PhD position: Epitaxial growth of InGaN-based nanostructures for the photo-electrochemical production of hydrogen

CRHEA : Centre Recherche sur l'Hétéroépitaxie et ses Applications
ICPEES : Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé

Keywords : Epitaxy - InGaN - Photoelectrochemistry – Low-carbon H_2

CONTEXT

Dihydrogen H_2 is involved in numerous chemical processes and is emerging as a future energy carrier that can be stored, transported and used on demand as a fuel or to generate electricity via a fuel cell. For economic reasons, 95% of hydrogen is currently produced from fossil fuels. To reduce greenhouse gas emissions, large-scale projects are being developed to produce "low-carbon" hydrogen by electrolysis of water, which can even be "green" by using electricity from renewable sources.
Indeed, photocatalytic water splitting and photoelectrochemical (PEC) approaches developed at research level do not require an external supply of electricity, since they rely solely on solar energy for the production of high-purity H_2, which is particularly suitable for fuel cell applications. The principle of these approaches is based on the use of semiconductor materials (SCs) that can efficiently absorb photons to generate charge carriers (electron-hole pairs), transport these charges to the reaction sites before they recombine and facilitate the targeted oxidation and reduction reactions.

Among the materials considered for these systems, **InGaN/GaN alloys** have the advantage of having a bandgap that can cover the entire visible range by varying the indium composition while maintaining good stability in an acidic environment. It is thus estimated that with 50% indium (with a band gap energy Eg≈1.7 eV) it is possible to collect a large part of the solar spectrum while having valence and conduction band levels ideally placed for the oxidation reactions and reduction of water. We could thus obtain theoretical STH efficiency of 27%, much higher than the metal oxides used such as TiO_2 or WO_3 [1].
Moreover, beyond the intrinsic properties of the material, we can increase the efficiency of the devices by optimizing their morphology. For example, the use of nanostructures such as **nanowires** increases the active surface area as compared to a planar layer ensuring a greater number of sites available for photoelectrochemical reactions.
The epitaxy of InGaN alloy with a high indium composition is, however, a challenge due to the phase separation phenomena between the two binaries InN and GaN and the formation of dislocations at the layer-substrate interface. Two approaches currently being explored at CRHEA are being considered. The first consists of carrying out the growth by MOCVD (Metal Organic Chemical Vapor Deposition) of InGaN on GaN nanowires in “core-shell” geometry in order to take advantage of the excellent structural quality of the nanowires and the growth on their non-polar lateral facets [2]. The second consists of carrying out the growth of InGaN on porous GaN to benefit from the relaxation of the substrate stress and increase the indium content.

OBJECTIVES

The objective of this thesis is to produce, following these two precedent approaches, nanostructures based on InGaN alloys with a high indium content and to use them as photoelectrodes for the PEC production of H_2 with a high efficiency greater than 10%. In addition, to improve the transfer of photogenerated charges and the stability of the material, the deposition on the surface of the SC of a transition metal oxide co-catalyst or a transition metal dichalcogenide of the $MoSe_2$ type is considered.

THESIS ENVIRONMENT

This thesis is funded by the CNRS MITI "HydroGaN" project bringing together CRHEA and ICPEES specialized respectively in the fabrication of nitride materials and heterogeneous catalysis processes. Figure 1 shows GaN nanostructures on silicon substrate produced in 2023 at CRHEA and the photo-electrochemical measurement bench available at ICPEES. The student will thus be able to benefit from the complementary expertise of the two laboratories.

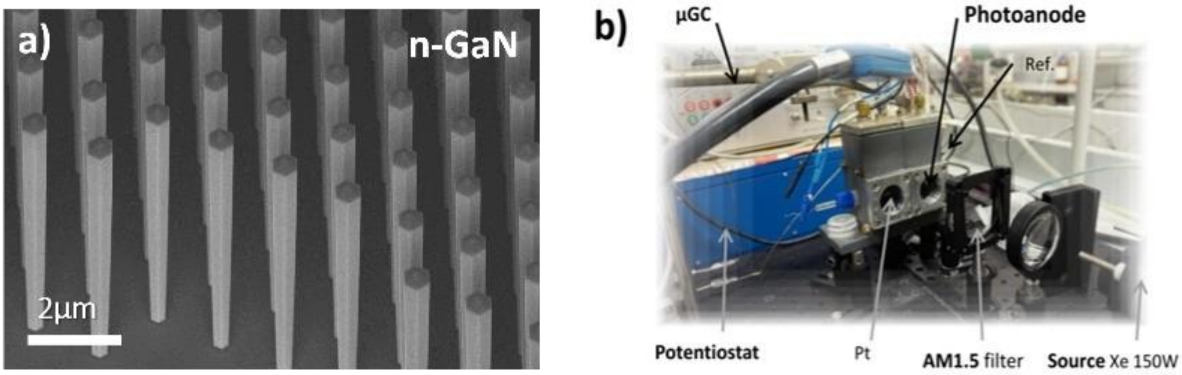

Figure 1 : (a) SEM images of GaN nanowires after MOCVD growth; (b) Image of the photoelectrochemical measuring bench and the photoelectrochemical cell used at ICPEES

More precisely, he/she will perform the epitaxial growth (MOCVD and MBE) and characterization by Scanning and Transmission electronic microscopy (SEM, TEM) and Cathodoluminescence at CRHEA and will participate in photoelectrochemical performance measurements at ICPEES [3] (cyclic voltammetry measurements for photo conversion, impedance spectroscopy, gas chromatography under irradiation for the production of H_2 and O_2). He/She will thus follow all the stages, from the growth of nanostructures to their photoelectrochemical characterization. In practice, the doctoral student will be based at CRHEA (located in Valbonne) and will make stays of one or several months depending on the results obtained at ICPEES (in Strasbourg) to characterize the samples he/she has produced. He/she will communicate the results through scientific publications as well as at conferences. The thesis will be carried out under co-supervision between the CRHEA (supervision Blandine Alloing) and the ICPEES (co-supervision Thomas Cottineau).

PROFILE

The candidate will have the opportunity to work on an interdisciplinary subject, on the border between materials physics and chemistry, and with strong environmental and societal issues. He/she must have a master degree (or equivalent) in materials science or condensed matter physics, enjoy experimental work with the desire to learn different fabrication and characterization techniques. He/she must be prepared to travel between the 2 partner laboratories. Good communication skills and team spirit are therefore required.

To apply, the candidates should send CV, Master's results, Cover letter and contact details of 2 referees to the following persons:

Blandine Alloing tel : 04 93 95 42 06 email : ba@crhea.cnrs.fr
Thomas Cottineau tel : 03 68 85 28 14 email : cottineau@unistra.fr

References:

[1] J. Lin et al. *Adv. Funct. Mater.* **30**, 2005677 (2020)
[2] J. Bosch et al. *Crystal Growth & Design*, **22**, 5206 (2022)
[3] T. Favet et al. *Materials Today Energy* **37**, 101376 (2023)