

Synthesis and characterisation of Ga₂O₃ nanowires

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Abstract: Ga₂O₃ nanowires (NWs) have been fabricated according to a vapour-liquid-solid growth mechanism. The synthesised NWs have been structurally and optically characterised using X-ray diffraction, Scanning and Transmission Electron Microscopy and photoluminescence.

I. INTRODUCTION

Gallium (III) oxide is a metal oxide with an appearance of white crystalline powder. It presents five crystalline structures, among which the monoclinic form β -Ga₂O₃, is the most stable chemically and thermally. This structure has semiconducting properties, a wide band gap of 4.9 eV and a melting point of 1900°C.

Moreover, it exhibits conductive and photoluminescence properties. It has applications as a transparent conducting material, in optoelectronic devices and in high temperature gas sensors.

We are interested in nanostructured material with nanowire (NW) morphology because its properties differ from bulk materials. The main advantage of using NWs for gas sensing is the enhancement of the surface to volume ratio, increasing the interaction area. In this work we have focused only on the synthesis of the β -Ga₂O₃ nanowires.

NWs can be fabricated by different methods, like solution-phase synthesis [1] or non-catalytic growth [2]. In this work, however, they were fabricated by the VLS growth mechanism, which was first reported by Wagner and Ellis [3]. It consists in the vapour transport of the precursor, its diffusion into a liquid droplet of catalytic material, its supersaturation and its precipitation, giving rise to nanowires.

The Ga₂O₃ synthesised NWs have been analysed by scanning (SEM) and transmission (TEM) electron microscopy, X-ray diffraction (XRD) and photoluminescence (PL) to gain information of the crystallographic and chemical properties of the NWs as well as the presence of lattice defects at their inside.

Before beginning the process, to ensure that the tube is totally clean, we heat it to 1000 °C and pass oxygen and argon through it during 6 hours.

The experimental process starts with the precursor material preparation: pure gallium (III) oxide (99.99%) nanopowder was mixed with graphite powder in a 2:3 weight proportion in an agate mortar. The graphite is used to decrease the melting point of the gallium oxide powder according to the carbothermal reduction process [4].

The process continues with the substrates preparation, which are 5x5x0,5 mm³ pieces cut from a 10 cm diameter Si wafer, with a 0.5 μ m thick SiO₂ layer. These substrates were Au sputter-covered for 5 or 20 seconds, which should give rise to a thin and discontinuous Au layer.

Each experiment contains 0.25 g of the precursor material; in the first place we prepare five small alumina boats. The first of them will contain the mixture powder, and on the other four we will lay ten silicon samples on each one (five sputtered with gold for 5 seconds and five for 20 seconds).

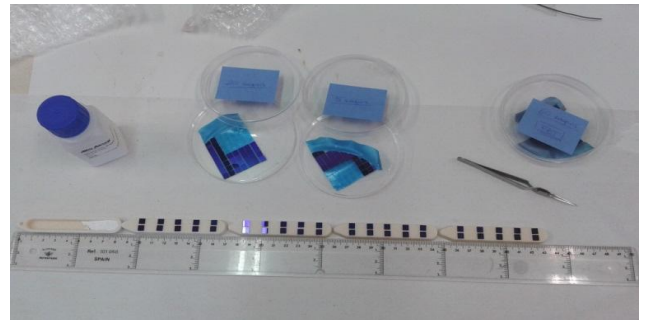


FIG. 2: Alumina boats with white Ga₂O₃ powder (first left) and with silicon samples (the other four).

II. EXPERIMENTAL PROCEDURE

The VLS mechanism used to synthesize the gallium oxide NWs, carried out by chemical vapour deposition (CVD) in a quartz tube furnace, consists in various steps, which are schematically represented in Figure 1.

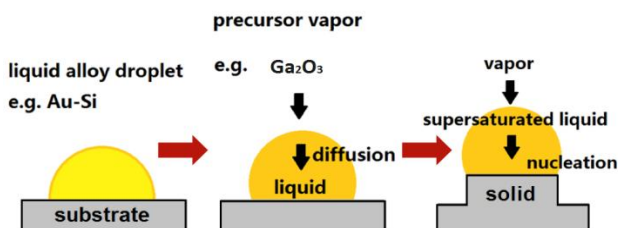


FIG. 1: Sketch of the different steps of the VLS process.

