Synthesis and Characterization of Ga_2O_3 and In_2O_3 Nanowires

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Abstract. *In this work, the thermal synthesis and characterization of gallium oxide and indium oxide nanowires using vapour-liquid-solid mechanism at atmospheric pressure were described. Au nanoislands formed by the solid-state dewetting process of various thickness metal layer were applied as growth catalyst of nanowires while high-purity metal reactants (In, Ga) were applied as AIII precursors. The catalytic layer thickness influence on the morphology of investigated nanostructures was studied. Material composition and structural properties were used for crystallographic quality of AIII-oxide nanowires examination.*

Keywords

Ga_2O_3, In_2O_3, nanowires.

1. Introduction

Oxides of AIII group as In_2O_3, Ga_2O_3 are physically and chemically stable materials with excellent properties. Materials based on these oxides, exhibiting good electrical conductivity and transparency, are widely used in various industrial applications as transparent and conducting coatings or electrodes. Quantum confinement effects and high surface-to-volume ratio occurring in one-dimensional (1D) nanostructures obtained by reducing sizes of bulk material assure its parameters modification. Thus, application of AIII-oxides nanostructures in various devices as UV photodetectors, conductive windows with anti-reflective and light trapping properties, transparent field-effect transistors and gas sensors [1], [2] and [3] could modify or improve their operation. The most popular method of AIII-oxides nanowires fabrication is synthesis using Vapor-Liquid-Solid (VLS) mechanism with the application of catalytic metal or the Vapor-Solid (VS) mechanisms directly on a substrate. The metallic (In, Ga) or oxide powders/bars/pills are used mainly as precursors of AIII atoms, and the thermal synthesis is conducted in an oxidizing gas atmosphere [4]. In this paper, we present a thermal synthesis and characterization of Ga_2O_3 and In_2O_3 nanowires using vapor-liquid-solid mechanism at atmospheric pressure.

2. Experiment

The 18×18 mm^2 Si (100) samples with 100 nm oxide layer deposited by Plasma-Enhanced Chemical Vapor Deposition (PECVD) method were used in the study. On the samples, the 1, 3, 5 and 10 nm thick Au layer was evaporated thermally (K. J. Lesker, PVD 225). These Au layers served as a catalyst for nanowires growth in the VLS method.

The Ga_2O_3 and In_2O_3 nanowires were synthesized in a high-temperature furnace with a horizontal quartz tube. Precursors of AIII atoms were metallic gallium (5N) and metallic indium (6N). During processes, the samples were arranged in a reactor at different ways and distances from the metallic source. To synthesis Ga_2O_3 nanowires the distance was 10 mm, and the samples were placed vertically in the tube. To synthesis In_2O_3 nanowires the distance was 50 mm and the samples were arranged horizontally. The growth of nanostructures was conducted at high temperature

