Manufacturable Aluminum Nitride Nanowire Films

K. Teker[1, 2]

[1]College of Engineering, Istanbul Sehir University, Istanbul, Turkey

[2]Mechanical Engineering, Frostburg State University, MD 21532, U.S.A.

Abstract

Aluminum nitride (AlN) is an important wide band gap (6.2 eV) III-V semiconductor material for electronic and optoelectronic applications. AlN has attracted great interest due to its inherent superior properties such as excellent thermal conductivity, low thermal expansion coefficient, high chemical stability, high electrical resistivity, and low electron affinity. Furthermore, one-dimensional AlN nanostructures are important for potential applications in several fields including power transistors, heat sinks, surface acoustic wave filters, resonators, sensors, piezoelectric nanogenerators, and spintronics. This paper presents a detailed investigation of AlN nanostrucures synthesis and characterization by chemical vapor deposition using Al and NH_3 as source materials. A wide variety of catalyst materials have been used (Co, Au, Ni, and Fe). The growth runs have been conducted at temperatures between 800 and 1100^{o}C under H_2 as carrier gas. The synthesis experiments have resulted in very high-quality and dense AlN nanowire array films. These results offer scale-up manufacturing opportunities of these nanostructures in many electronic and optoelectronic applications.

Key words: Aluminum nitride nanowires, chemical vapor deposition, nanomanufacturing.

1. Introduction

Controlled fabrication of nanoscale building blocks with various sizes and shapes are critical for the progress of nanotechnology and integration into large-scale manufacturing. Aluminum nitride (AlN) is a very important semiconductor material for electronic and optoelectronic applications. As a wide band gap (6.2 eV) III-V semiconductor, AlN has attracted great interest due to its inherent superior properties such as excellent thermal conductivity, low thermal expansion coefficient, high chemical stability, high electrical resistivity, and low electron affinity [1-3]. One-dimensional AlN nanostructures are important for potential applications in several fields including power transistors, heat sinks, surface acoustic wave filters, resonators, sensors, piezoelectric nanogenerators, and spintronics. Consequently, significant research has been devoted to the synthesis of 1-D AlN nanostructures with various fabrication methods. These fabrication methods include metal organic vapor deposition (MOCVD) [4], arc discharging process [5], chloride-assisted growth [6], carbothermal reduction [7], gas reduction nitridation [8], and CVD [9-15].

Corresponding author: Address: Faculty of Engineering, İstanbul Şehir University, 34660, Üsküdar, İstanbul, TURKEY. E-mail address: kasifteker@sehir.edu.tr, Phone: +902165599000

This paper presents a systematic investigation of both catalyst-assisted and catalyst-free 1D AlN nanostructure synthesis by chemical vapor deposition using Al and NH_3, as source materials; and physical properties of the AlN nanostructures. The catalyst-free AlN nanostructures have directly been fabricated on the alumina boat without any substrate. This very simple and effective fabrication approach has resulted in very high-quality and dense AlN nanowire array films. In attempts to compare with catalyst-assisted growth, studies with various catalyst materials have also been presented (Co, Au, Ni, and Fe). Consequently, free-standing catalyst-free nanowire films provide great opportunities due to enabling easy transfer of these into any substrate for the development of new devices for many technological applications.

2. Materials and Method

AlN nanowire growth has taken place in a resistively heated hot-wall 25-mm horizontal LPCVD reactor. Si and SiO_2/Si substrates were used for the catalyst-assisted growth. 400 nm thick SiO_2 was formed by thermal oxidation of Si. Various catalyst materials including Ni (20 nm size nanoparticle and thin film), Au of 20 nm, Fe of 40 nm, and Co of 25 nm were used. All the catalyst materials have been placed on SiO_2/Si substrate except Ni film, which was pre-deposited on Si substrate by sputtering. The substrate was ultrasonically cleaned in acetone, isopropyl alcohol, de-ionized water and dried with nitrogen. Nanoparticle solution was applied to the substrate surface and dried. An alumina boat containing both the substrate and Al (99.97 % purity, about 30 mg) was loaded into the CVD reactor. Al powder as source material was used for the direct nitridation studies. Moreover, the Al powder was placed into alumina boat and the growth took place directly on top of the source. Following loading, the reactor was evacuated and purged three times with hydrogen (99.999 %). After purging cycles, the reactor was heated to the growth temperature (typically between 800 and 1100^{o}C) under hydrogen. Then, the growth was carried out by flowing NH_3 (99.99%) and H_2 gases through the reactor for typically about 15 min. The gas flow rates were controlled by mass flow controllers and set to 300 sccm for both H_2 and NH_3. After the growth, NH_3 was shut off and the reactor cooled down under H_2 flow until 250^{o}C. Then, the furnace naturally cooled down to room temperature.

