Ga$_2$O$_3$ nanowires preparation at atmospheric pressure*

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An attempt has been undertaken to produce gallium oxide nanowires by thermal synthesis from metallic gallium source at atmospheric pressure. Silicon substrates of (1 0 0) and (1 1 1) orientation with and without silicon oxide layers (0.5 μm) were used as support. Evaporated thin gold films were deposited on the top of those silicon carriers as a catalytic agent. After thermal treatment by Rapid Thermal Processing RTP (at various temperatures and times), which was applied to make small Au islands with the diameters of about several tens of nanometers, the substrate surfaces were observed by SEM. The Ga$_2$O$_3$ syntheses were made at various conditions: time, temperature and gas mixture were changed. As a result, monoclinic gallium oxide β-Ga$_2$O$_3$ nanostructures with dominant [1 1 1] and [0 0 2] growth directions were grown. The obtained nanostructures of several tens micrometers length were studied by SEM, PL and X-ray methods.

Keywords: *Ga$_2$O$_3$; nanowires; nanobelts; thermal synthesis; atmospheric pressure*

1. Introduction

Properties of the monoclinic gallium oxide β-Ga$_2$O$_3$ are very interesting for researchers: a wide bandgap (E$_g$ = 4.9 eV), refractive index of 1.97, high breakdown filed (8 MV/cm) and a high thermal stability. As a conducting transparent semiconducting oxide it can be used as a material for solar-blind UV detectors [1] and gas, chemical or humidity sensors [2, 3]. Gallium oxides have been studied in terms of their catalytic properties too. Gallium oxide nanowires GaONWs or nanobelts GaONBs because of their large active area (large surface-to-volume ratio) and size effect are particularly suitable for those purposes.

A typical, simple way of GaONWs or GaONBs synthesis is low-pressure thermal evaporation or sublimation. An atmospheric pressure synthesis is applied rather seldom. The reason is low partial pressure of gallium, although some investigators carry out their works in a reactor open to air [4].

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2. Experimental

A high-temperature furnace with a horizontal tubular quartz tube was used as a reactor for GaONWs synthesis. Metallic gallium of 99.9999 % purity was a source of gallium, silicon plates (15 mm × 15 mm in size) with gold thin layers were used as supports for nanostructures growth. Gas mixture consisting of nitrogen (99.9999 %) and nitrogen flowing through the bubbler with DI hot water was the working atmosphere in the quartz reactor. Silicon wafers were put into suitable place in the reactor at the ambient of the fixed gas mixture.

The surface morphology of the samples with nanostructures was observed by scanning electron microscope (SEM) Hitachi SE6600. X-ray diffraction (XRD) spectra were obtained using a PHILIPS MRD diffractometer supported by the parallel beam optics and CuKα1 = 1.540597 × 10^{-4} μm radiation source. 2 Theta scans with a constant incident beam were performed. Photoluminescence (PL) spectra were performed at room temperature using 213 nm CryLaS laser as an excitation source and Ocean Optics HR4000 spectrometer as a PL signal receiver.

2.1. Silicon carrier preparation

At first, it was necessary to prepare silicon substrates (supports). To verify which kind of the support would be better for GaONWs synthesis, silicon wafers with two orientations were used, with and without oxide layers and prepared (*ex-situ*) Au island layers.

Si wafers with (1 0 0) and (1 1 1) orientations (15 mm × 15 mm in size) were used. A part of them (with both orientations) was thermally oxidized to obtain 500 nm thick SiO$_2$ layers. All substrates (oxidized and not oxidized) were covered by a gold layer which acted as a catalyst for GaONWs growth. Au thin films with a thickness of 5 nm were deposited with a deposition rate of about 2×10^{-1} nm/s on the samples by thermal evaporation in a UHV system (Kurt J. Lesker PVD225).

To form Au particles from quasi-continuous metallic layer, Rapid Thermal Processing (RTP) treatment was applied to a part of processed samples. Solid-state dewetting process (SSD) of thin metal films is caused by a pursuit to reduce the total interfacial energy of the system. Due to dewetting process, the metallic layer forms island on the substrate surface [5]. Time and temperature of RTP were changed: 1 min and 3 min, and 600 °C, 700 °C, 800 °C and 900 °C in ambient of nitrogen (purity better than 99.99999 %). Some samples were not subjected to RTP treatment.

