DEPENDENCE OF GALLIUM NITRIDE NANOWIRES
PROPERTIES ON SYNTHESIS PRESSURE AND TEMPERATURE

M. Danilyuk1*, A. Messanvi2

1Belarusian State University of Informatics and Radioelectronics, P. Brovki 6, Minsk, Belarus
2Institute National des Sciences Appliquées de Rennes, Rennes, France
*e-mail: maxim_danilyk@mail.ru

Abstract. The main task of the investigation was to perform the synthesis of gallium nitride nanowires using a low pressure chemical vapor deposition system. The nanowires were grown via a catalyst-assisted reaction based on the vapor-liquid-solid mechanism. The influence of catalyst, temperature and pressure on the growth of gallium nitride nanowires was explored. Optimal results were obtained at a temperature of 750 °C and at a pressure of 400 to 500 mTorr.

1. Introduction

Next generation of integrated circuits could be realized according to a bottom-up approach in contrast with the current top-down paradigm. This approach would be based on the assembly of nano-size structures such as nanowires, nanotubes or nanobelts. In particular, nanowires have shown promising properties and are envisioned as building blocks for nanoelectronic and photonic devices. Single nanowire LEDs, lasers and transistors have already been demonstrated opening the path to the realization of functional devices based on one-dimensional structures. Among the various kind of nanowire systems investigated today, Gallium Nitride (GaN) nanowires are of particular interest because this III-V semiconductor has already shown interesting properties in a bulk form. GaN is well-known for its resistance to temperature, strain and high electric fields. As a result, it is a material of choice for high power/high temperature applications. In addition, the optical properties of GaN are useful for optoelectronic device operating at ultraviolet and blue wavelengths [1].

GaN has interesting optical properties based on its direct and wide bandgap of 3.44 eV at room temperature [2]. With a direct bandgap, GaN is a natural candidate for light emission and detection (unlike silicon which cannot be used for optical applications because of its indirect bandgap). Besides, GaN belongs to the family of wide bandgap semiconductors similar to AlN (6.2 eV) and InN (1.9 eV). Its large bandgap places it as a material of choice for optoelectronic devices that operate in the blue and UV part of the spectrum which for a long time were inaccessible.

Alloying GaN with InN or AlN enables creating compounds of different compositions that could potentially cover the entire range of the visible spectrum from the infrared to the ultraviolet [3]. Addition of indium shifts the emission of GaN towards the red part of the spectrum while aluminum incorporation results in a blue-shift of the emission. Because of this ability to tune the emission wavelength by varying the composition, III-nitride alloys (Al-In-Ga-N) are very attractive materials for light emitting devices. Applications of this bandgap engineering are the green and blue LEDs made of InGaN as well as blue and ultraviolet laser diodes and detectors.

© 2014, Institute of Problems of Mechanical Engineering
Furthermore, GaN is well-known for its superior electrical properties and resistance to temperature and strain. GaN has above average mechanical and thermal stability. Because of its wide bandgap, GaN becomes intrinsic at a much higher temperature than Si or GaAs. This allows the devices made from GaN to be operated in high temperature environments. GaN benefits also from a high thermal conductivity (compared to Gallium Arsenide) that helps heat dissipation. Another feature that shows the strength of GaN material is its high breakdown field, estimated to be superior to 4 MV which is equivalent from ten to sixteen times the breakdown voltage of GaAs and Si respectively.

Last but not least, GaN possesses remarkable electronic properties. It has high electron mobility and its saturated drift velocity reaches $3 \cdot 10^7$ cm/s, three times superior to that of silicon [2, 4]. Because of these outstanding transport properties, GaN is widely used in high frequency applications. For instance, this potential for elevated mobility is exploited in High Electron Mobility Transistors (HEMT) based on AlGaN/GaN heterostructures. If we consider the combined figure of merit for high temperature/high power/high frequency applications, GaN is the best semiconductor in this category followed closely by SiC [2].

