Modification by chemical treatment of the surfaces of nitride nanowires – CL and XPS study

Bogdan J. Kowalski, Anna Reszka, Marcin Klepka, Anna Wolska, Marta Sobanska, Zbigniew R. Zytkiewicz

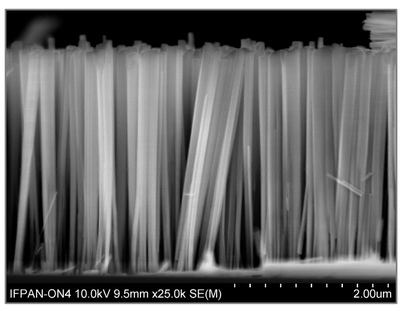
Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, 02-668 Warsaw, Poland

Introduction

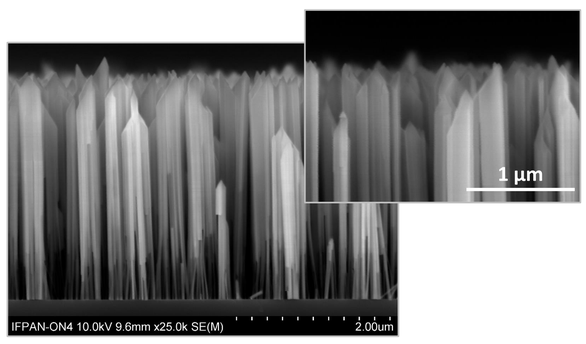
Although the influence of surface conditions on transport and optical properties of semiconductor nanowires (NWs) has been identified, the methods of controlling it and inhibiting its detrimental impact on the NW characteristics still remain an important subject of research. As the depth of the depletion or accumulation layer induced by surface band bending may become comparable with the diameter of the NW, its part available for transport, charge carrier injection and light generation can be markedly reduced. This applies also to NWs made of the group III nitrides. Therefore, we carry out complementary studies of luminescence of GaN NWs vs. chemical and electronic conditions on their surfaces. We report the results of CL and XPS experiments on the GaN NWs modified by etching their surfaces in KOH and HCl solutions. Both substances are used as media that etch, deoxidize or passivate nitride surfaces [D. Priante et al., Optic.Mat.Express **9**, 203 (2019); M. Biswas et al., ACS Appl. Nano Mater. **1**, 1968 (2018); C.Y. Lee et al., Jpn. J. Appl. Phys 51, 076503 (2012)].

Samples

The GaN NWs were grown on in-situ nitridated 3" Si (111) substrates using plasma-assisted molecular beam epitaxy (PA MBE) in a Riber Compact 21 system with elemental sources of Ga, Al, Si, and Mg. A radio frequency Addon nitrogen plasma cell, controlled by an optical sensor of plasma light emission, was used as the source of active nitrogen species. No catalyst was applied to induce nucleation of NWs. The morphology of the samples was assessed by scanning electron microscopy (SEM) using a field-emission Hitachi SU-70 scanning electron microscope.