2.2. Nanowires synthesis

Three methods of gallium supply were applied. The first one (A) was wetting a silicon substrate by liquid gallium containing Au particles with a quartz stick. In the other method (B), a small drop of liquid gallium was laid on a quartz plate and silicon wafer was placed near the gallium perpendicularly to the substrate. And the third one (C) consisted in putting the silicon samples with active side (covered by gold) over a small gallium droplet placed on a quartz plate in a distance of few millimeters. The processes of NWs synthesis were performed in the ambient of nitrogen (99.9999 % of purity) and water steam from a bubbler with DI water transported by nitrogen. Two values of temperature were applied: 912 °C and 1012 °C. The gas mixture was fixed to 0.5 slm of nitrogen and 0.8 slm of nitrogen passing through the bubbler with DI hot water (97 °C). For the first (A) method of gallium supply, the time of the synthesis was 2 h and for the remaining (B and C) methods, the time was 0.5 h.

2.3. SEM observations

For the surface topography measurements of the samples, scanning electron microscopy was applied. SEM examinations were performed on the samples after Au deposition, after RTP treatment and after GaONWs synthesis. SEM analysis of Si surfaces aimed to determine which combination of time and temperature of the RTP processing gives better effect for creation regular in shape, small in size and uniformly distributed Au islands. GaONWs nanostructures on silicon substrates, which were oxidized (SiO$_2$ layers 500 nm) were difficult to study due to static charges accumulated on the surface.

2.4. X-ray measurements

X-ray diffraction method has been used to study the phase contents of the samples. XRD is one of the basic methods, which allows determination of structural parameters of a material, calculation of particle size and phase identification.

One of the basic measurement methods in XRD is so-called 2Theta scan with a constant incident beam, which involves measuring the diffraction pattern from the sample surface while changing the diffraction beam angle. This may be realized by measurement of an X-ray beam incident on the sample at a constant small angle (<7°, typically 4°) [6]. At low angle, the beam slips over the surface and does not penetrate deeply into the sample, thus, probing the near-surface region of the sample. The method enables obtaining reflections from all crystal planes of the measured sample and cut-off strong reflections from the single crystal substrate.

2.5. Photoluminescence measurements

Some GaONWs structures (the same as the ones measured by X-ray) were studied at room

temperature (RT) on a photoluminescence PL stand. 213 nm CryLaS laser as an excitation source and Ocean Optics HR4000 spectrometer as a PL signal receiver were used.

3.   Results and discussion

3.1.   Scanning Electron Microscopy survey

Dewetting observations of as-deposited Au layers

In case of the thin Au films deposited on SiO_2, the beginning of spontaneous solid-state dewetting process without any additional heating was observed (Fig. 1a). This effect was also observed for the as-deposited Au films thicker than 5 nm [7]. The nucleation of Au layer starts from small grains or islands and then, upon successive atoms supply, a layer with a lace-like structure, finally becoming a continuous layer, is formed. So, the SSD process is accelerated with decreasing film thickness [8]. On the other hand, Au film deposited on unoxidized silicon has no cracks (Fig. 1b). The topography of the metallic layer surface on Si substrates indicates that probably the state of eutectic occurred between the thin film of silicon and gold. However, the *in-situ* temperature measurement during the deposition process has not been carried out to confirm this supposition. Nevertheless, the as-deposited layer should reproduce almost perfectly flat silicon surface but this has not occurred.