The five boats are introduced in the quartz tube of the furnace, as shown in figure 3, which is controlled by a computer, and allows independently setting the temperatures in three zones and several steps. Its configuration limits the temperature difference among the zones to about 150 °C. Several experiments with different growth temperature, flow and gas mixtures were done.

As first step, which takes 30 minutes, we raise the first and second furnace's zone temperatures linearly to between 750 and 950 °C, leaving the third zone at ambient temperature. During this step the gold catalyst will agglomerate into small droplets, few tens of nm in diameter. As second step, the temperature is maintained at the growth values during one or two hours depending on the experiment. The third step is the cooling down up to room temperature.

The system is kept at atmospheric pressure and increases to 780 mmHg in the second step due to the flow of 100 ml/min of pure argon gas, 5 N quality, into the tube during the whole experiment.

Then we ensure the tube is airtight to avoid leakages, we close the furnace and pump the tube down to 10 Pa to start the growth from a clean ambient.

At this moment we can set all the parameters on the software and start the process; the furnace will heat up and argon will flow into the tube increasing the pressure. Once the furnace reaches a temperature of about 600 °C the powder will start to evaporate, the gas flow will transport it and will be deposited on the samples.

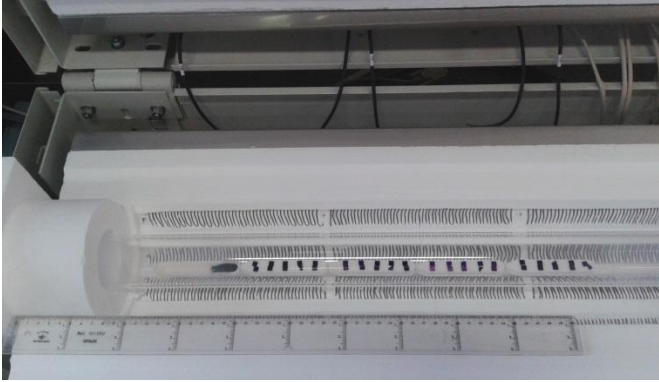


FIG. 3: Boats inside the tube in the furnace.

III. RESULTS AND ANALYSIS

A. Scanning electron microscopy SEM

All our samples have been analysed by the Jeol-7100 Field Emission SEM, operated at 20 KeV.

We have used the secondary electrons generated by the primary beam to form the images, which give information of the sample's surface topography and, to a certain extent, of the composition.

The observed samples reveal NWs with the gold catalyst observable as a bright spot at the end of the wire, confirming the VLS mechanism. Some nanoplateaus also found are observables in figure 4. Furthermore, NWs were found to grow vertically and horizontally depending on the source-substrate distance [5].

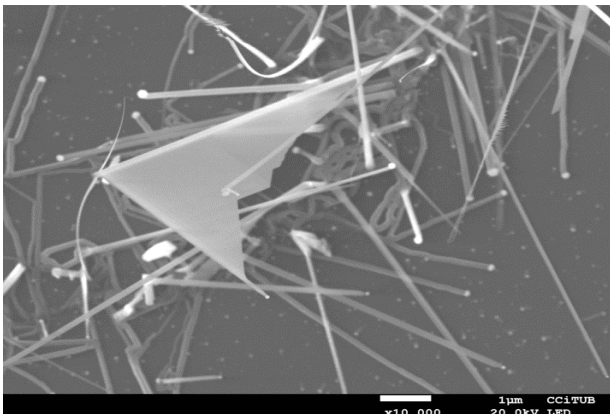


FIG. 4: Ga₂O₃ nanoplateau on top of NWs.

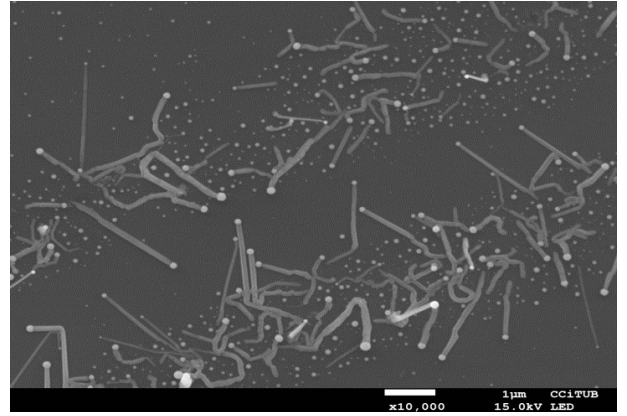


FIG. 5: Horizontal Ga₂O₃ NWs.