2. Experimental part
The nanowires were grown via a catalyst-assisted reaction based on the vapor-liquid-solid mechanism [5]. The following experiments were performed with nickel as the catalyst as successful growth of nanowires was obtained with this metal. Silicon monocrystal wafers with orientation (100) were utilized as substrates. The first growth parameter to be varied was a temperature. In our case, four temperatures were tested: 700 °C, 750 °C, 800 °C, and 850 °C. SEM images below show typical nanowire morphology obtained for each temperature.

Fig. 1. SEM images of GaN nanowires obtained at different growth temperatures.
Temperature is a very important parameter to tune in nanowire growth as changes of a few tens of degrees have been reported to produce nanowires with very different morphologies. It can clearly be seen that temperature has a stringent impact on the nanowires morphology. At the highest temperatures (850 °C), the nanowire yield was extremely low and the rare nanowires that could be observed had a short length of a few hundreds of nanometers. However their diameter was quite small, between 20 and 50 nm. Most of the substrate was covered with 3-D nanostructures exhibiting triangular faceting as shown in Fig. 1a. It appeared that the edges and corners of these irregular islands served as nucleation sites for the growth of the few nanowires observed; the nanowires emerged laterally from the already grown nanostructures.

To examine the influence of pressure on the nanowire morphology, the temperature was fixed at 750 °C which yielded promising results in terms of density and dimensionality. The pressure was varied from 250 mTorr to 600 mTorr. SEM images below show the typical morphology of the nanowires obtained for each pressure.

![SEM images of GaN nanowires obtained at different pressures.](image)

**Fig. 2.** SEM images of GaN nanowires obtained at different pressures.

SEM observation of the nanowires showed that their morphology remained rather consistent over the range of pressures experimented (Fig. 2). From 250 mTorr to 500 mTorr, the nanowires exhibited a straight and elongated shape. Zigzag and curved shapes were also present but to a lesser extent. At the highest pressure (600 mTorr), two distinct morphologies could be observed: some nanowires exhibited a relatively smooth surface whereas others had rough surfaces with a variable diameter along their length. Apparition of stacked-cone nanowires at higher pressures could be explained by the fact that more gaseous species reached the growth interface. Therefore nanowires grew thicker and cones formed along the growth direction.
The photoluminescence (PL) spectra of the GaN nanowires were obtained under excitation at 260 nm [6]. Fig. 2 shows the PL spectrum obtained for GaN nanowires at different temperatures. For each temperature, the spectrum is characterized by two main peaks: an intense and broad peak which corresponds to the near band-edge emission and a much weaker peak centered around 300 nm. Influence of the growth temperature on the PL spectrum of the GaN nanowires is clearly visible. As the temperature increases from 700 °C to 800 °C, the emission peak becomes broader: peak fitting rises from 65 nm at 700 °C to 200 nm at 800 °C. Moreover, at 800 °C, the near band-edge emission seems to result from the overlapping of multiple peaks centered at 407 nm, 425 nm and 440 nm. A red-shift of the emission peak can also be observed with the increasing temperature from 390 nm at 700 °C to 425 nm at 800 °C. The near-band-edge peak normally located around 360 nm for GaN material is shifted towards red wavelengths for our GaN nanowires by more than 30 nm. Previous comparisons between luminescence from GaN bulk and nanowires have shown that emission from nanowires is usually broader and red-shifted due to strain as well as surface and impurity states. Therefore, the decrease in peak broadening seems to indicate that the structures grown at lower temperatures exhibit a lower density of defects than those grown at higher temperatures. Correlation between the previous observations and the nanowire morphology shows that the stacked-cone nanowires grown at 800 °C have a quite broad luminescent peak whereas the very thin nanowires grown at 700 °C exhibit a narrower emission peak; however the peak intensity in the latter case is reduced by one third.

Fig. 3. PL spectra of GaN nanowires synthesized at different temperatures.