3.2.   Rapid Thermal Processing results

From the SEM observations, after RTP annealing, one can notice the influence of time and temperature on the samples morphology. In Fig. 2 the evolution of the morphology of the samples with SiO_2 dielectric layer is shown. At elevated temperature the SSD process leads to the formation of Au islands. For higher temperatures, the quality of self-organizing structures has been improved. At temperatures below 800 °C, even for a longer time (3 min), there is not enough energy to form islands with spherical shape on the oxide surface. However, time of 1 min is sufficient for temperature of 800 °C and higher to get well-formed gold droplets.
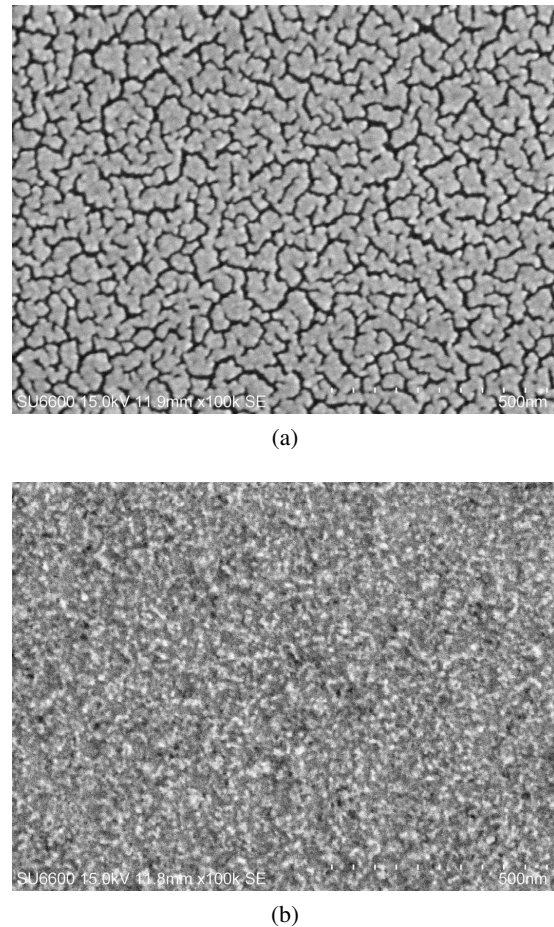

(a)

(b)

Fig. 1. Surface of the thin Au films deposited on Si substrate without thermal processing: (a) self-cracking (dewetting) of Au film on the oxidized silicon surface, (b) continuous Au film on the unoxidized silicon surface.

In case of Si substrate without oxide, the SSD process does not occur as easily as in the previous case (Fig. 3a). Even the second processing of the same sample at higher temperature cannot improve the morphology of the self-organizing Au structures (Fig. 3b). The islands have irregular shapes and a much larger sizes. The reason for this could be the creation of a eutectic thin layer between Au and Si, as mentioned above.

3.3.   Definition of Au islands parameters after RTP treatment

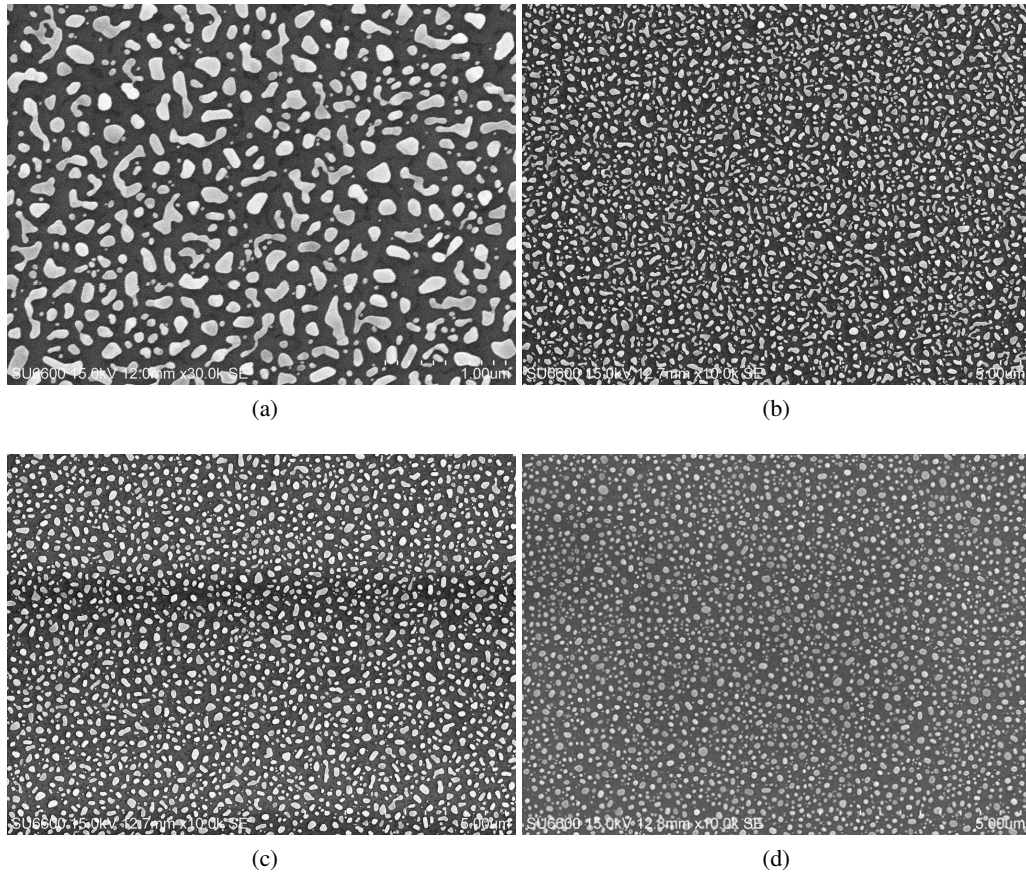SEM images were analyzed by ImageJ software (Public domain Java Image Processing