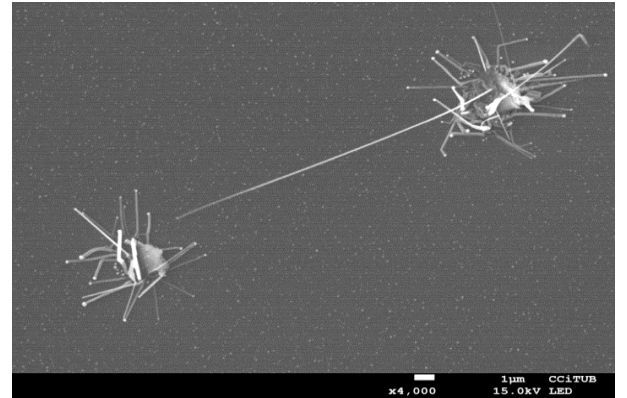


FIG. 6: Vertical NWs accumulated in clusters.

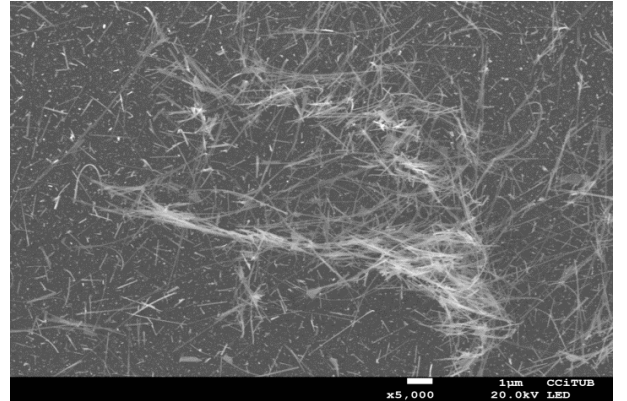


FIG. 7: Spiderweb shaped NWs.

The NWs dimensions were measured, giving lengths between 1 and 20 μm and diameters between 10 and 50 nm. Figures 4, to 7 show images obtained from the NWs. Some unreacted gold droplets are also seen as white spots on the substrate.

B. Photoluminescence PL

PL is the spontaneous emission of light from a material under optical excitation. The excitation energy and intensity are chosen to probe different regions in the sample.

We analysed the luminescence emission of two of our samples, one with vertically (5 s) and the other with horizontally (20 s) grown NWs, being excited with a HeCd

laser that emits UV light (325 nm), with an estimated power density at the sample of 2 mW/cm^2 , and the measurement range is between 360 and 850 nm.

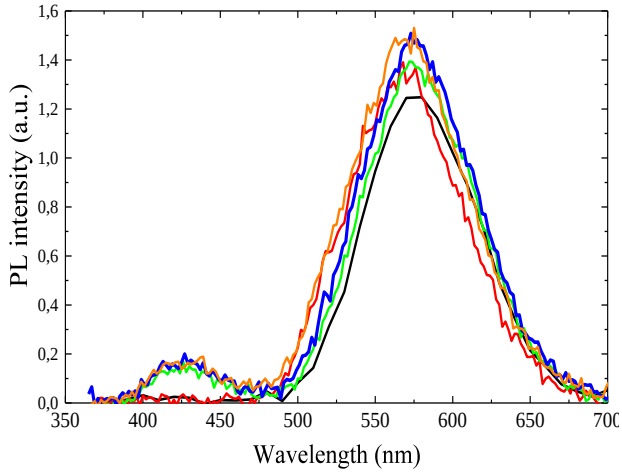


FIG 8: Spectra from different spots of the 20 s sample.

Figure 8 shows the spectra collected from several different positions of the spot over the 20 s sample, corresponding to horizontally grown NWs. Two different bands can be observed, the first one, centered at about 578 nm (yellow), is the strongest one and is present in all the spectra, meaning that is quite uniform along the sample surface. A weaker band centered at about 428 nm (blue) does appear only in some measured regions of the surface, far from the center of the square sample. The shape is Gaussian in both cases and the width of each band is compatible with other reported experiments [6], where the PL bands have been assigned to exciton recombination at defects sites, which may be oxygen vacancies or more complex ones, but related to oxygen-vacancies.