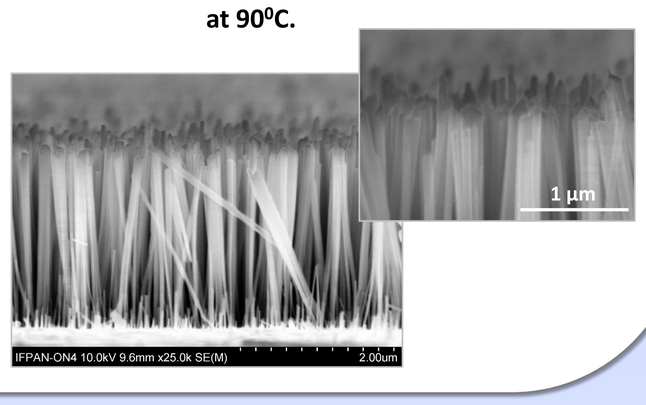


GaN NWs grown by PA MBE on a Si wafer



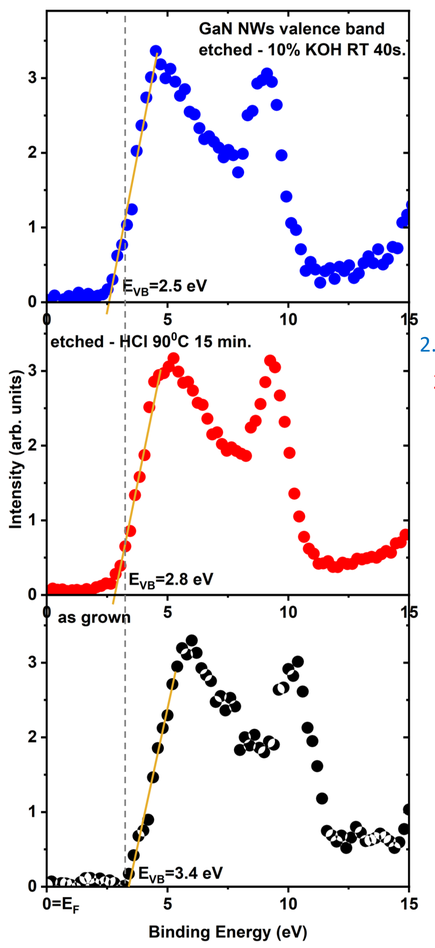
GaN NWs etched in HCl, 15 min. at 90^{0}C.

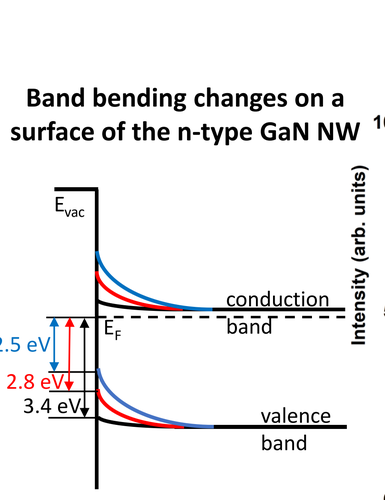
GaN NWs etched in a 10% solution of KOH in water, 40 s at RT.

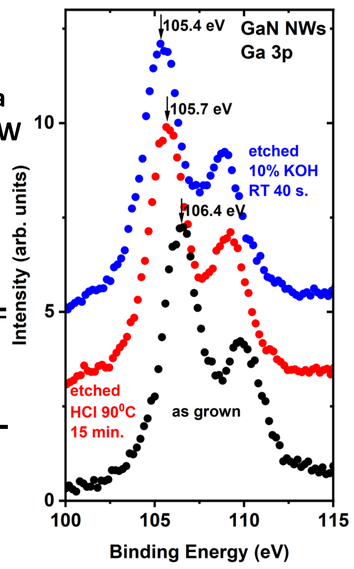


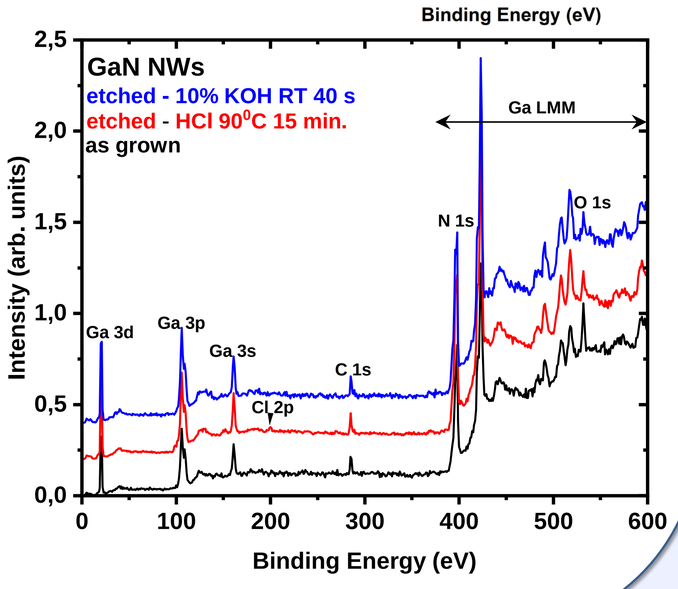
X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy enabled us to measure the shifts of the valence band maximum with respect to the Fermi level (i.e. to assess changes in the surface band bending) as well as reveal changes in the chemical composition of the surface. XPS spectra were recorded with use of the set-up made by PREVAC equipped with a high-intensity monochromatic X-ray Al Kα (1486.69 eV) source (Scienta MX 650) and Scienta R4000 hemispherical analyzer. No charge neutralization was used during measurements. The spectra were acquired at the emission angle of 60^0.