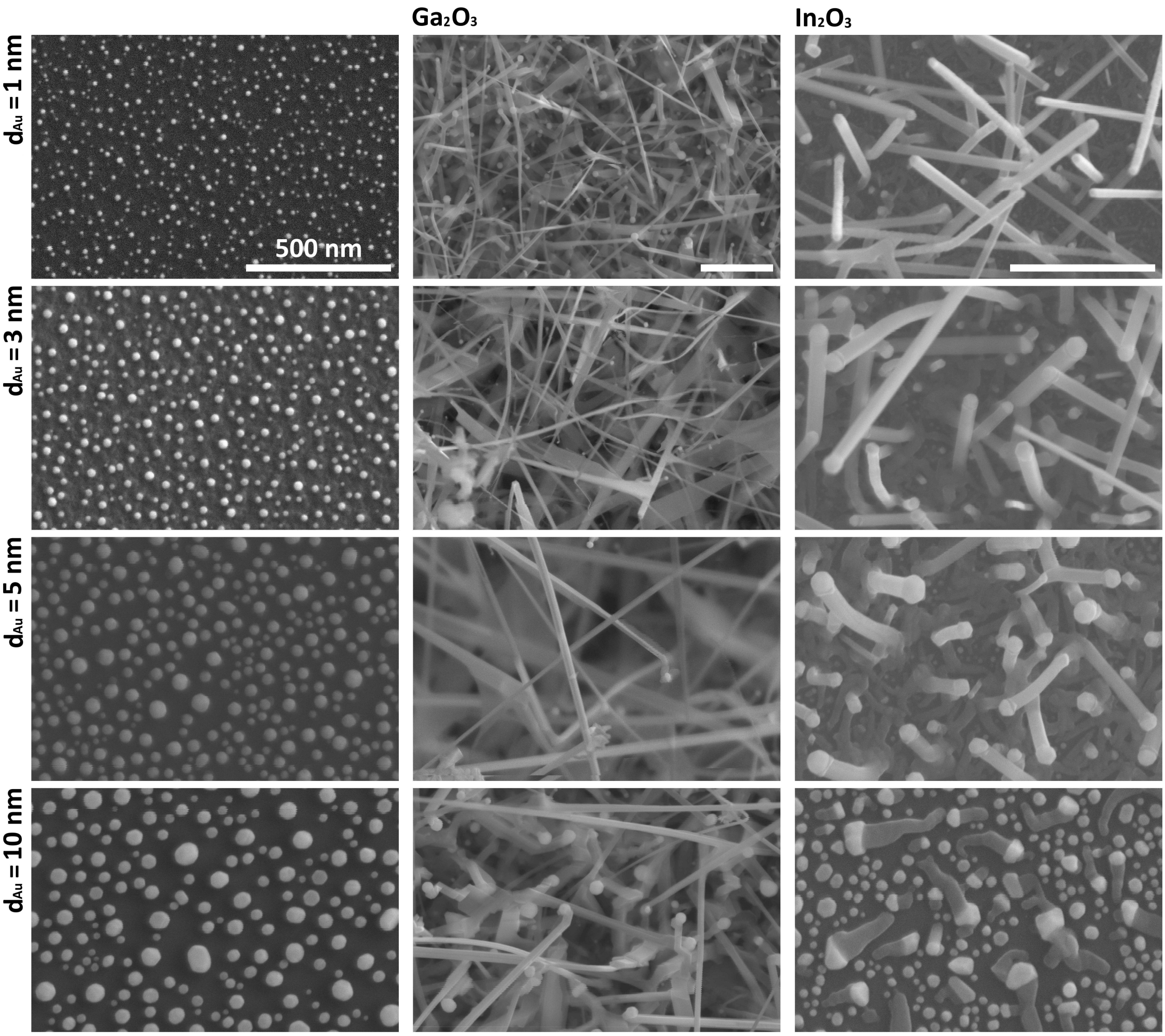

Fig. 1: The SEM images of 1, 3, 5 and 10 nm Au layers on SiO_2/Si substrates annealed at 1012 °C temperature for 2 min, Ga_2O_3 (middle column) and In_2O_3 (right column) nanowires grown using the VLS mechanism. Scale – 500 nm.

(Ga_2O_3 – 1012 °C, 2 min; In_2O_3 – 800 °C, 10 min) at atmospheric pressure. During the process, a gas mixture consisting of nitrogen and DI water vapor was flowing through the reactor with a constant flow of 1300 sccm.

The morphology of obtained nanostructures was observed by a Scanning Electron Microscope (SEM). Structural and material composition characterization was performed by X-Ray Diffraction (XRD) and Energy-Dispersive X-ray Spectroscopy (EDS).

3. Results and Discussion

Prior to nanostructures synthesis, the Solid-State Dewetting (SSD) process of Au layers occurred, and the metal formed itself into the spherical islands with nanometric dimensions. This effect could be observed in Fig. 1 in the left column where the Au layers were annealed at 1012 °C temperature for 2 min. In Tab. 1, the analysis results of the islands size and their surface density are shown. The surface densities of the islands decreased and their size increased with the increasing of the Au layer thickness.