For nanowires grown under various pressure conditions, the PL spectra exhibit a more consistent shape. This is in agreement with the observed morphology of the wires. The PL spectra present a near band-edge emission around 390-395 nm and a UV-emission centered at 300 nm. We can observe an increase in the peak intensity and width when the pressure increases from 400 mTorr to 600 mTorr; the tops of the fitted peaks go from 115 nm at 400 mTorr to 158 nm at 600 mTorr. The broadest emissions are obtained at 250 mTorr and 600 mTorr. This seems to confirm that rough surface nanowires induce peak broadening as they incorporate a higher amount of defects than smooth and thin nanowires.

These results indicate that the optical quality of 1-D GaN nanostructures can be improved by controlling their dimensions and its diameter in particular. In our case, the lowest growth temperatures (750 °C-700 °C) at which thin nanowires have been produced gave the best optical results. PL spectra at these temperatures exhibited narrower emission
peak and a reduced red-shift. However it can be observed that the decrease in peak broadening is also associated with a reduction in peak intensity.

**Effect of temperature and pressure on the Raman spectra of GaN NWs.** The Raman spectra were taken with the spectral resolution of 3 cm$^{-1}$ in the backscattering geometry at ambient conditions using a 532 nm wavelength excitation laser, in 400-850 cm$^{-1}$ range. Power, beam spot and acquisition time were identical for all the Raman spectra presented in this work. Figures 5 and 6 collected the Raman spectra reordered from the samples synthesized at varied temperatures and pressures, respectively. All experimental spectra contain two peaks centered at $\sim$565 cm$^{-1}$ and 725 cm$^{-1}$ assigned to E$_2$ and A$_1$(LO) Raman-active modes of wurtzite space group.

![Graph showing PL intensity vs. wavelength for GaN nanowires at different pressures.](image)

**Fig. 4.** PL spectra of GaN nanowires synthesized at different pressures.

![Graph showing Raman intensity vs. frequency for GaN nanowires at different temperatures.](image)

**Fig. 5.** Raman spectra of GaN nanowires synthesized at different temperatures.

In contrast to the usual observations [7] in our experiment the intensity of E$_2$ mode is weaker than that of A$_1$(LO). The influence of the low intensity ratio of $I_{E2}/I_{A1(LO)}$ on the Raman spectrum from the GaN straight nanowires was already reported by other groups [8]. The low $I_{E2}/I_{A1(LO)}$ ratio can be attributed to the fact that nanowires have a good crystallinity with dominated orientation. The similarity of all Raman spectra shapes can
indicate that crystal orientation of nanowires is identical for all experiments. We should only notice that for the sample prepared at 700 °C nanowires are less straight, according to the SEM observation, and peak attributed to the E_2 is more pronounced.

The strong dependence of the Raman scattering intensity on the sample synthesis temperature (Fig. 3) we attribute to the change in the sample morphology. Indeed, samples with higher array density (see Fig. 1) provide stronger Raman scattering intensity. However, the Raman spectra taken from the sample synthesized at varied pressures do not show strong dependence of the intensity on the sample process pressure that is in agreement with electron microscopy observation (see Fig. 2).

![Raman spectra of GaN nanowires synthesized at different pressures.]

**Fig. 6.** Raman spectra of GaN nanowires synthesized at different pressures.

### 3. Conclusion

In summary, we have performed scanning Raman and photoluminescence spectroscopy studies of gallium nitride nanowires grown by low pressure chemical vapor deposition technique on silicon substrate. The Raman spectroscopy studies show the low intensity ratio I_E2/I_A1(LO) what can be attributed to the specific crystal orientation of grown nanowires. The similarity of all Raman spectra shape indicates that crystal orientation of nanowires is identical for all experiments. The intensity of Raman scattering strongly correlated with array nanowires density. The best optical results were obtained for the samples grown at the lowest growth temperatures (700°C-750°C). PL spectra of the samples synthesized at these temperatures exhibited narrower emission peak and a reduced red-shift. The presented results indicate that the optical quality of 1-D GaN nanostructures can be improved by controlling their dimensions and its diameter in particular by growth parameters.

### References

