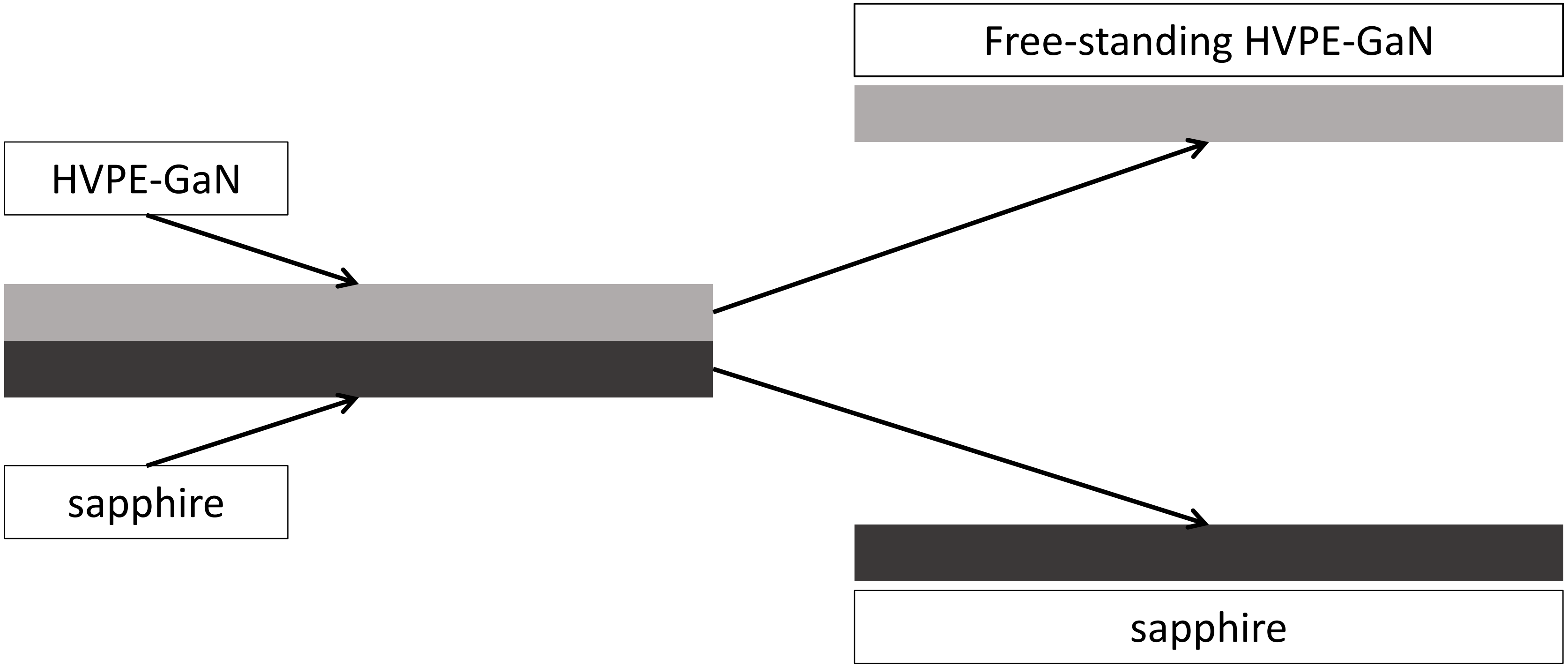
Analysis of self-lift-off technique during HVPE growth of GaN on sapphire templates with photolitographically patterned Ti mask*

Among methods used for GaN crystallization, one of the most perspective for substrates mass production seems to be HVPE. Main advantages of this technique are relatively fast growth rate and high purity of obtained material. HVPE is generally based on crystallization on a foreign material, mainly GaAs or sapphire. In case of sapphire, one of the problems is to separate the GaN crystal from the foundation.



