INSTITUT PASCAL – Axe Photon - Equipe Surface

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Title of PhD subject: Functionalization of nano-structured surfaces of III-V semiconductors for energy conversion.

Summary:

Photovoltaic energy conversion technologies are advancing in terms of efficiency and cost to compete with fossil fuels. However, the development of large-scale solar power plants poses challenges related to the storage and transportation of the generated energy. Solar-powered water splitting, inspired by photosynthesis, represents a promising approach to hydrogen production. In photoelectrochemical cells, semiconductor photoelectrodes facilitate the cathodic hydrogen evolution reaction and the anodic oxygen evolution reaction using the two most abundant resources: sunlight and water [1].

III-V semiconductors are particularly attractive for this application due to their favourable properties, including high light absorption, enhanced charge carrier mobility, and efficient charge transfer to the electrolyte. However, their high cost and rapid corrosion in electrochemical environments limit their widespread use [2].

This study aims to exploit gallium arsenide (GaAs) and gallium nitride (GaN) by leveraging the advantages of ion bombardment as an effective tool for nano structuring and surface functionalization. Ion cluster bombardment is an efficient technique for modifying the surface properties of III-V semiconductors. This method enables surface cleaning by removing contaminants and oxides while preserving the underlying crystalline structure. Additionally, it can induce controlled changes in surface chemical composition, thereby influencing key properties such as bandgap energy and charge carrier mobility. Moreover, ion cluster bombardment allows the creation of self-organized nanostructures on the surfaces of III-V semiconductors. By precisely controlling irradiation parameters such as ion energy, angle of incidence, fluence, and cluster size, it is possible to fabricate nanostructures with specific dimensions and shapes, offering a potential pathway for improving the performance of these materials.

First, the impact of cluster ion bombardment on semiconductor surfaces will be analysed, particularly in terms of surface structuring and functionalization. The main objective is to gain an understanding of and control over the induced modifications and/or new physicochemical properties, including electrochemical and optoelectronic behaviours as well as crystallographic properties. To this end, in situ characterizations will be carried out using electronic spectroscopies, such as X-ray photoelectron spectroscopy (XPS) for chemical analysis of surface modifications and ultraviolet photoelectron spectroscopy (UPS) or angle-resolved photoemission spectroscopy (ARPES) to examine induced changes in valence band energy and alignment. These results will be complemented by ex situ microscopy studies and electrical and optical measurements.

In the next phase, the resulting structures will be chemically stabilized via nitrogen plasma treatment. This treatment is known to generate a nitrided upper layer that exhibits good stability in corrosive solutions. These controlled modifications will optimize the use of the developed electronic structures as efficient photoanodes. Chemical and electrochemical tests will be conducted to evaluate their stability and performance.

[1] M. Grätzel, Photoelectrochemical cells, Nature. 414 (2001) 338–344. https://doi.org/10.1038/35104607.

[2] Mekan Piriyev et al., Dual bandgap operation of a GaAs/Si photoelectrode, Solar Energy Materials and Solar Cells. 251 (2023) 112138. https://doi.org/10.1016/j.solmat.2022.112138