The metal nanostructures catalysed the VLS process in the presence of gas precursors. At elevated temperature, the metal nanostructures become liquefied. The mechanism of structures growth in VLS method is based on achieving a proper relationship between the surface energies of the three boundary phases: gas - liquid, liquid - solid, gas - solid. At the gas-liquid interface, the atoms of growing material are adsorbed faster than on the surface of the substrate. Maintaining the

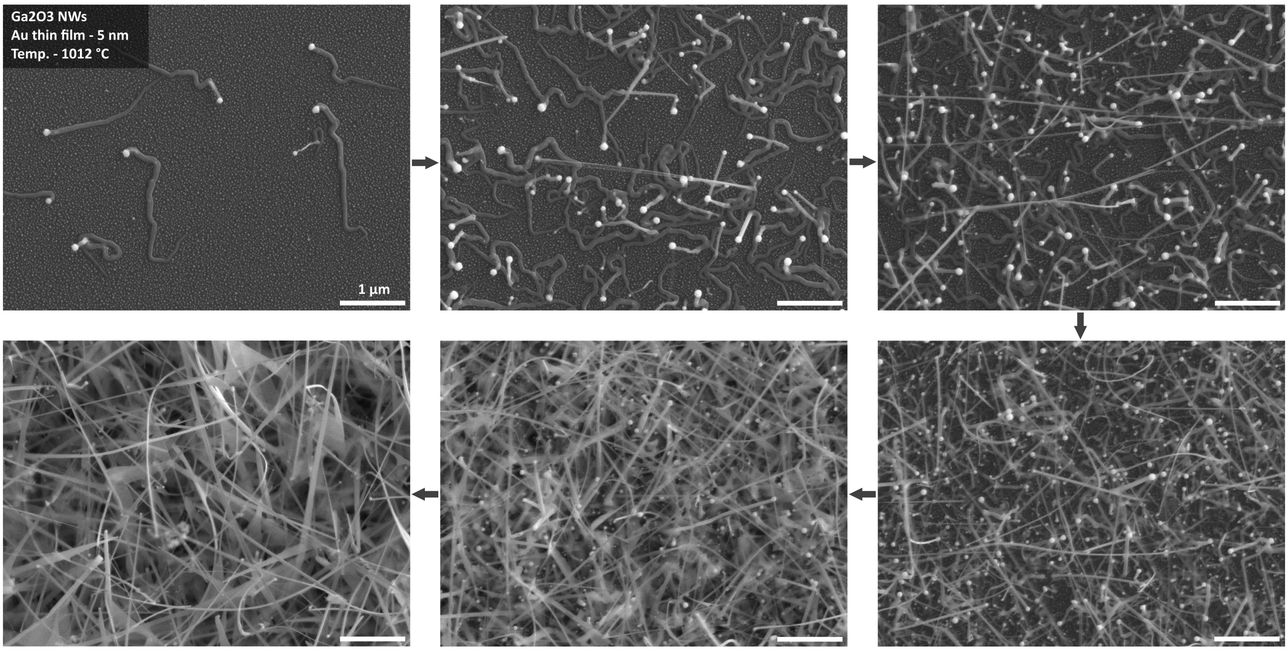

Fig. 2: The juxtaposition of early stages of Ga_2O_3 nanowires growth. The SEM images of nanowires from sample with 5 nm Au layer. Scale bare – 1 µm.

process temperature, which is higher than the eutectic temperature, the supersaturation of the metal alloy is obtained and crystal growth occurs on the interface of the alloy and substrate. In Fig. 1, the SEM images of Ga_2O_3 nanowires (middle column) and In_2O_3 nanowires (right column) made by thermal synthesis using the VLS mechanism are presented.

Tab. 1: The results of SEM analysis of the Au islands size and their surface density for various thicknesses of Au layers (samples were annealed at 1012 °C temperature for 2 min).

d_{Au} (nm)	Density (μm^{-2})	Radius (nm)
1	436	10.2
3	331	11.5
5	223	18.3
10	118	24.9

The Ga_2O_3 nanowires were successfully grown on all samples with different thickness of the Au layer. Nanowires synthesized from smaller Au nanoislands were narrower, which is typical for the VLS method where the catalytic metal sphere defines the shape of the wire. The average radius of the obtained Ga_2O_3 nanowires was 21.7 ± 8.5, 31.6 ± 12.4, 54.9 ± 13.8 and 61.3 ± 15.9 nm for samples with Au layers with thickness 1, 3, 5 and 10 nm, respectively.

