2020-2021 Internship proposal at LMGP Lab.

Synthesis of lamellar metal dichalcogenides 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 Atomic Layer Deposition/Molecular Layer Deposition of sulfide thiolate thin films (Ti- and Sn-thiolates), in a dedicated reactor located in LMGP, while monitoring the growth by *in situ* ellipsometry. Specific equipment will be used to further anneal the thiolates and study the amorphous to crystalline transition by *in situ* X-ray diffraction (CMTC). 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 transition metal dichalcogenides (TMD) [1], have recently received considerable attention since they are emerging as a class of exceptional semiconductor materials with many potential applications (supercapacitors, batteries, electronics and opto-electronics, flexible electronics, ...). However, a sizeable bottleneck for their full deployment stems from the lack of scalable fabrication methods with atomic scale precision. In the recent years, a 2-step Atomic Layer Deposition/Molecular Layer Deposition process and annealing has been used for the synthesis of 2D MoS_2 and WS_2 [2,3]. It has the advantage of being compatible with the manufacturing environment and avoid the use of toxic sulfur molecules as for instance H_2S (“green” chemistry). However, as far as MoS_2 and WS_2 are concerned, the 2D crystallization is obtained by an annealing at a rather high temperature (> 800°C), which severely hinder the integration capabilities of those materials. Alternatively, Tin disulfide (SnS_2), which is a semiconductor with a band gap in the range [2.2-2.35eV] (depending on the layer thickness), appears as a good candidate since it has a low melting point (865°C) in comparison to those of MoS_2 and WS_2. Moreover, Tin is an earth-abundant metal with almost all of its oxide and sulfide derivatives (SnS, Sn_2S_3, SnS_2, SnO et SnO_2) being semiconductors and non-toxic.

The internship 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) [4-6].

Under the guidance of a PhD student, the successful Master candidate will achieve Atomic Layer Deposition/Molecular Layer Deposition of Sn-thiolates thin films in the MOON reactor at LMGP, while monitoring the growth by *in situ* ellipsometry (and possibly by residual gaz analysis). Some of the post ALD/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).

[1] Y.P. Venkata Subbaiah et *al* (2016), Adv. Funct. Mater **26**, 2046 ; [2] S. Cadot et *al*. (2017), Nanoscale **9**, 538 ; [3] S. Cadot et *al*. (2017)., J. Vac. Sci. Technol. A **35**, 061502. [4] R. Boichot et *al*. (2016), J. Chem. Mater. 28, 592. [5] M. H. Chu et *al*. (2016), Cryst. Growth Des. **16**, 5339. [6] E. V. Skopin et *al*. (2018), Nanoscale, 10, 11585.

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 (C2P2, 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

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