Free-standing HVPE-GaN

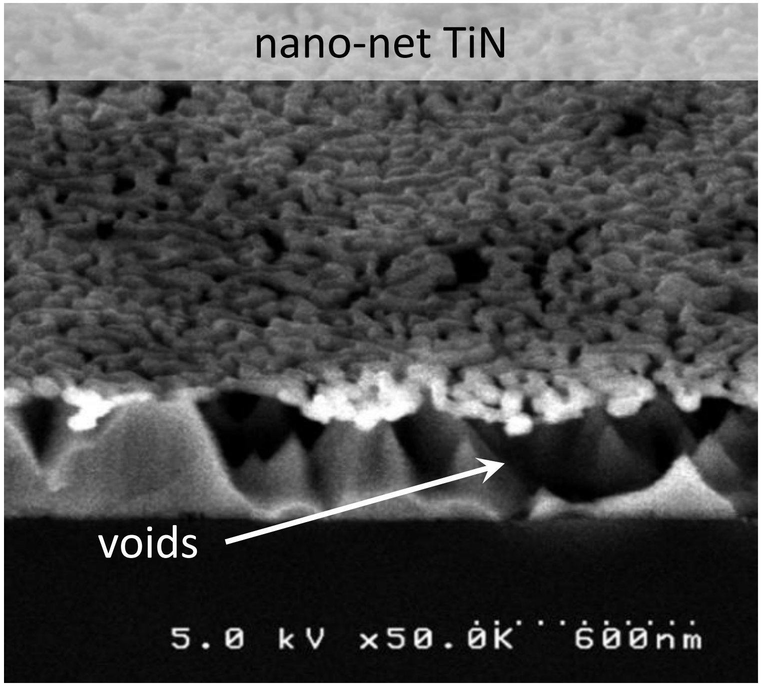
HVPE-GaN

sapphire

sapphire

*M. Amilusik et al., Journal of Crystal Growth 380 (2013) 99-105

When sapphire is used as the foundation for making GaN free-standing substrates, one of the best results is obtained with a technique known as Void Assisted Separation (VAS)*. With this approach, pioneered by Hitachi Cable, growth proceeds on a sapphire substrate coated with an ultra-thin layer of MOCVD-GaN and nanometric continuous layer of Ti. Application of such a substrate requires a nitridation process.



SEM image of the GaN template after annealing.
VAS method – Y. Oshima et al.*

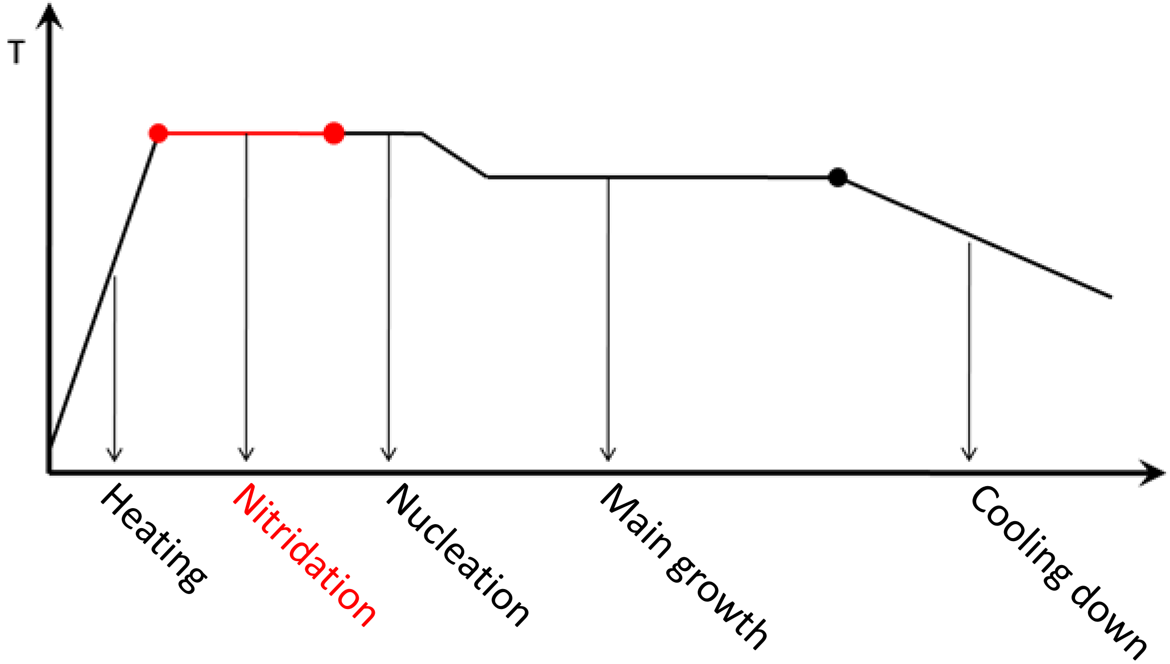
This process consists on annealing of the substrate in a gaseous mixture of H2 and NH3 at 1060°C and leads to the formation a nano-net TiN and voids in the MOCVD-GaN layer.

