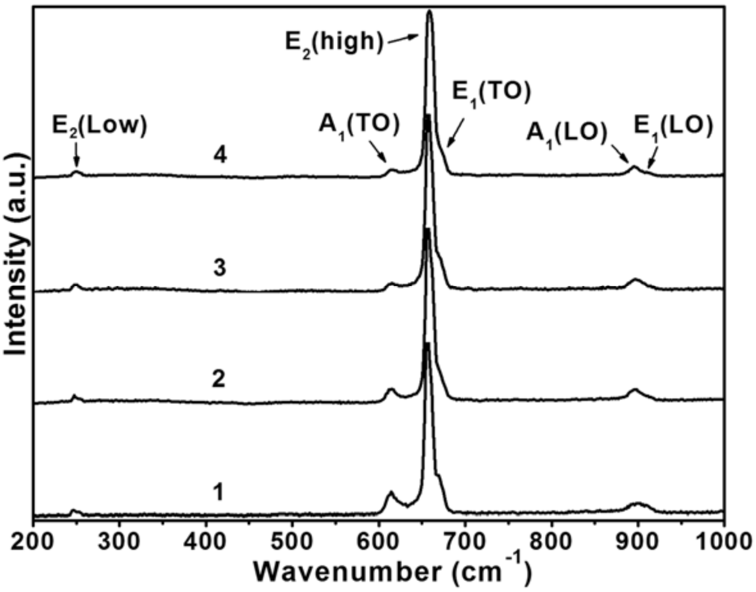

Fig. S5 The corresponding Raman spectrum of the AlN architectures. (1–4) correspond to Samples 1–4, respectively.

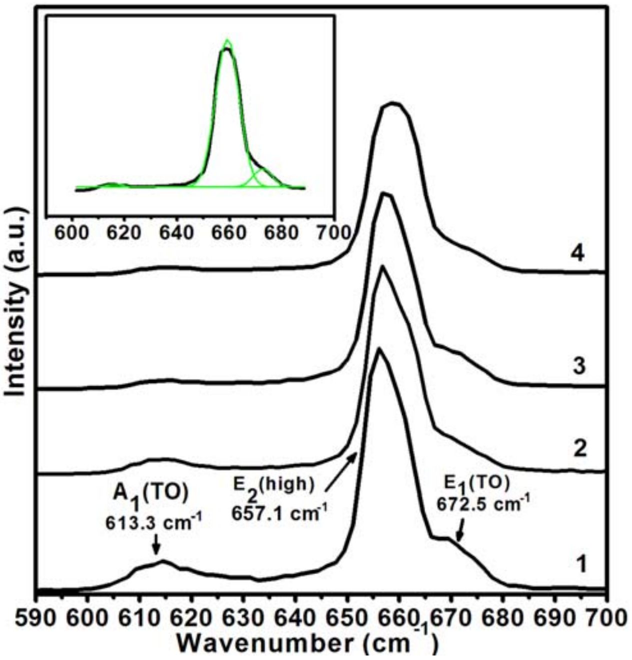

Fig. S6 The corresponding Raman spectrum of the AlN architectures. (1–4) correspond to Samples 1–4, respectively. The inset is Gaussian fitted Raman spectrum of Sample 4.

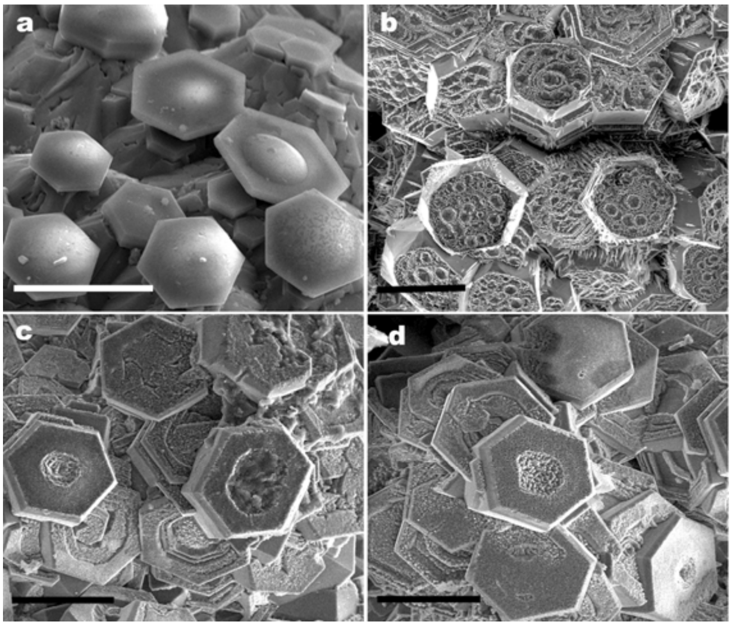

Fig. S7 SEM image of AlN nanostructures obtained for (a) 10 min; (b) 20 min; (c) 25 min; (d) 30 min. The scale bar is 100 μm.

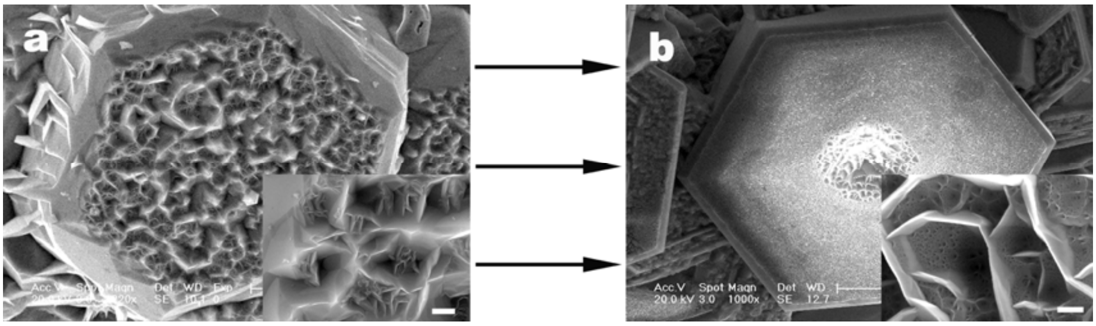

Fig. S8 SEM image of AlN nanowalls on the top surface of microbox obtained for (a) 28min; (b) 30 min. The scale bar is 250 nm.

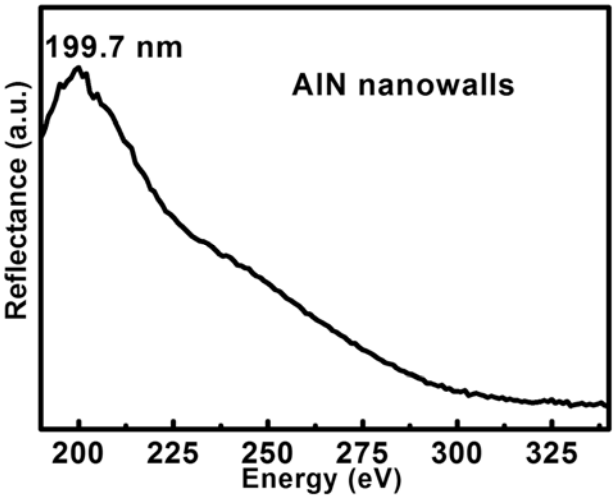

Fig. S9 Reflection spectra of the as-synthesized AIN nanowalls.