The samples have been characterized by scanning electron microscopy (SEM, JEOL JSM 6060 and JEOL 7600F SEM with Oxford Inca EDS), Raman spectroscopy (Renishaw inVia Raman Microscope with 532 nm laser excitation wavelength and Leica DMLM microscope), and x-ray diffraction (XRD, Rigaku 300 and Bruker D8 Discover).

3. Results and Discussion

Figure 1 shows SEM images of the AlN nanowires grown on 20-nm Ni coated Si and SiO_2/Si with 25 nm Co nanoparticles at 1100^{o}C under H_2 as carrier gas. The AlN nanowire diameters grown on Ni-film are in the range of 20 nm to 30 nm and lengths about few microns. It is worth mentioning that the metal catalysts were observed at the end of the nanowires. This observation indicates that AlN nanowire growth has taken place via vapor-liquid-solid (VLS) growth mechanism. In the VLS mechanism, the metal droplet acts as a catalyst for decomposing the crystalline constituents. As the constituents for nanostructures become supersaturated within the liquid solution, crystal growth proceeds by precipitation of source materials from the solid-liquid interface. In general, the VLS mechanism results in highly anisotropic nanostructures, since nucleation and growth process is mainly controlled by the liquid catalyst droplet. The AlN nanowire diameters grown with Co nanoparticles are in the range of 25 nm to 35 nm and lengths about several microns. Majority of the AlN nanowires grown with Co have kink morphology. The growth runs have been repeated at the same conditions with different catalyst materials including Fe and Au. Nevertheless, Fe or Au catalysts did not yield any nanowire growth. Following that, AlN growth was carried out at different temperatures with the most active catalysts (Ni and Co). In the temperature range of 800-950^{o}C, no nanowire growth was observed. AlN nanowires appeared at 1000^{o}C; and the nanowire growth yield has increased with temperature and reaching its peak at 1100^{o}C.

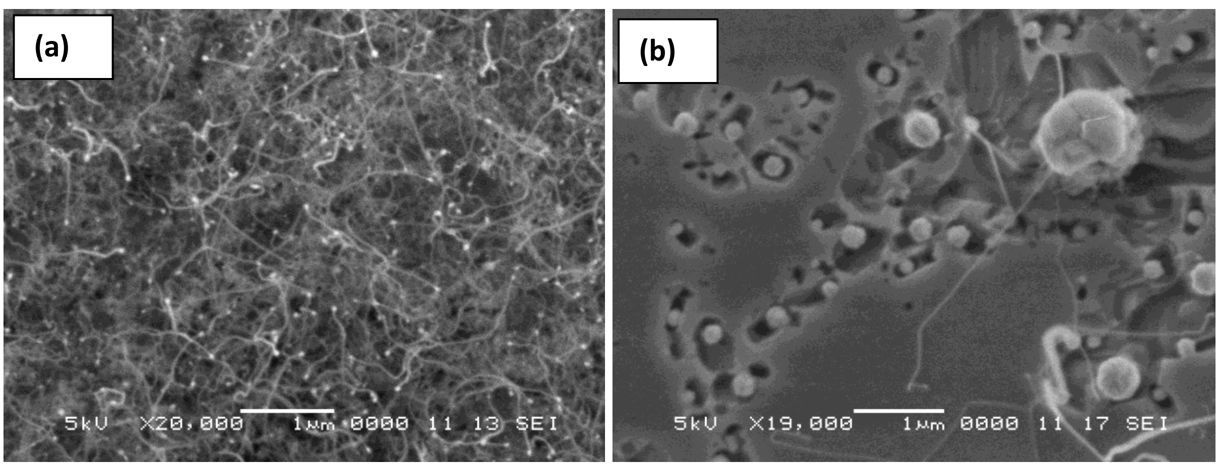
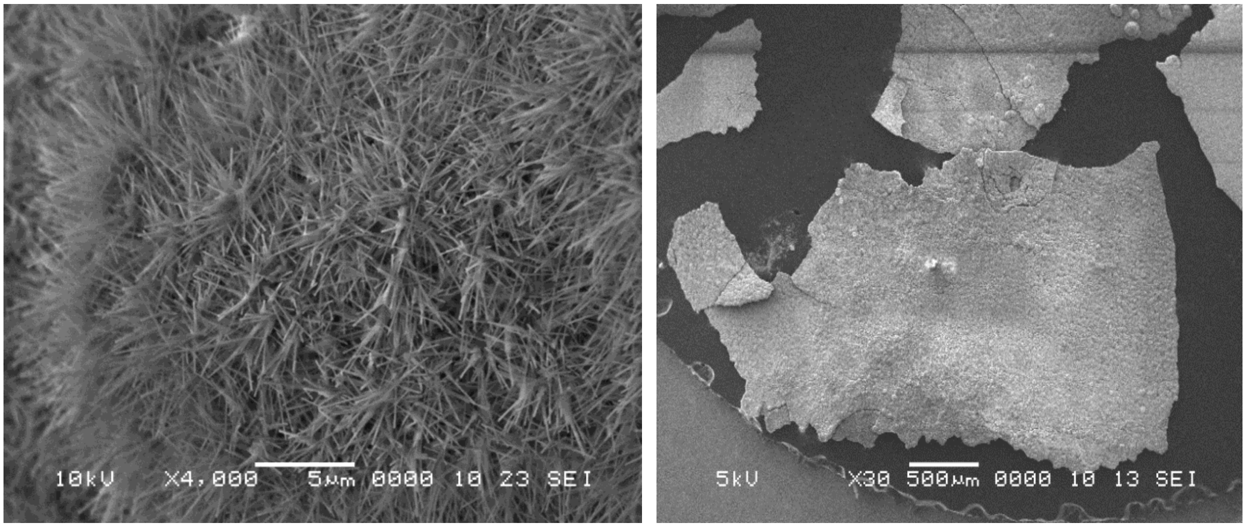


