Third year PhD Report

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Research activity

During the third year of my PhD, I continued my research on 2D semiconducting materials, with a focus on overcoming the key challenges associated with the real-world implementation of Transition Metal Dichalcogenides (TMDs). My primary goal was to enhance the feasibility of integrating TMDs into practical devices, guiding my efforts towards addressing several critical bottlenecks in their synthesis and manipulation.

These challenges include the lack of homogeneous and scalable synthesis techniques for producing replicable, large-area devices; the reliance on high-temperature processes that are incompatible with most industrial applications and materials; the significant difficulties in creating heterostructure configurations through the stacking of different TMDs; and the absence of effective methods for tuning and improving the electrical performance of TMDs when fabricating metal electrodes for device configurations.

1 Large-area, low-temperature deposition of amorphous a-MoSx by Ion Beam Sputtering

1.1 Fabrication and characterization of Hybrid 2D/3D junction

Building on last year's initial attempts, I continued studying and implementing amorphous MoSx (a-MoSx) films deposited by IBS using a custom-built setup and proximity masks. I fabricated vertical 2D/3D junctions with a-MoSx thin layers over HF-treated p-doped silicon substrates. After selecting appropriate metals for the bottom contacts on silicon, I created and characterized various devices by varying the MoSx thickness and/or top metal electrode materials. Electrical characterization of the vertical junctions revealed rectifying behavior with modest short-circuit current and open-circuit voltage, as well as good photoconductivity in forward bias. This suggested that as-grown a-MoSx may act as a selective carrier layer. Based on this idea, as an additional study, different devices with a-MoSx layers on silicon-based photovoltaic devices were fabricated in collaboration with ENEA (Portici division). The study of this kind of configuration is ongoing.

1.2 a-MoSx as active layers for Li-button cells

MoS_2 has recently shown promising properties in energy storage for lithium batteries. Exfoliated MoS_2 layers, obtained through mechanical or liquid phase exfoliation, have demonstrated good performance as active anode materials with high specific capacities. However, the limitations of exfoliation, such as micrometric size and stochastic transfer, pose challenges for real-world applications. Exploiting our ability to deposit a-MoSx over large areas at ambient temperature, I began growing MoSx films of various thicknesses on copper substrates for use as active material in Li button batteries, in collaboration with ENEA (SSPT-PROMAS-MATPRO division in Rome). Initial experiments have shown promising specific capacitance values during charge-discharge cycles. Ongoing studies are focused on film composition, Li-induced modifications, and other influencing factors.

1.3 Electrical characterization of a-MoSx via deterministic lithographic devices

In parallel with the characterization and implementation of a-MoSx in the above mentioned collaborations, I have also explored the characterization of these films through on-demand growth and the fabrication of a-MoSx-based devices. Utilizing the recently developed t-SPL fabrication technique [1], I achieved deterministic deposition of a-MoSx patches with arbitrary geometries. Additionally, after several optimization attempts, I successfully fabricated metal electrodes on the a-MoSx patterns. Preliminary electrical characterization has been conducted, paving the way for further investigations, such as modifications via Ion Beam Irradiation or local annealing using t-SPL's hot tip.

2 Local recrystallization of meta-stable MoS2 via t-SPL local annealing

The idea of using the heat stimulus from the t-SPL hot tip is not only promising for modifying a-MoSx but also for inducing local recrystallization in metastable stoichiometric films. A similar approach would i) enable on-demand, localized recrystallization of MoS2 with arbitrary geometries in a maskless manner, and ii) avoid subjecting the entire substrate to high temperatures processes. In collaboration with Politecnico di Milano (POLIMI), I initiated local annealing experiments on few-nanometer-thick MoS_2 stoichiometric films deposited by Pulsed Laser Deposition (PLD). Building on the knowledge gained from similar experiments with IBS-deposited a-MoSx and MoS_2, the films were deposited on silicon nitride free-standing membranes provided to the POLIMI group. The annealing experiments, conducted in an inert nitrogen atmosphere to prevent oxidation, led to a selective recrystallization process, confirmed by Raman spectroscopy through the analysis of MoS_2 vibrational features. While this is a significant achievement, further experiments are planned to enhance the spatial resolution of this deterministic process.

3 Strain-engineering of exfoliated MoS2 flakes on Grayscale nanopatterns

Building on last year's successes in multi-level grayscale fabrication and flake exfoliation on patterned substrates, I have expanded these efforts in two main directions. In this context, I have utilized exfoliated crystalline material as an ideal platform to investigate the localized effects of strain induced by arbitrarily nanopatterned substrates, paving the way for similar studies on large-area TMDs.