In case of In_2O_3 wires, the nanowires grown much efficiently on substrates covered with smaller Au nanoislands from 1 and 3 nm thick catalytic layers. For samples with 5 nm Au layer, In_2O_3 nanorods were obtained. However, in the case of samples with 10 nm Au layer, one-dimensional structures did not grow. The average radius of the obtained In_2O_3 nanowires was 32.4±5.4, 48.2±5.9 and 54.6±10.2 nm for samples with Au layers with a thickness of 1, 3 and 5 nm, respectively. In_2O_3 nanowires were more homogeneous than Ga_2O_3 nanowires where a more varied shape including nanoribbons and membranes could be observed.

In Fig. 2, the early stages of Ga_2O_3 nanowires growth are presented for a sample with 5 nm Au layer. The SSD process of Au layer led to the formation of separated metallic nanoislands that catalysed the growth process of Ga_2O_3 worm-like structures on the SiO_2 surface. Gas precursors adsorbed on the surface of Au islands, dissolved and then the crystal grew on the interface of the alloy and the substrate. However, the lateral growth was observed. This was probably because the continuous supply of mass material into the islands resulted in their enlargement in size, thus preoccupation the neighbouring Au islands. The surface tension of the connecting islands forced the movement along the substrate surface of the bigger and new island. When the saturation level of the alloy reached some supersaturation, the vertical growth of NWs began. Connecting the islands to the larger ones caused that relatively larger diameter of wires than initially the diameter of Au islands.

In general, wires easier synthesized for thinner layers of the catalytic metal. In small islands, much faster supersaturation of precursors was achieved. For In_2O_3 nanostructures, the saturation process was longer (the growth process was five times longer than for Ga_2O_3). The wires were shorter, and in case of a 10 nm thick catalytic layer, the growth of nanostructures did not occur. In order to improve the growth efficiency of In_2O_3 nanostructures, the catalytic islands should be relatively small or have a much lower surface density to avoid the connection of islands in the initial stage of growth.

In Fig. 3, the EDS spectra of Ga_2O_3 and In_2O_3 nanowires synthesized from 5 nm Au layer are shown. The accelerating voltage of EDS measurements was set to 6 kV in order to limit the penetration of electrons into the sample and in order to obtain the signal originated mostly from the surface. It was over one and a half times more than higher excitation energy than the critical ionization energy of last counted emission line. Thus overvoltage requisite to make reliable measurements was ensured.

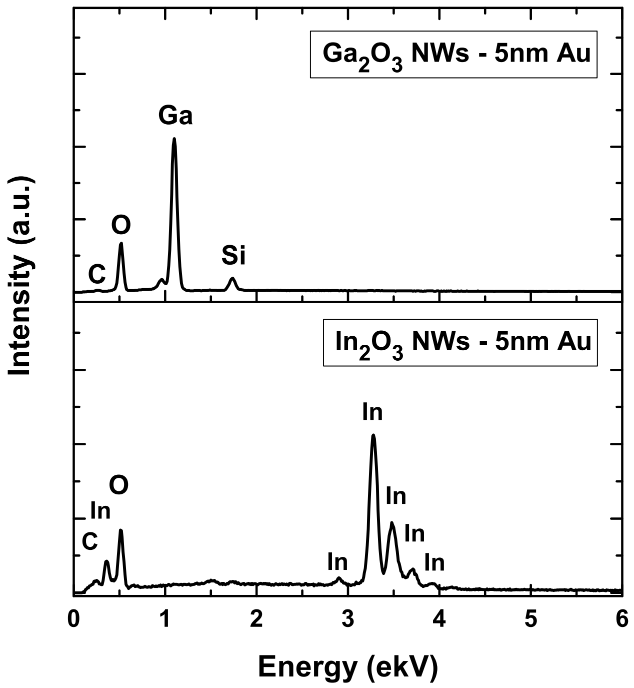

Fig. 3: The EDS spectra of Ga_2O_3 and In_2O_3 nanowires synthesized from 5 nm Au layer.