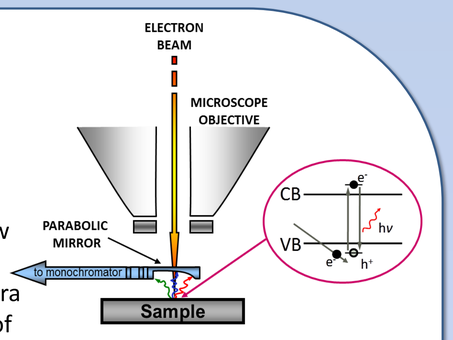




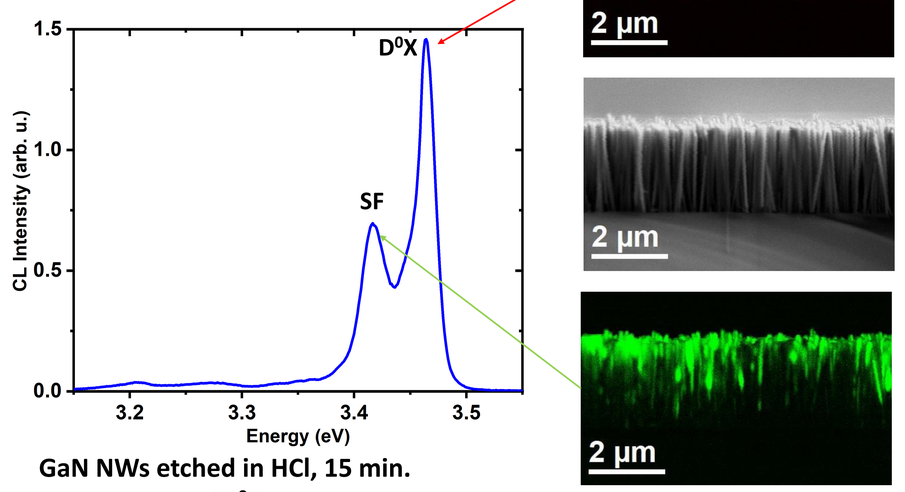


Cathodoluminescence

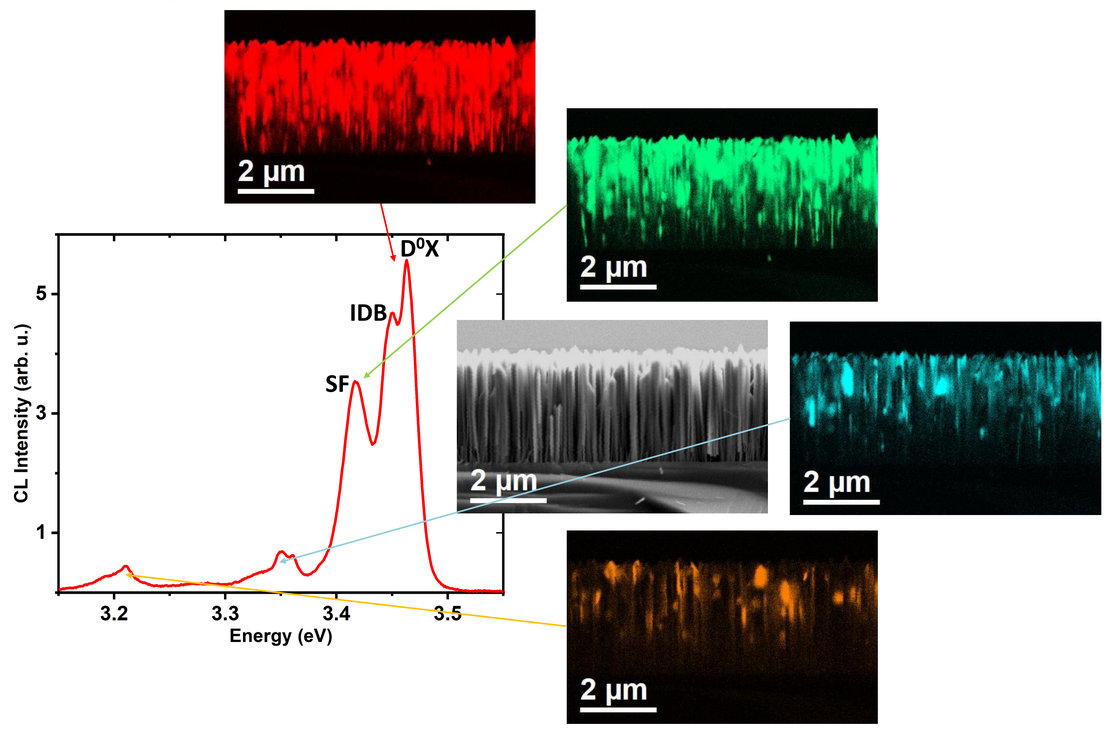
The electron microscopy techniques and related spectroscopic methods, like cathodoluminescence (CL), allow us to study morphology and optical properties of individual nanorods with the submicron lateral resolution. The SEM machine, equipped with a Gatan MonoCL3 CL system, including the continuous-flow liquid helium cryo-stage enabled studies of the local optical properties of single GaN NWs. The cathodoluminescence spectra and maps were taken at 5.3 K with the primary electron beam of 5 kV and 0.34 nA.