Figure 1. SEM images of AlN nanowires grown at 1100^{o}C under H_2 with different catalysts: (a) Ni-film, (b) Co-nanoparticles solution.

Figure 2 shows SEM images of the catalyst-free grown ultra-dense AlN nanostructure films at 1100^{o}C. The AlN nanostructures were grown on the source Al, which was placed directly to the alumina boat without any substrate. These free-standing nanostructure films were attached to conductive carbon tape before placing to the SEM sample holder. The AlN nanorod tip diameters are about 30 nm and lengths up to 10 microns. The growth takes through a VLS mechanism with Al droplets serving as the self-catalyzing agents. The size uniformity of the AlN nanorods suggests very fast and spontaneous nucleation.



(a) (b)

Figure 2. SEM images of catalyst-free grown ultra-dense AlN nanostructure films at 1100^{o}C: (a) high magnification (AlN nanorods with 30 nm tip diameter and ~10 µm length); (b) low magnification films

XRD measurements were carried out using Cu K_α radiation (λ = 0.154 nm) to determine the structure and crystal quality of the AlN nanostructures; and a typical spectrum is shown in Figure 3. The diffraction peaks in the spectrum were indexed to a hexagonal wurtzite crystal structure. The lattice constants derived from the peak positions were a = 0.3114 nm and c = 0.4979 nm (JCPDS: No. 25-1133). The diffraction peaks and their positions from the AlN nanostructures can be listed as: (100) - 33.2^o; (002) - 36.04^o; (101) - 37.92^o; (102) - 49.82^o; (110) - 59.35^o.

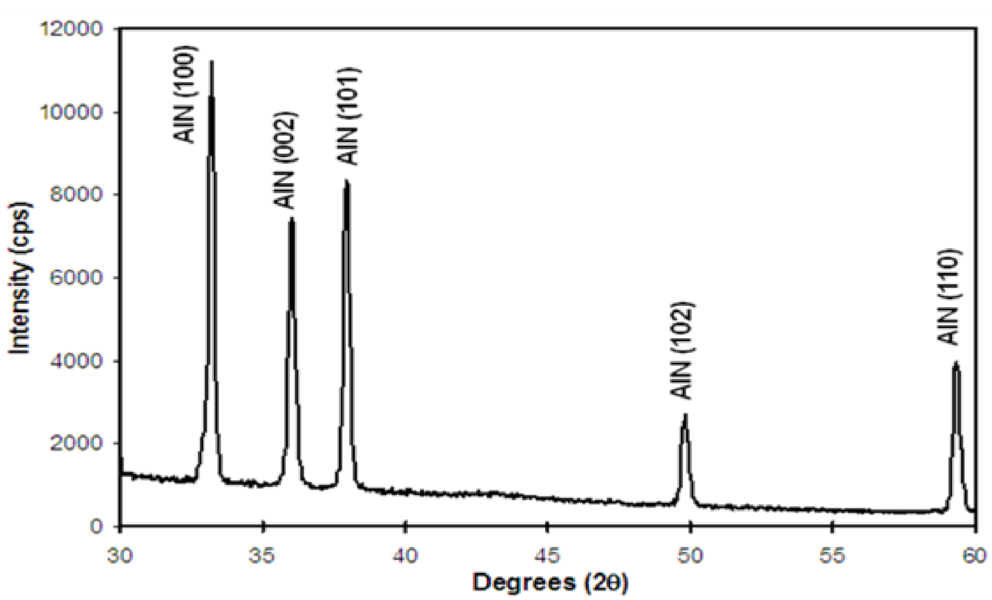


Figure 3. XRD pattern of the AlN nanostructures indicating hexagonal wurtzite structure.