This nano-net and voids are helpful in the subsequent procedure to separate the new grown HVPE-GaN from sapphire.

*Y. Oshima et al.; Chapter 4 in *Technology Of Galium Nitride* edited by D. Ehrentraut et al. (Springer-Verlag, Heidelberg, 2010, ISBN 978-3- 642-04828-9)

Heteroepitaxial HVPE process in the Crystal Growth Laboratory at Unipress is based on GaN deposition on 2-inch MOCVD-GaN/sapphire templates with photo-litographically patterned Ti mask. Thickness of the MOCVD-GaN layer is 500nm. The Ti mask has openings of 3µm in diameter with a distance of 9µm between the openings.

Typical growth run included the following steps:



The nitridation process is the key to a correct and full separation of the GaN crystal from its sapphire foundation.

Experiment – optimization of nitradation

The experiments were divided in two parts. First, the nitridation duration time at fixed flows was changed:

Process no.	I	II	III	IV
Time [min]	**20**	**40**	**60**	**80**
Flow of NH_3 [ml/min]	260	260	260	260
Flow of dilution gas of ammonia - H_2 [ml/min]	100	100	100	100
Flow of carrier gas - H_2 [ml/min]	1900	1900	1900	1900

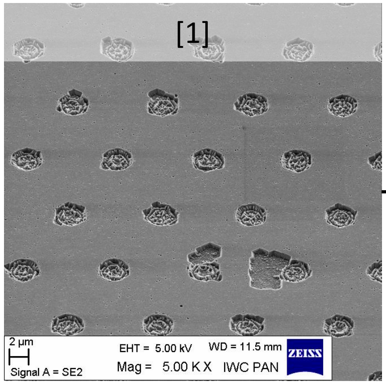
Next, the nitridation duration time was fixed and the reagent flows were modified:

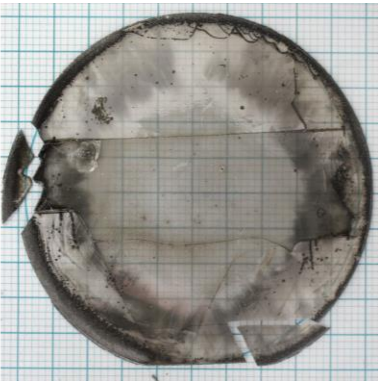
a) Flow of NH3 – 200ml/min; Flow of dilution gas – 600ml/min

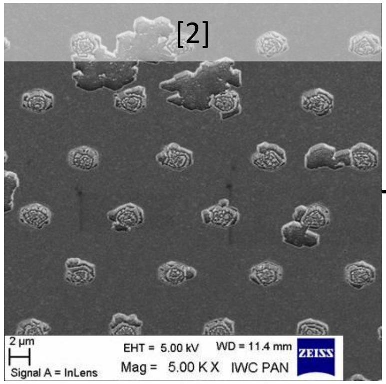
b) Flow of NH3 – 600ml/min; Flow of dilution gas – 200ml/min

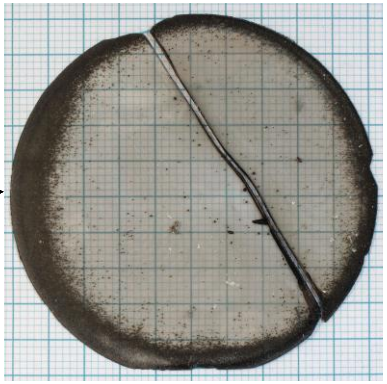
All experiments were carried out at T=1060°C and p=800 mbar.