Fig. 2. Dewetting Au films process on Si/SiO$_2$ substrates after RPT at: (a) 600 °C 3 min, (b) 700 °C 3 min, (c) 800 °C 1 min, (d) 900 °C 1 min.

Table 1. Parameters of Au droplets calculated by ImageJ software.

Au – 5 nm	Area [10^{-3} μm^2]	Radius [nm]	Roundness	Density [μm^{-2}]	Coverage [%]
600 °C 3 min	7.1±7.9	47.5	0.68±0.18	36.7±3	26.3
700 °C 3 min	8.5±9.1	52.0	0.70±0.19	28.8±0.6	25.1
800 °C 1 min	10.7±9.1	58.4	0.72±0.16	22.0±0.7	23.5
900 °C 1 min	6.0±6.2	43.7	0.86±0.28	37.3±2.4	21.9

Program) which allows one to determine parameters of the particles, such as quantity, area or roundness (describes the shape of the particles according to 4*area/π*(major axis)^2). Some example-data are shown in Table 1. The radius values were calculated from the islands areas under assumption of an ideal case that the islands are circular.

In Fig. 4, stages of an image treatment by ImageJ software are shown as an example.

3.4. Ga$_2$O$_3$ nanowires observation

Morphology of synthesized gallium oxide nanostructures depends on the kind of gallium source. The manual lubrication of liquid gallium with a quartz stick on the silicon support surface with gold nanostructures is unsatisfactory: independently of the treatment of silicon substrates. We suppose that gallium layers were always too thick and neither the fact that silicon was
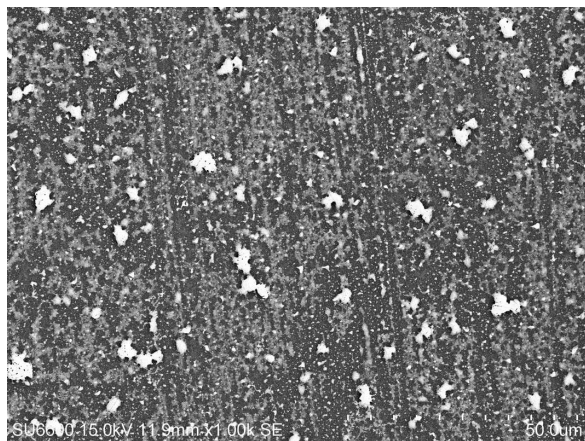
(a)
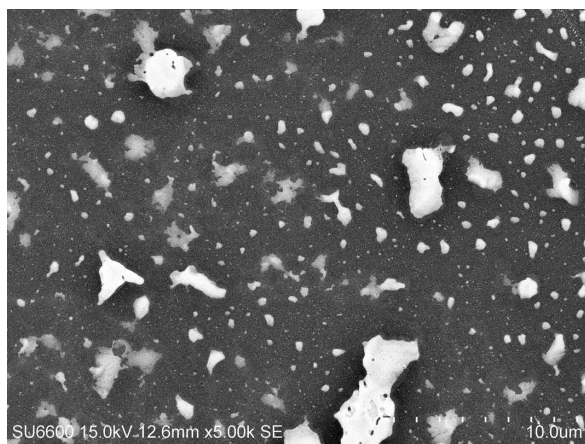
(b)