Optical properties of the AlN nanostructures have been analyzed through Raman spectroscopy; and a typical spectrum is shown in Figure 4. The Raman spectrum yields peaks at 611 cm^{-1} (A_1; TO), 656 cm^{-1}(E_2; high), 668.3 cm^{-1}(E_1; TO), and 907.4 cm^{-1} (A_1; LO); which agrees well with the high-quality single-crystalline bulk AlN [16].

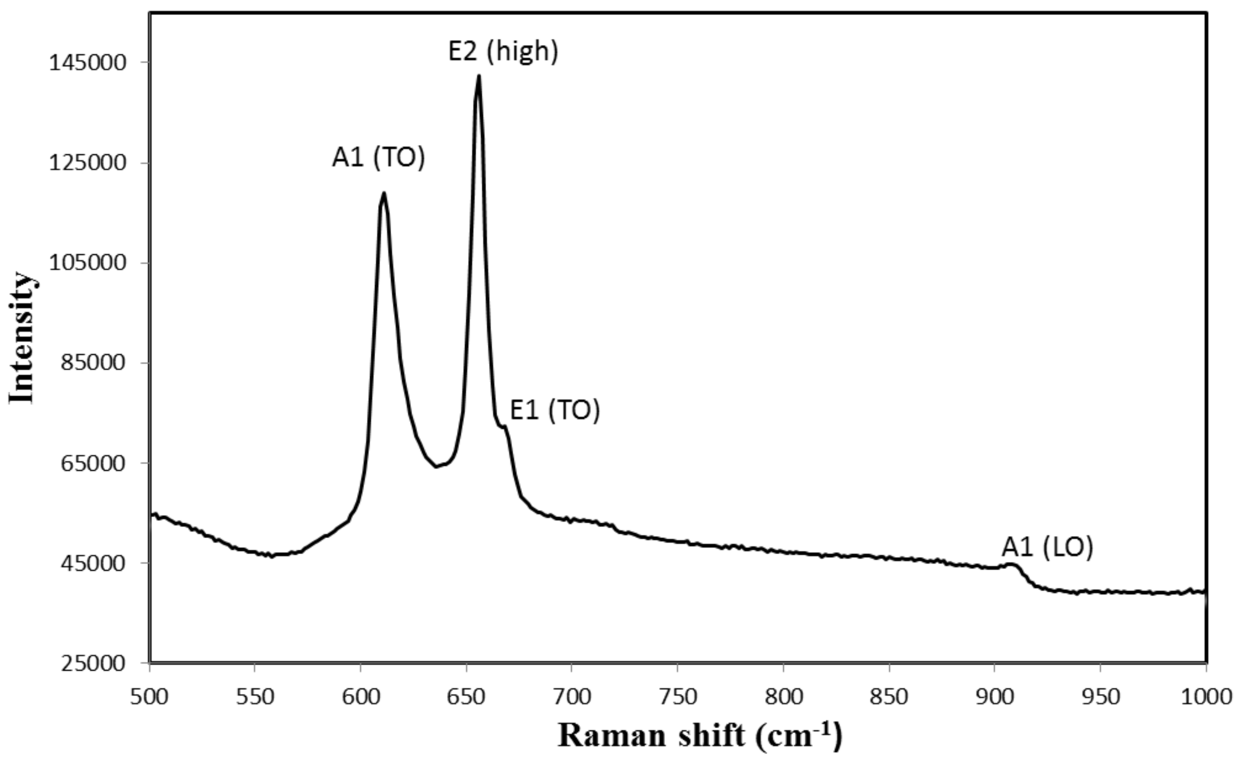


Figure 4. Raman spectrum of the AlN nanostructures.

Conclusions

The synthesis of both catalyst-assisted and catalyst-free growth of AlN nanostructures by chemical vapor deposition using Al and NH_3 as source materials has successfully been demonstrated. The catalyst-assisted growth on Ni-coated film resulted in small diameter (20 – 30 nm) AlN nanowires with lengths of about several microns. In fact, the yield, as measured with the degree of surface coverage by nanowires, has been the highest for the Ni catalyst at 1100^{o}C. Moreover, no significant growth has been observed at temperatures lower than 1000^{o}C presumably due to the low vapor pressure of Al metal. The direct nitridation of Al powder by NH_3 has resulted in very dense AlN nanostructure films. The AlN nanorod tip diameters are about 30 nm and lengths up to 10 microns. The growth takes through a VLS mechanism with Al droplets serving as the self-catalyzing agents. Consequently, free-standing catalyst-free nanowire films provide great opportunities due to enabling easy transfer of these into any substrate for the development of new devices in many technological avenues including energy applications.

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