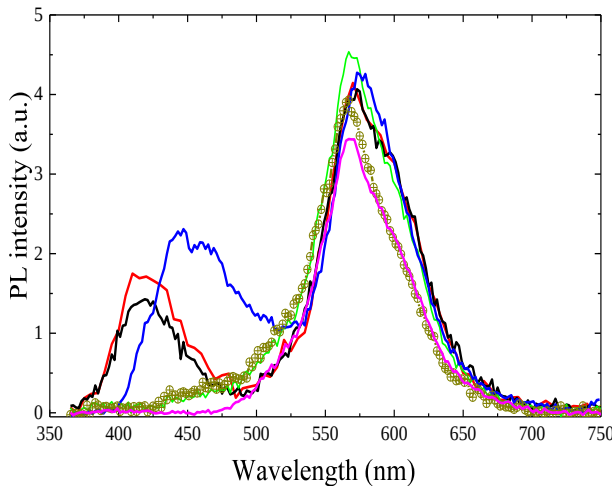


FIG 9: Spectra from different spots of the 5 s sample.

Figure 9 shows the spectra collected from several different positions of the spot over the 5 s sample. The PL emission of this sample is much stronger and the two bands have almost comparable intensity, meaning that the density of emitting blue centers is almost the same as the one of the yellow emitters [7].

A Gaussian de-convolution of the yellow band, indeed, reveals that it is formed by two bands, and the main one is the one found in the sample 20s, as to say, the band centered at 578 nm. This is further confirmed by the width of the band, which corresponds to the value found in the previous sample. Surprisingly, the additional band is quite weak and narrow, but somehow is related to the whole nanowire population, as it is present at each measuring point, as the band at 578 nm, and its relative intensity respect to that one is also quite constant.

This uniformity in the ratio among the two sub-bands seems to indicate that both have a similar origin.

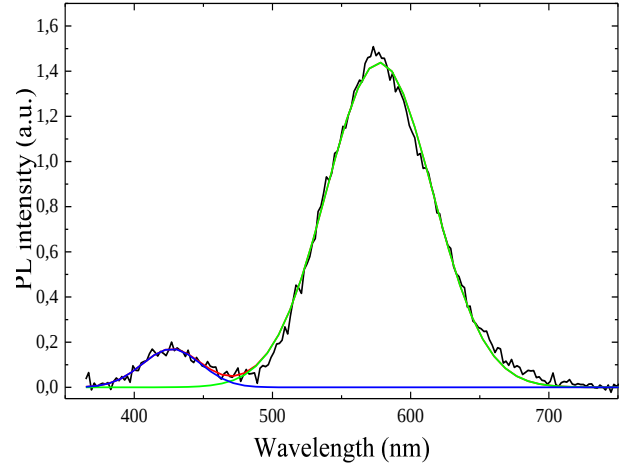


FIG 10: De-convolution of the 20 s sample.

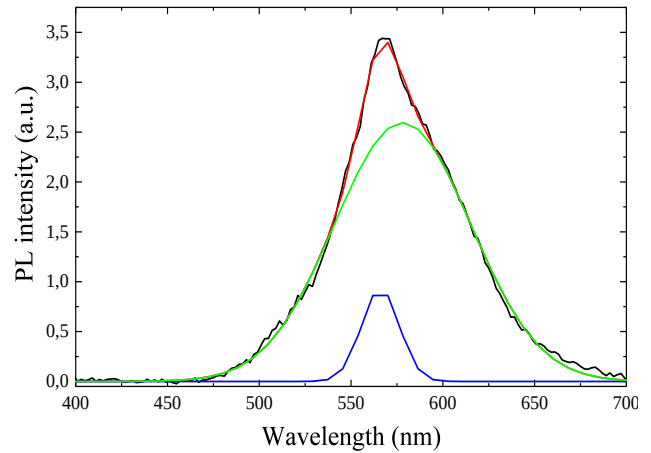


FIG 11: De-convolution of the yellow line of the 5 s sample.

Figures 10 and 11 show the theoretical de-convolution of the 20 s sample spectra and of the yellow line of the 5 s sample spectra, respectively.

C. X-ray diffraction XRD

Three of our samples (one sputtered for 5 seconds and two for 20 seconds, corresponding to vertical and horizontal NWs) have been analysed with a PANalytical X'Pert PRO MRD diffractometer, which emits X-Rays coming to the $K\alpha$ line of Cu ($\lambda=1.541874\text{\AA}$), with a power of 45 kV and 40 mA.