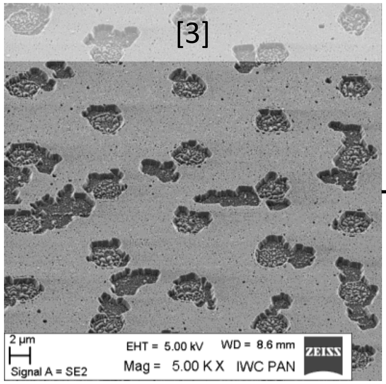
Results – first step of the experiment

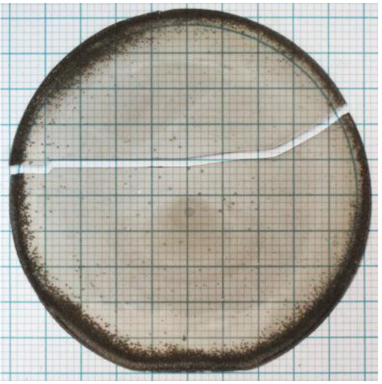

[1]

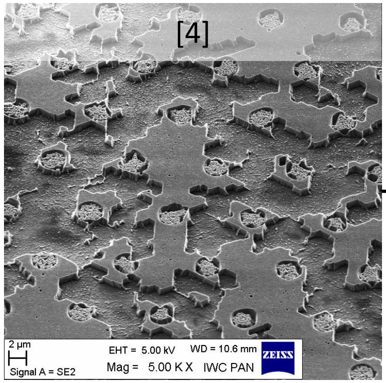



[2]




[3]




[4]

Due to an excessive degradation of the substrate and peeling off of the Ti mask the crystallization process with 80min of nitridation was not performed.

Figures [1], [2], [3], and [4] present SEM micrographs of MOCVD-GaN/sapphire substrates' surfaces after:

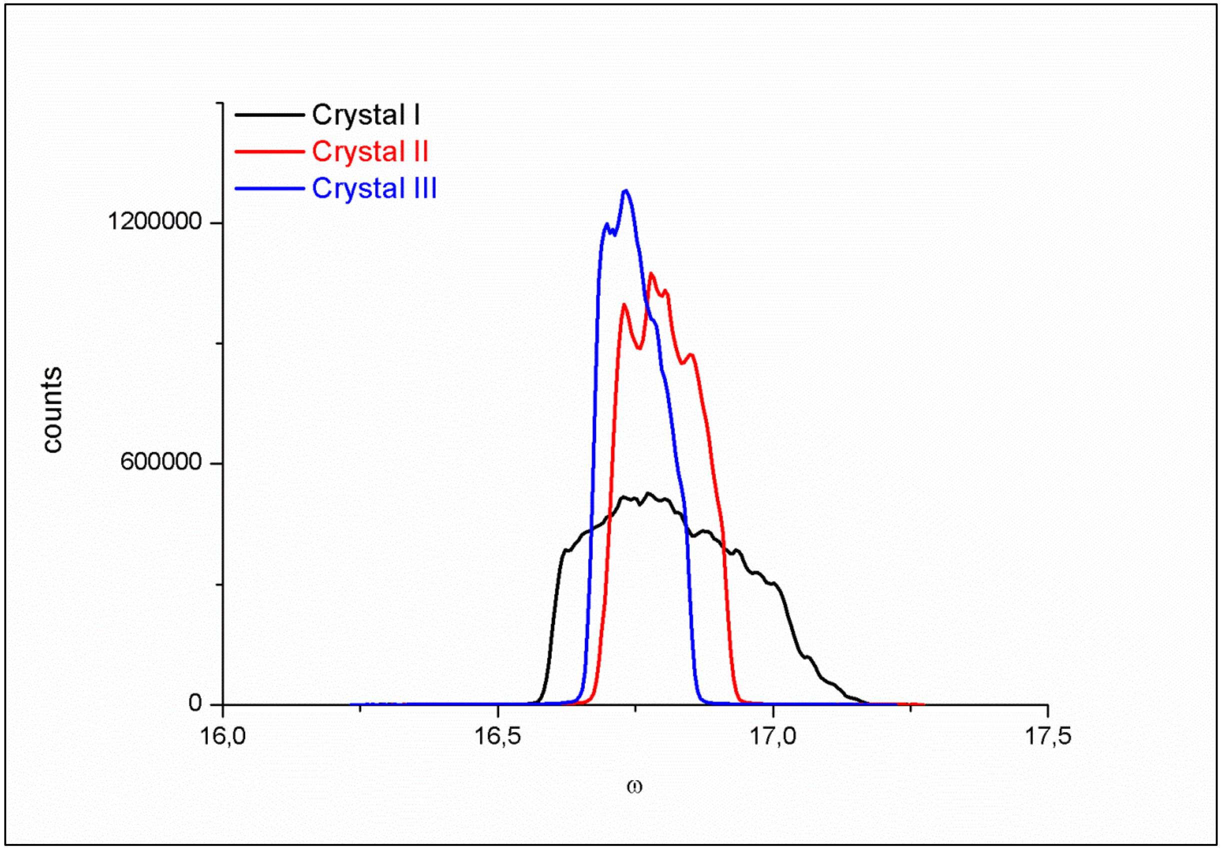
a) 20 minutes,
b) 40 minutes,
c) 60 minutes,
d) 80 minutes,

nitridation processes.

After 20min of nitridation the separation occurred during the crystal growth process (after 2h of growth). Similar situation was observed for the 40-min nitridation (after 5.5h of growth). However, if the nitridation procedure was extended to 60 min, the lift-off occurred after the growth process, thus during the cooling down procedure.

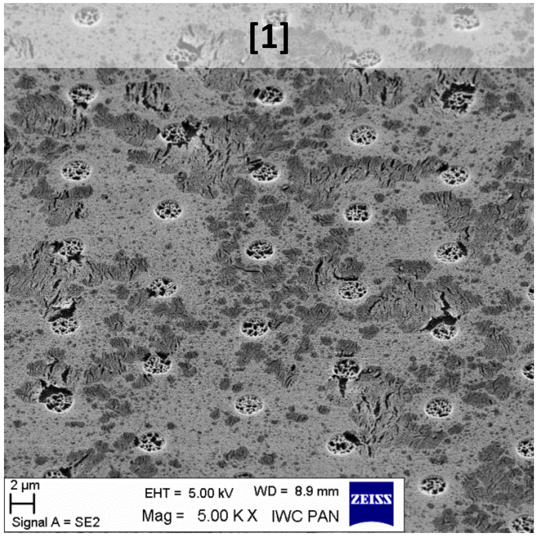
Rocking curves of obtained crystals:

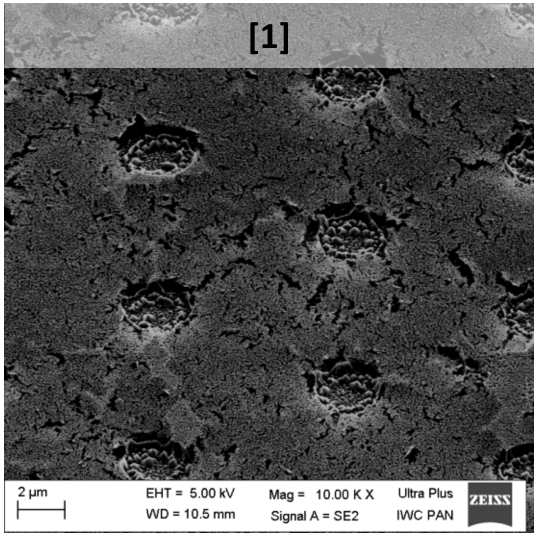
- Crystal I – crystal grown with 20 min of nitridation, FWHM=0.42°
- Crystal II – crystal grown with 40 min of nitridation, FWHM=0.23°
- Crystal III – crystal grown with 60 min of nitridation, FWHM=0.16°