The microanalysis of the surface chemical composition showed mainly the desired elements. The samples with Ga_2O_3 nanowires contained the atomic composition of the Ga and O elements at 34 % and 43 % level, respectively. The samples with In_2O_3 nanowires contained In and O elements at 40 % and 54 % level. In both cases, the content of metal atoms was slightly higher than that resulting from the stoichiometric material.

To confirm the structural quality of nanowires, X-ray diffraction measurements were made. The XRD spectra of Ga_2O_3 and In_2O_3 nanostructures synthesized from 5 nm Au layer are shown in Fig. 4. All the diffraction peaks can be identified and assigned exactly to β-Ga_2O_3 in monoclinic crystal system or to In_2O_3 in cubic crystal system (JCPDS# 87-1901, JCPDS# 8 0-5364). For Ga_2O_3 NWs, the strongest signals were observed to planes: (111), (002) and (400). The In_2O_3 NWs were more preferentially oriented in [222], [400], [440] growth direction. The results of XRD analyzes were very similar to those obtained by other groups [5] and [6].

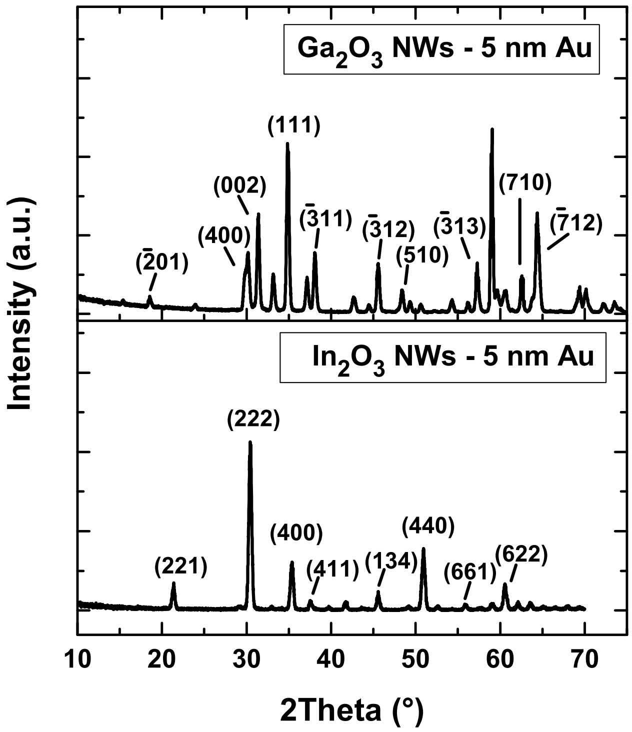

Fig. 4: The XRD spectra of Ga_2O_3 and In_2O_3 nanowires synthesized from 5 nm Au layer.

4. Conclusion

The thermal synthesis of In_2O_3 and Ga_2O_3 NWs using vapor-liquid-solid mechanism at atmospheric pressure was successfully performed. As the growth catalyst, the Au nanoislands formed by the SSD process of thin Au layer and colloidal Au nanoparticles were applied. In order to provide AIII precursors, the sublimation of high-purity metal reactants (In, Ga) in water vapor ambient was carried out. The influence of the catalytic layer thickness on the morphology of obtained structures was investigated. The initial stage of nanowires growth where the lateral growth dominated was analysed. The microanalysis of the surface chemical composition of oxide nanostructures showed that the content of metal atoms was slightly higher than that resulting from the stoichiometric material. Structural characterization confirmed the crystallographic quality of AIII-oxide nanowires. For Ga_2O_3 NWs [111], [002] and [400] dominant growth direction was observed. In the case of In_2O_3 NWs, the dominating signals were observed for (222), (400), (440).

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