Fig. 3. Surface morphology of the sample (Si) T20 after RTP at: (a) 600 °C and (b) 900 °C.

oxidized or not, nor the kind of thermal treatment of gold film and gallium oxide synthesis temperature had no influence on the result. No nanowires, nanoribbons or nanobelts on the substrate have been found. The typical artefacts shown in Fig. 5 are bulky oxide crystals, sometimes with dendritic growth beginning (Fig. 5a and Fig. 5b). Fig. 5d to Fig. 5f show gallium oxide crystals, which grew on gallium droplets. Perhaps, if the synthesis lasted many hours (e.g. day and night), it could be enough to achieve a good result.

Two other gallium supply methods gave better results. Surfaces of the supports became covered by white fur of oxide nanostructures (Fig. 6). The nanowires and remaining nanostructures are

several tens of micrometers in length. A part of them creates ribbons or belts, a few micrometers wide. We have not observed the influence of silicon carrier orientation on the order of nanostructures growth.

3.5. X-ray measurements

X-ray spectra of the as-synthesized β-Ga$_2$O$_3$ show a plenty of sharp diffraction peaks in the patterns of measured samples (Fig. 7). The strongest dominant signals can be assigned to two planes: (1 1 1) and (0 0 2). Therefore, it is difficult to determine which growth direction is preferable: [1 1 1] or [0 0 2]. Independently of this consideration based on the obtained results, the β-Ga$_2$O$_3$ crystal phase has been identified which is described in JCPDS# 11-0370.

A comparison of example spectra of as-synthesized β-Ga$_2$O$_3$ is shown in Fig. 8. All data come from the samples prepared by B (T29a and T29b) and C (T30) methods of gallium supply (mentioned in the Section 2.2).

In addition, the average sizes of the crystallites for two lattice planes – (0 0 1) and (1 1 1) – were determined. The peaks are located at positions: 15.71° and 35.17°, respectively. For this calculation, the Scherrer's equation [9] was used:

$$d = \frac{0.9 \cdot \lambda}{\beta \cdot cos(\theta)} \tag{1}$$

where λ is the wavelength of the X-ray radiation, β is the full width at half maximum of the peak from which the crystallite size is determined and θ is the Bragg angle of the considered diffraction peak.

The average sizes of the Ga$_2$O$_3$ nanowires and nanobelts are presented in Table 2. The uncertainty of Scherrer's equation depends on the value of β, and for this range of crystallite size it is 5 % [10]. Moreover, the d-spacing of (1 1 1) and (0 0 1) lattice planes have been specified. These values for not stressed crystal are 5.64980 Å and 2.549420 Å, respectively.