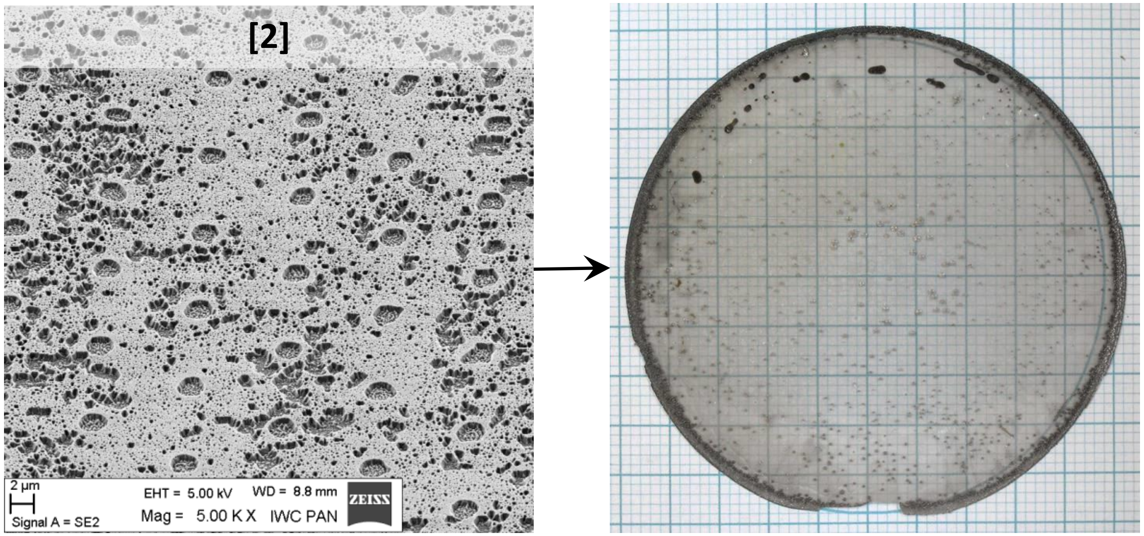


Since, in sense of the crystal quality, the best result was obtained for the crystallization with 60min of nitridation, the second set of the experiments (modification of the reagents flows) was performed with just the 60min nitridation.

Results – second step of the experiment







Figures [1] present SEM micrographs of TiN mask after nitridation with:

- Flow of NH3 – 600ml/min;
- Flow of dilution gas – 200ml/min.

The nitridation, with increasing in amonia flow, led to the peeling off of the Ti mask.

Therefore, the crystallization run with such nitridation procedure was not performed.

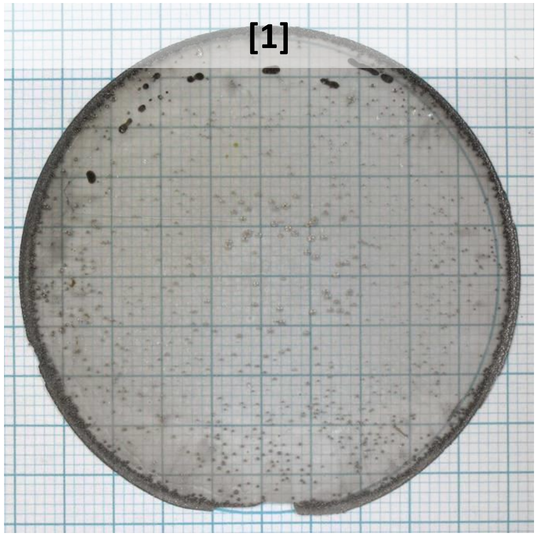
Figure [2] presents SEM micrographs of MOCVD-GaN/sapphire substrates' surface after nitridation with:

- Flow of NH3 – 200ml/min;
- Flow of dilution gas – 600ml/min.