First measurements are done under grazing incidence $\theta=0.5^\circ$, a parabolic mirror was needed in the primary beam and a parallel plates collimator in the secondary beam. In this case sample should be rotated to avoid peaks due to the silicon substrate. This configuration is used in order to increase the interaction of the thin Ga_2O_3 nanowire at the surface with the incident X-rays. Figure 12 shows a spectrum collected under these conditions.

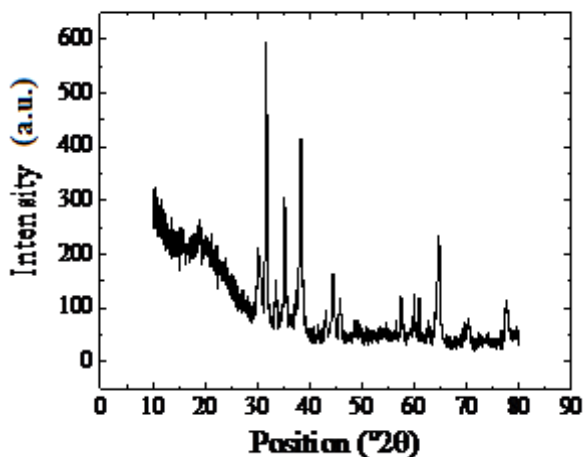


FIG 12: Grazing incidence diffraction pattern.

Second measurements are performed in conventional conditions, a parabolic mirror in the primary beam and divergent optics in the secondary beam. In this case micrometric shifts in the diffraction peaks position have appeared. Figure 13 shows a spectrum collected under these conditions, however peaks haven't appeared owing to the fact that the interaction of the Ga_2O_3 with the X-rays was not enough.

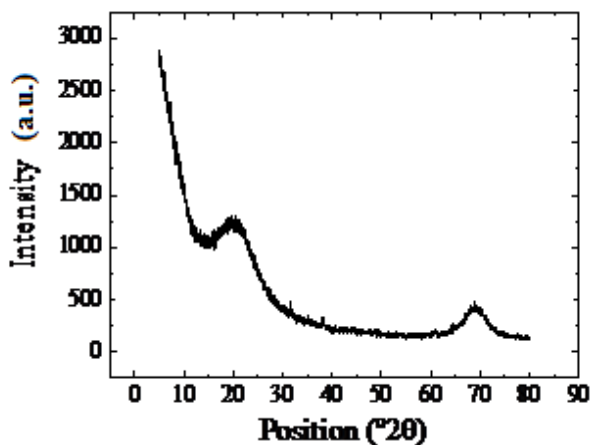


FIG 13: Conventional conditions diffraction pattern.

We can compare the spectra obtained with the theoretical one shown in figure 14, which contains 55 peaks with different intensities I (proportional to the number of X photons detected), in incident angular positions 2θ among 15° and 89° . Effectively the peaks observed in figure 12 are the same that the peaks expected in figure 14. Besides, additional peaks have appeared due to the gold droplet or the silicon substrate.

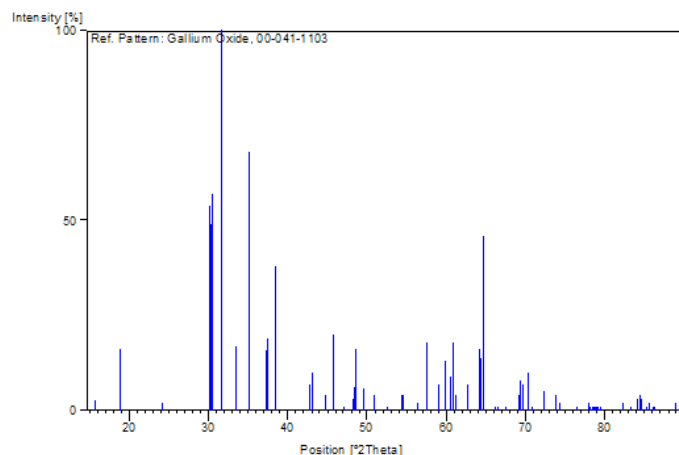


FIG 14: XRD peaks of Ga_2O_3 reference material.

From the peaks obtained we can deduce that gallium oxide has a monoclinic crystalline structure with the distances $a=12.2270 \text{ \AA}$, $b=3.0389 \text{ \AA}$, $c=5.8079 \text{ \AA}$ between its atoms and the angles $\alpha=90^\circ$, $\beta=103.82^\circ$, $\gamma=90^\circ$ in the lattice vertexes and a density of 5.93 g/cm^3 .

