First year PhD Report

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Research activity

The activity of my first year of PhD has been focused on the nanofabrication of two-dimensional (2D) Transition Metal Dichalcogenides semiconductors (TMDs) and on the study of their optoelectronic response. This family of 2D materials is characterized by exceptional optoelectronic properties and have shown lots of interesting effects, such as layer-dependent energy bandgap, quantum emission, sensing and electronic transport capabilities. The most diffused platform for the study of the 2D TMDs optoelectronic properties are currently 2D micro-flakes achieved by mechanical exfoliation. However, the limited sizes of exfoliated flakes prevent TMDs from reaching employability in real-life applications, which require scalable synthesis approaches for defining replicable TMDs based devices, possibly with nanoscopic resolution. The first aim of my work is the investigation of novel growth and nanofabrication methods of 2D TMD semiconductors to enable their applications to large-area devices. The second aim is the investigation of the electronic transport and of the optical properties of few-layer TMDs (MoS_2, WS_2) grown over large-area. To achieve this second aim, I am currently exploiting the new thermal-Scanning Probe Lithography system installed at DIFILab (Nanofrazor) to re-shape and/or locally tailor the optoelectronic response of 2D TMDs layers. The optoelectronic and electronic transport properties of the functionalized layers are finally investigated via optical micro-spectroscopy and scanning probe microscopy techniques. To achieve the aims of my project, I have worked on different experimental activities that are discussed below.

1 Nanofabrication of 2D TMDs nanocircuits and study of their electronic properties

Deterministic nanopatterns based on few-layers MoS_2 have been fabricated by combining thermal- Scanning Probe Lithography, (t-SPL, Nanofrazor instrument) and a custom-developed physical deposition process of large-area TMDs. The latter is based on the Ion Beam Sputtering deposition of few-layer TMDs and subsequent recrystallization. The semiconducting response of the fabricated MoS_2 nanopatterns was confirmed by micro-Raman spectroscopy maps, which showed the effective presence of MoS_2 with its characteristic vibrational response in clearly confined areas. Furthermore, 2D TMDs nanodevices have been fabricated via t-SPL and characterized by optimizing Conductive AFM and Kelvin Probe Force Microscopy imaging. Such analysis allowed the extraction of the local transport properties and Fermi energy level of the 2D layers [1]. These results demonstrate a novel route for large-area growth and deterministic nanopatterning of few-layer TMDs, which represents an enabling technology for the future fabrication of in-series devices based on 2D semiconducting Van der Waals materials.

The same 2D TMDs have been also exploited to create large-area flat-optics nanopatterns for photoconversion and photocatalysis [2].

2 Lithographic 2D TMDs heterostructures for on-demand photoconversion devices

The addictive fabrication of 2D TMDs nanostructures via t-SPL have been exploited to develop on-demand TMDs heterostructures without the restraints typically imposed by mechanical exfoliation of 2D flakes. More specifically, a design consisting into a bilayer graphene – WS_2 – MoS_2 heterostack has been developed. This work (which is currently in-progress) aims at filling the gap between fundamental studies on photoconversion of non-replicable heterojunctions made from exfoliated 2D materials, and the fabrication of replicable and in series devices. Indeed, the non-invasive hot tip of the Nanofrazor and the direct-overlay approach, allow the in-situ imaging of the nanostructured layers, leading to relatively easy fabrication of heterostacks and aligned metal nanoelectrodes. A few-layer WS_2-MoS_2 heterostructure device have been fabricated on top of commercial bi-layer graphene by t-SPL with the aim to develop a deterministic type II heterojunction device for photonic and energy harvesting applications.

3 Physical modification of 2D TMDs layers by local thermal stimuli

The thermal stimulus induced by a nanoscopic tip, such as the one used in t-SPL, is able to locally modify physical properties of the 2D layers. The ability to tailor the optoelectronic response of few-layer TMDs in localized areas is appealing since it could be a route towards the creation of 2D materials-based devices without the need for standard lithographic techniques. For this purpose, I introduced a platform which aims at favoring the thermal effects of the hot tip on a few-layer thick MoS_2 film. Commercial free-standing membranes (200nm of Si_3N_4 on a silicon frame) were covered with a 4nm thick MoS_2 grown with the same process described in the first section. Under this configuration the characteristic optical and vibrational response of few-layer MoS_2 can be modified by local heating of the 2D layers, without changing the morphology of the film. The samples were analyzed by Raman micro-spectroscopy maps (which I performed at DIFILab), thus suggesting that this treatment may induce the local degradation of the crystalline MoS_2 structure. Additionally Scanning Near field Optical Microscopy imaging (SNOM) was performed in collaboration with *NeaSpec* with the aim to image the layer changes at the nanoscale. These results will be exploited to better control local changes of 2D TMDs with the aim to engineer their electronic transport properties in flat TMDs nanodevices characterized by high-resolution domains without any change in their composition and morphology.

4 Grayscale nanopatterning towards strain engineering

Another interesting way for tailoring TMDs properties can be strain engineering, namely the ability to address optical/electronic behavior by applying a controlled mechanical stress on the crystal lattice. To achieve control of the crystal bending, it is interesting to gain high control on the morphology of nanopatterned substrates. In view of a similar goal, I have recently worked on grayscale t-SPL nanolithography, able to create multi-level 3D designs with very high resolution. My goal is to create substrates with anisotropic nanostructures with a-priori defined curvature radiuses. These templates will host exfoliated or physically grown 2D TMDs to tailor their optoelectronic and electronic transport properties. Under this condition interesting effect could be observed, such as enhanced localized photoemission or anisotropic electrical conductivity. As for now, patterns with curvature radiuses as low as 50 nm have been created on polymer films. It is my intention to transfer such patterns into Si/SiO_2 substrates by Reactive Ion Etching (RIE), to develop optimal templates for the study of strain effects in 2D TMDs.

As a parallel work, the same t-SPL grayscale approach has been used for nanofabrication of on-demand photonic nanocavities embedded into thin functionalized polymer films that have been studied in collaboration with Polytechnic University of Turin [3].

PUBLICATIONS

1. M. Giordano, G. Zambito, M. Gardella, F. B. de Mongeot *et al.*, "Deterministic Thermal Sculpting of Large-Scale 2D Semiconductor Nanocircuits", currently under review.
2. Ferrando *et al*. "Flat optics Hybrid MoS2/polymer films for photochemical conversion", under submission
3. Marcucci *et al*. to be submitted

ATTENDED COURSES

Passed: Applied Cryogenics

Exam in preparation: Optical properties of nanomaterials, Quantum optics, Surface science

CONFERENCE PRESENTATIONS

- Epioptics 16 – International school of physics – <u>ORAL CONTRIBUTION</u>
- EMRS Fall meeting 2022 **–** <u>ORAL CONTRIBUTION</u> (end of September 2022)