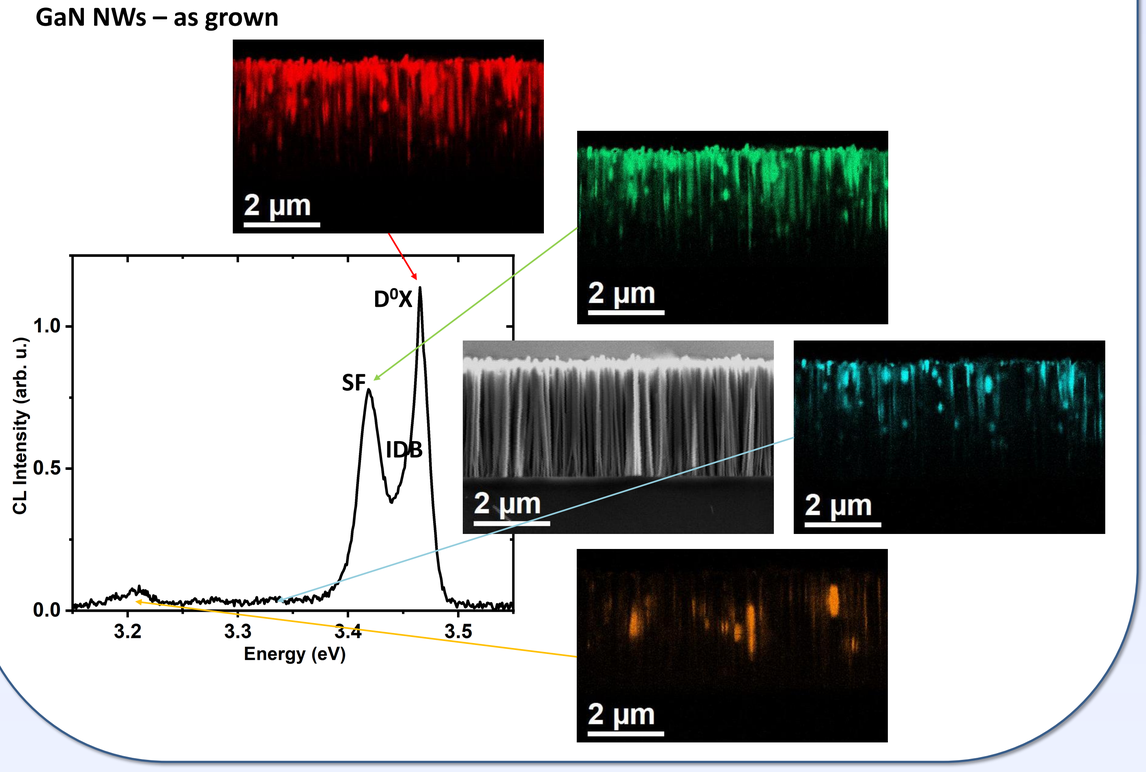
GaN NWs etched in a 10% solution of KOH in water, 40 s at RT.



GaN NWs etched in HCl, 15 min. at 90^{0}C.



GaN NWs – as grown



CONCLUSIONS

- Etching of the GaN NWs in HCl or 10% solution of KOH changes morphology of the NWs and reduces the surface contamination with O; the presence of the etching solution components on the NW surface is negligible. This procedure increases the band bending at the surface of GaN NWs by 0.6 and 0.9 eV, respectively.
- The etching of GaN NWs in HCl enhances cathodoluminescence from the lower parts of the NWs, presumably due to removal of luminescence-killing surface centers, even though the increase of the band bending may increase carrier depleted subsurface layer.
- The etching of GaN NWs in 10% KOH solution suppresses emission at 369 and 386 nm which reveals surface related character of those luminescence bands.

The authors are grateful to D. Płużyński for acquiring XPS spectra of the samples. Financial support by the Polish National Science Centre (NCN) under the Grants No. UMO-2022/45/B/ST5/02876 and UMO-2021/43/D/ST7/01936 is gratefully acknowledged.