2021-2022 Internship proposal at LMGP Lab.

Synthesis of lamellar metal dichalcogenides (Ga_xS) by a Molecular Layer Deposition route with atomic level control by *in situ* characterization techniques

Abstract

The objective of this research internship is to contribute to the fabrication of sulfide-based lamellar materials, in particular ultra-thin films of metal dichalcogenide, a recognized class of emerging materials. The student will achieve Molecular Layer Deposition and thermal treatment of sulfide thiolate thin films (Ga-thiolates) in a dedicated reactor located in LMGP, while monitoring the process by *in situ* ellipsometry. If relevant, specific equipment will be used to study the amorphous to crystalline transition of the thiolate thin films by *in situ* X-ray diffraction. The internship student will participate in an experiment at the synchrotron SOLEIL (St Aubin) to study the thiolate deposition and annealing by *in situ* X-ray techniques. Further structural and chemical analysis of the thin films will be performed after synthesis, such as Raman scattering spectroscopy, X-ray photo electron spectroscopy (XPS) and Transmission Electron Microscopy.

Project description

2D-materials, especially metal dichalcogenides (MDs)[1,2], have received considerable attention recently since they are emerging as a class of exceptional materials with many potential applications. Beside the prototypical transition metal dichalcogenide (TMDs) MoS_2, WS_2, TiS_2, … there are several interesting lamellar MDs to investigate as precursors of new hybrid composites for emerging devices. The internship work will focus on **layered gallium sulfide (GaS) materials**. Gallium sulfide (**Ga_xS**) has two stable forms: **GaS and Ga_2S_3**[3]. Both forms are wide-band-gap semiconductors (Eg = 3.0 - 3.6 eV), making them promising candidates for optoelectronics and photovoltaics[4]. In particular, gallium sulfide thin films have been proposed as passivation layers in III-V semiconductors [5], anodes for Li-ion batteries[6] and buffer layers in CdTe solar cells[7]. Atomic Layer Deposition (ALD), as well as Molecular Layer Deposition, are based on sequential, self-limiting surface reactions that allow conformal film growth with precise thickness control. They are ideal techniques for depositing scalable ultrathin inorganic and organic films. Beside the conventional Atomic Layer Deposition (ALD) process, we develop an innovative **2-step process**[8] one advantage of which is to avoid the very toxic H_2S molecule currently used for the growth of 2D MDs by ALD. The 2-step process consists in depositing a metal-thiolate thin film by MLD. Then, the metal-thiolate, which was formed after the reaction of the metal precursor and organic sulfide molecule (1,2-ethanedithiol), is transformed into the target material by annealing in a controlled atmosphere[8,9].

Under the guidance of a PhD student, the successful Master candidate will achieve MLD of Ga-thiolates thin films in a dedicated reactor in LMGP, on thermal SiO2 and InGaAs substrates, while monitoring the growth by *in situ* ellipsometry (and possibly by residual gaz analysis). If applicable, post MLD thiolate thin films will be transferred into specific equipment to perform *in situ* Raman scattering measurements at the LETI characterization platform or *in situ* XRD at Grenoble-INP characterization platform (CMTC), to study the amorphous to crystalline transition during the thermal treatment. Post annealed samples will be checked by high resolution X-ray fluorescence, X-ray reflectivity, grazing incidence X-ray diffraction, X-ray photoelectron spectroscopy (CMTC, Grenoble INP) and Transmission Electron Microscopy (LMGP). The internship student will participate in an experiment at the synchrotron SOLEIL (St Aubin) to be carried out by July 2022.

This internship work takes part of the collaborative ULTiMeD project, funded by the French ANR, which aims at the atomic-level control over ultrathin layers of lamellar metal dichalcogenides by a Molecular Layer Deposition route. The project mainly focusses on the investigation of the early stage of deposition and crystallization of lamellar metal dichalcogenide ultra-thin films processed with organosulfides (as Sulfur source alternative to H_2S) in a custom-built portable reactor for Atomic Layer Deposition (ALD) [10-12].

[1] Y. P. Venkata Subbaiah et *al.* (**2016)** Adv. Funct. Mater. 26, 2046 ; [2] W. Hao et *al*. (2019) 2D Mater. **6** 012001 ; [3] R. M. A. Lieth *et al* 1966 *J. Electrochem. Soc.* **113** 798 **;** [4] X. Meng et *al*. (2014) Adv. Funct. Mater. 24, 5435 ; [5] X. Cao, *JVST. B* **1998**, 2656 ; [6] X. Meng et al. *Adv. Funct. Mater.* **2014,** 5435 ; [7] E. Cuculescu et al. *J. Optoelectron. Adv. Mater.* **2006**, 1077 ; [8] S. Cadot et *al*. *Nanoscale* **2017**, 538 & S. Cadot et al. *JVST. A* **2017**, *35*, 061502 ; [9] P. Abi Younes et *al*. To be published ; [10] E. V. Skopin et *al*. *Nanoscale* **2018**, 11585 ; [11] R. Boichot et *al*. **2016**, DOI 10.1021/acs.chemmater.5b04223; [12] M. H. Chu et *al. Cryst. Growth Des.* **2016**, 5339.

Scientific environment:

The master candidate will work within the LMGP (Materials Science and Physical Engineering), in team **NanoMAT** in close collaboration with a PhD student, in the framework of the ULTiMeD project and with the other partners of the ULTiMeD project (IRCELYON, Lyon ; IPVF, Palaiseau, SOLEIL), as well as scientists at CEA Leti. Located in the heart of an exceptional scientific environment, the LMGP offers the applicant a rewarding place to work.

Profile & requested skills:

The candidate must be engaged in a research master program in physics, chemistry or material science or closely related science. She/he should also have ability and initiative to get to the heart of the problem and take it effectively through to completion; good interpersonal, communication and scientific presentational skills; good organizational and planning skills. Self-motivation.

Allowance: Internship allowance will be provided

CONTACT : Pr Renevier (last name), Hubert (first name) ; hubert.renevier@grenoble-inp.fr; Tel: 04 56 92 48