3.1 Contact engineering via periodically strained flakes

After creating 1D periodic ripples using grayscale t-SPL, exfoliated MoS_2 monolayer flakes were identified through PL measurements and deterministically transferred onto the PPA rippled patterns. This configuration, where the MoS_2 monolayer conforms to the engraved patterns, was examined using Kelvin Probe Force Microscopy (KPFM), revealing a periodic variation in the MoS_2 surface potential. This suggests that nanoscale electronic modifications are induced by the strain from the nanostructured surface. To investigate the effects of the strained crystal on a metal-TMD junction, gold was deposited at a grazing angle, resulting in the formation of spatially confined gold nanowires (NWs) due to the shadowing effect of the ripples. Further KPFM studies demonstrated an asymmetric behavior in the semiconductor-metal junctions, with the junction nature (Schottky or Ohmic) being dependent on the previously strain-modified surface potential. A draft related to these findings is currently being prepared for submission [5].

3.2 Hybrid TMD-Plasmonic structures for enhanced photoluminescence

The above process was repeated in reverse order to create a configuration that enhances photoluminescence (PL) in a hybrid TMD-plasmonic structure. After grayscale lithography of the appropriate rippled structure, gold was again thermally deposited at a grazing angle, confining gold NWs that exhibited plasmonic behavior, as observed by polarized micro-spectroscopy in the VIS-NIR range. MoS_2 monolayer flakes were exfoliated and transferred after the NWs deposition, positioning the active semiconducting layer on top of the plasmonic Au-NWs. In this configuration, polarized PL measurements were conducted to observe the effects of the plasmonic NWs, including PL shifts and/or enhancement. To further explore the nanoscale features of these effects, tip-enhanced Raman spectroscopy (TERS) and tip-enhanced photoluminescence (TEPL) characterizations are being performed in collaboration with CNR (Messina group).

PUBLICATIONS

1. Giordano, M. C., Zambito, G., Gardella, M., Buatier de Mongeot, F., ‘’*Deterministic Thermal Sculpting of Large-Scale 2D Semiconductor Nanocircuits*’’. Adv. Mater. Interfaces 2023, 10, 2201408. (2^{nd} Year)
2. Giordano, M. C.; Pham, D.; Ferrando, G.; Si , Hieu N.; Ha, C.; Mai, T. H.; Zambito, G. *et al.*; *‘’Self-Organized Plasmonic Nanowire Arrays Coated with Ultrathin TiO2 Films for Photoelectrochemical Energy Storage’’*, ACS Applied Nano Materials 2023 6 (23), 21579-21586, DOI: 10.1021/acsanm.3c03546
3. Gardella, M.; Zambito, G. et al., ‘’ *Large area van der Waals MoS2–WS2 heterostructures for visible-light energy conversion*’’, RSC Appl. Interfaces, 2024, Advance Article, DOI: 10.1039/d3lf00220a
4. Gardella, M.; Zambito, G. et al., ‘’*Maskless synthesis of van der Waals heterostructure arrays engineered for light harvesting on large area templates’’,* under revision
5. Zambito, G. et al., ‘’Inducing and observing non-homogeneus periodic strain on MoS2 flakes via t-SPL and KPFM’’, in preparation.

Exams

Surface science – passed

Optical properties of nanomaterials – scheduled in September

Quantum Optics – scheduled in September

Nanophotonics and nanofabrication – scheduled in early october

CONFERENCE PRESENTATIONS

- ‘’MNE23’’, Berlin, September 2023 (Poster) – ‘’ Shape-engineering of 2D TMD semiconductors via thermal-Scanning Probe Lithography’’
- ‘’8^{th} thermal probe workshop’’, Zurich, March 2024 – ‘’ Reshaping TMDs: Strain-induced effects
- and on-demand nanocircuitry’’
- ‘’MRS Spring Meeting 2024’’, Seattle (USA), April 2024:
    - Oral contribution: ‘’Large area van der Waals MoS2-WS2 heterostructures for visible-light photocatalysis and energy conversion’’
    - Oral contribution: ‘’Growth of Arbitrary 2D TMDs Nanopatterns via thermal Scanning Probe Lithography’’
- Workshop ‘’Maskless Laser Lithography and Direct Write Technology for the Advanced Micro- and Nanofabrication’’, Montpellier, Invited talk – *‘’Inducing non-homogeneous strain on MoS2 via grayscale t-SPL*’’