3.6. Photoluminescence of GaONWs

Fig. 9 depicts photoluminescence spectra of the GaONWs at room temperature. The samples were
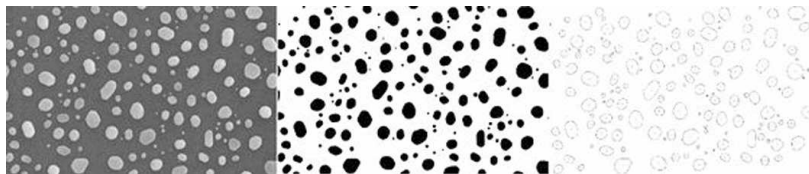
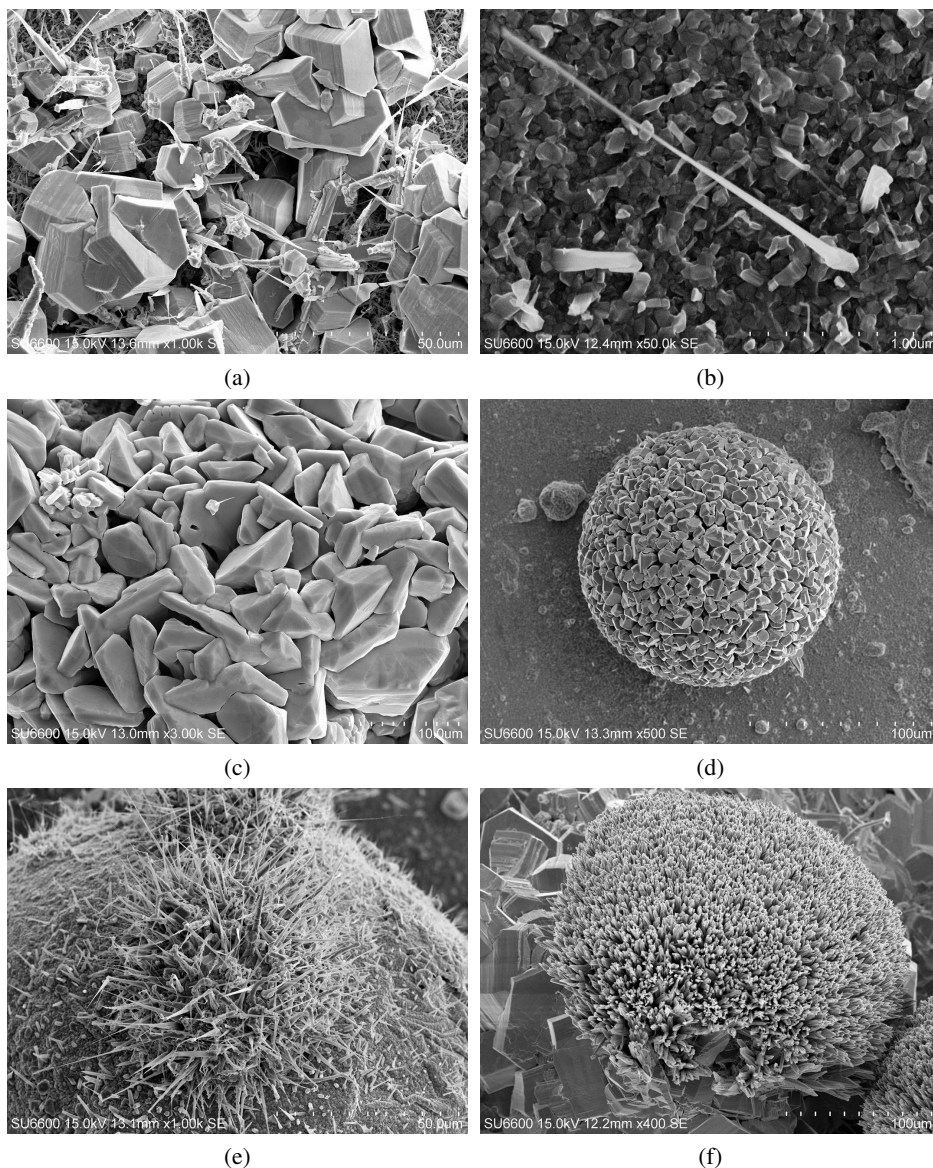Fig. 4. Module of ImageJ software for particles analysis; threshold 100 nm^2.