D. Transmission electron microscopy TEM

The TEM experiments were carried out in a Jeol 2100 microscope operated at 200 kV and equipped with an Electron Dispersive X-Ray (EDX) detection system.

For preparation of a sample of NWs to be analysed by TEM, one of our 20 seconds sputtered gold samples that contains NWs is submerged in a recipient with hexane C_6H_{14} and then exposed to ultrasounds during 15 seconds. With this process NWs are detached from the substrate and are dispersed in the C_6H_{14} liquid. Afterwards, we take a micropipette and deposit small droplets, which contain NWs, onto a copper grid covered by a holey carbon film. Once the grid dries, it can be observed with the TEM.

Figure 15 shows a TEM image of a single Ga_2O_3 NW with its gold droplet at the tip, and figure 16 shows the electron diffraction pattern of the NW. This diffraction pattern consists of spots that denote the monocrystalline nature of Ga_2O_3 .

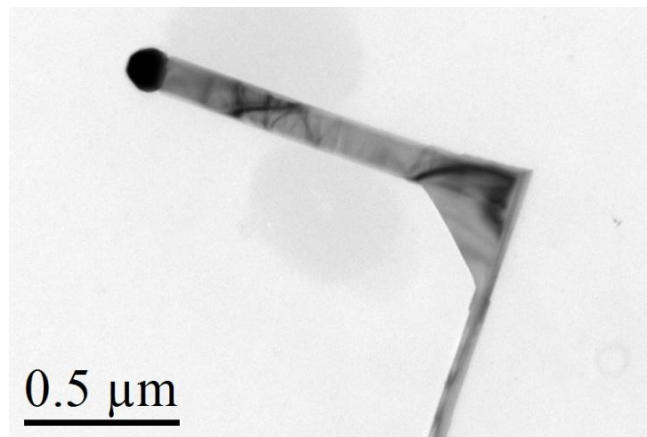


FIG 15: Ga_2O_3 NW observed with TEM, showing the Au catalyst (dark in the image).



FIG 16: Electron diffraction pattern of the NW of Fig. 15.

Moreover, the high energy electrons, interacting with the sample, can produce the emission of X-rays characteristic of the different elements present in the sample and, thus, can provide information of the chemical composition. In figure 17 we can see the spectrum obtained for Ga_2O_3 . As expected, it shows gallium and oxygen peaks and in addition carbon and copper peaks from the grid.

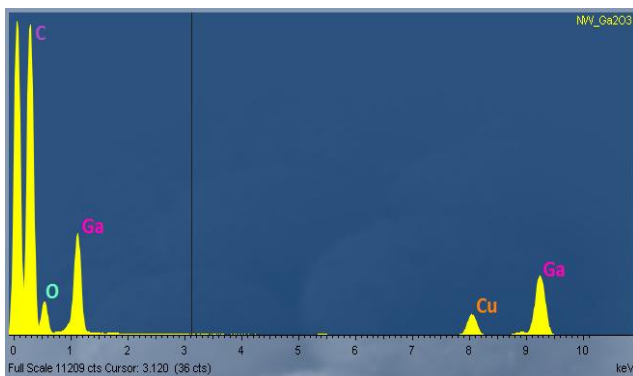


FIG 17: EDX spectrum of Ga_2O_3 NW, showing characteristic X-ray peaks corresponding to the sample's material.

IV. CONCLUSIONS

In this work the growth of gallium oxide NWs via VLS method by CVD using a quartz tube furnace has been carried out. The optimal conditions were obtained at a growth temperature of 950 °C during 1h, using argon as carrier gas.

While changing growing conditions, additional nanostructures have been formed, like nanoworms or nanoplateaus.

The synthesised NWs have been structurally and optically characterized, confirming their monocrystalline nature and the presence of oxygen vacancy-related defects in their body. The obtained results are in agreement with other authors [8].

I would like to conclude by saying that this work has allowed me to go into detail about some techniques learned in some subjects of the degree like *micro and nanotechnology* and *solid state physics*.

V. ACKNOWLEDGEMENTS

First of all I would like to acknowledge Guillem Domènech, who has taught me how to develop all the Ga_2O_3 fabrication experimental procedure, and also has always helped me with it patiently even when things went wrong. Secondly I acknowledge my advisor Albert Romano to guide me on how to do all this project.

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