The nitridation with the increase in the dilution gas of ammonia was chosen for the HVPE crystal growth run.

This improved the uniformity of the degradation degree of the MOCVD-GaN/sapphire template.

Rocking curve of the obtained crystal:



FWHM=0.08°
R=2.2m

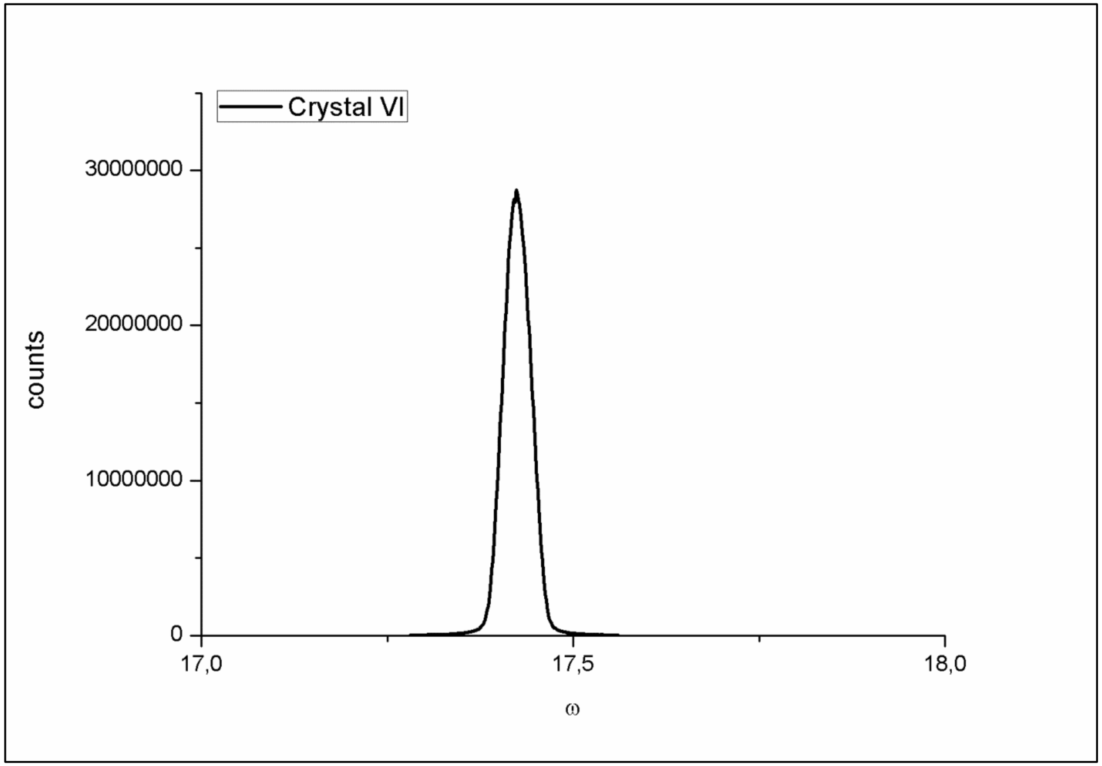


Figure [1] shows the final result of the experiment. The obtained crystal was separated from the foundation after the growth, during the cooling down step. This crystal was not cracked.

Not only the degree of degradation but also homogeneity of degradation is important for obtaining nocracked crystals of good structural quality. It was shown that the relationship between the conditions of nitridation and the moment of the lift-off exists and that the best free-standing HVPE-GaN crystal, in sense of structural quality, can be obtained if GaN is separated from the substrate during the cool-down procedure.