Fig. 5. SEM images of typical Ga$_2$O$_3$ artefacts caused by too thick gallium films.

excited by 213 nm CryLaS laser (shown on the left side of the diagram). One can observe strong blue emission with the signal at ∼391 nm (∼3.2 eV). Structures T28 and T30 were made by "C" method of synthesis, while for preparation of T29b "B" method was used (mentioned in Section 2.2). Very interesting is the fact that silicon substrates used for samples T29 and T30 were without oxide layers,

(a)

(b)

(c)

(d)

(e)

(f)
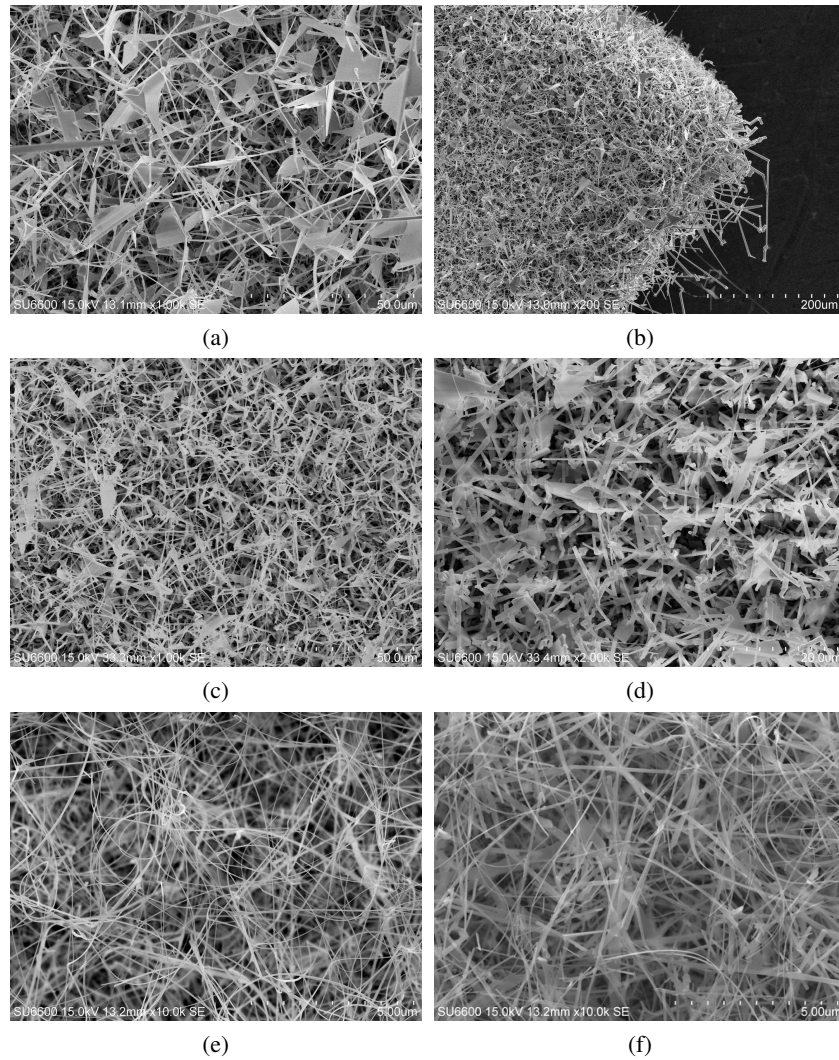
Fig. 6. SEM images of Ga$_a$O$_3$ nanostructures with various morphology.

Table 2. The average sizes of the Ga$_2$O$_3$ nanowires and nanobelts.

Sample ID	Size in [0 0 1] direction [nm]	Size in [1 1 1] direction [nm]	d-spacing (0 0 1) [Å]	d-spacing (1 1 1) [Å]
T30	110	278	5.72251	2.56263
T29a	>1 µm	198	5.74910	2.57053
T29b	84	121	5.71297	2.56178

and their gold thin films were not treated by RTP. Most likely, the rapid increase in temperature during inserting into the oven is sufficient to Au thin layer dewetting.

The signal which can be observed at ∼391 nm has the same position for all samples independently of the synthesis method or type of Si substrate surface treatment (oxidized or not oxidized prior gold films depositions and using or not RTP processing).

4.   Conclusions

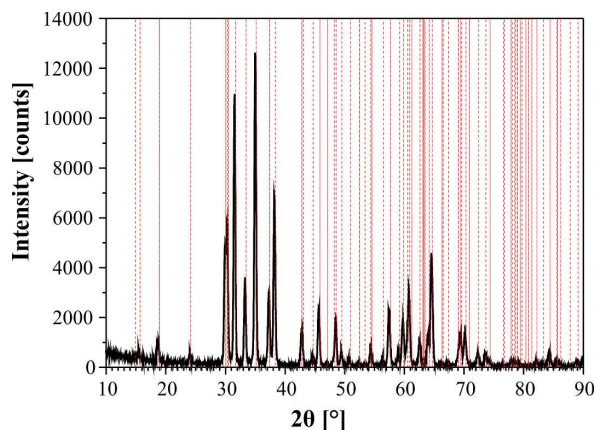In summary, thermal synthesis of monoclinic gallium oxide Ga$_2$O$_3$ at atmospheric pressure has

Fig. 7. Typical X-ray diffraction spectrum of as-synthesized β-Ga$_2$O$_3$ (sample T30). Dashed lines come from JCPDS# 11-0370.
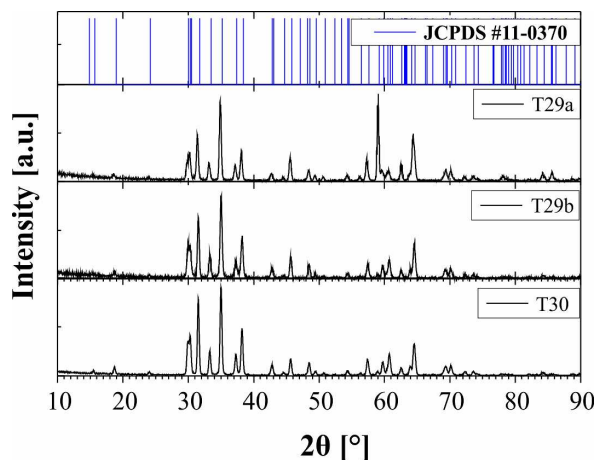

Fig. 8. Composition of X-ray spectra and data from JCPDS# 11-0370.

Fig. 9. Room temperature PL spectra of β-Ga$_2$O$_3$ nanowires.

probably not necessary: Au films rebuilding takes place during Si substrates heating. It was found that very good results were obtained for the samples without thermal treatment of Au film as well those which were subjected to RTP. Reconstruction (dewetting) of the Au layer, probably takes place when the sample is placed in the hot zone of a furnace.

Acknowledgements

References

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been performed using different methods of gallium supply. Three methods of gallium supply were tested. Manual lubrication with a quartz stick gave unsatisfactory results. We suppose that if this synthesis process (A type) lasted many hours, it could be successful. Two other methods of gallium supply are very promising. Our as-synthesized gallium oxide β-Ga$_2$O$_3$ nanostructures (nanowires, nanoribbons/nanobelts) have the length up to one hundred micrometer. Monoclinic space structure of the synthesized oxides, i.e. β-Ga$_2$O$_3$, has been confirmed. Dominant growth axes are [1 1 1] and [0 0 2]. From the PL spectra it can be concluded that preliminary RPT processing of gold films is
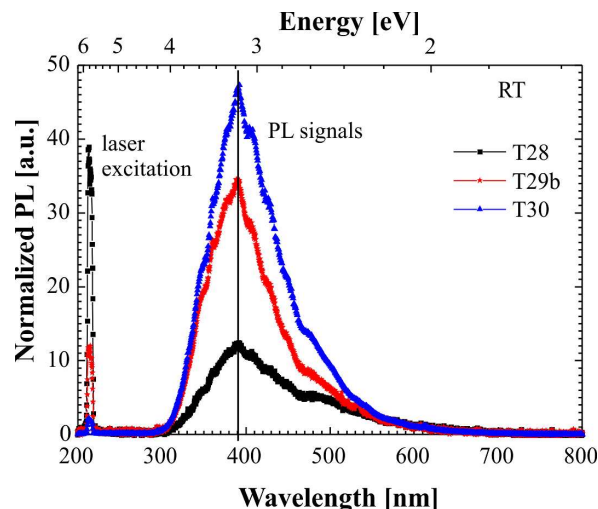
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