Second year PhD Report

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Research activity

The second year of my PhD aimed at continuing the work on nonconventional uses of thermal Scanning Probe Lithography (t-SPL) and the study of the peculiar properties of two-dimensional (2D) Transition Metal Dichalcogenides semiconductors (TMDs). In this context, the unique nanofabrication approach by t-SPL is exploited i) to engineer deterministic 2D TMDs nanocircuits and heterostructures and ii) to induce vertical and lateral modification of optically active layers. In parallel, novel large-area growth processes for few-layers TMDs has been further investigated, dealing with one of the main bottlenecks that limit their integration in competitive technological devices. The different activities I have been working on are discussed below.

1 Deterministic fabrication and characterization of TMDs-based nanostructures via t-SPL

1.1 Nanofabrication of 2D TMDs nanocircuits and nano heterostructures

Following last year results, which allowed to gain control in terms of fabrication of arbitrary 2D MoS_2 nanocircuits [1], I proceeded to test the fabrication technique for the creation of multi-materials nanopatterns. To do so, I subsequently applied the developed fabrication method both to WS_2 and MoS_2, engineering deterministic TMDs nanowires heterostructures, which represent a first example of on-demand junctions based on reshaped 2D materials with spatial resolution at the nanoscale. Such high-resolution heterostructures have been investigated by AFM and SEM techniques, as well by Kelvin Probe Force Microscopy measures to detect the electrical work function variations induced by the nanostructures. The latter measures have been performed within a collaboration with the Jagiellonian University in Kraków. As a follow-up nanodevices based on these deterministic TMDs heterojunction are currently in progress in order to study their photoconversion response in view of energy conversion and storage applications.

1.2 Electrical characterization of few-layer TMDs nano- and micro-circuits

While electrical transport properties of exfoliated TMDs flakes have been widely studied in literature, only few examples of fundamental transport measures can be found regarding large-area few-layers polycrystalline TMDs films. Thanks to the custom large area synthesis of MoS_2 and WS_2 here developed [1], together with our deterministic nanofabrication approach, it is possible to precisely create controlled geometries, down to the micro- and submicrometric scale, based on few-layer TMDs and subsequently fabricate high resolution electrical nanocontacts via t-SPL. The engineering of these devices based on the Transfer Length Method (TLM) configurations is an on-going activity that will allow the precise measurement of electrical transport properties such as the contact resistances of the metallic nanoelectrodes and the sheet resistance of the semiconducting layer (MoS_2 and WS_2). Under this condition the possibility to tailor and improve the electronic transport properties of the layers via electron- or low-energy ion beam irradiation will be investigated.

2 Non-conventional patterning via t-SPL for functional active layers

2.1 Study of MoS_2 flakes onto grayscale nanopatterned polymer films

The ability to engrave thermally sensitive polymeric films with arbitrary three-dimensional nanopatterns by gray-scale t-SPL has been further consolidated. This approach has been exploited for the fabrication of faceted nanopatterns endowed with geometric features defined a-priori in order to engineer the shape and the photonic properties of crystalline 2D TMD layers behaving as directional photon emitters. To this final goal a microscope-assisted setup for the exfoliation and deterministic transfer of MoS_2 crystalline flakes has been developed in collaboration with a PhD colleague. Such approach allows to precisely transfer MoS_2 mono- and few- layer flakes onto the patterned polymer surfaces. This kind of flakes, which possess well-known vibrational response and photoluminescent behavior, are then characterized by AFM and Raman micro-spectroscopy. Also, to detect possible variations in the electronic behavior induced by the presence of an underlying rippled structure, I performed Kelvin Probe Force Microscopy measurements. In order to resonantly amplify the 2D TMDs photon emission an hybrid 2D-plasmonic metasurface has been devised by coupling periodic arrays of plasmonic nanoantennas to the 2D TMD flakes. The nanoantenna arrays have been fabricated by grazing angle thermal gold evaporation onto the grayscale t-SPL nanopattern. Under this condition the mutual shadowing effect given by the facets promotes the growth of laterally disconnected nanowires endowed with tunable plasmonic response in the Visible and Near-Infrared spectrum. The final goal will be to create an integrated ultra-thin configuration that promote the enhancement of the photoluminescence emission of a 2D TMD layer by i) strain engineering in the nanostructured surface, and ii) plasmon-exciton coupling in hybrid metasurfaces. Additionally, the possibility to devise directional nanoemitters by controlling the directionality of the signal in these configurations will be investigated.

2.2 Nanopatterning PPA/AZO polymer blends onto 1D photonic crystals

An interesting class of optically active materials is represented by azopolymers, being them capable of undergoing a photoisomerization process from -trans to -cis structure when interacting with polarized light. The light- induced alignment of molecules dipoles perpendicularly to the polarization axis leads to physical and chemical changes that allows to optically control the material behavior, inducing dichroism and/or birefringence. The ability to nanopattern flat-optics components directly onto these thin films is appealing since it allows the manipulation of light at the nanoscale without the use of bulky optical components. However, standard nanolithography tools such as Electron Beam Lithography (EBL) are generally not suitable for these films due to charging effects and lack of spatial resolution in the final pattern. We thus developed a stable polymer blend (PPA/AZO) that combine the thermal sensitivity for t-SPL nanolithography with the azopolymer dye. This way thin films polymer blend have been directly patterned by t-SPL creating metalenses based on polymer subwavelength nanostructures. We fabricated linear and circular periodic nanocavities engraved on the polymer blend, aiming at the excitation and spatial confinement of Bloch Surface Wave modes supported by a 1D photonic crystal used as a substrate. We obtained a photonic device showing polarization-controlled Bloch Surface Waves localization [3]. The optical characterization has been performed in Turin within a collaboration with ''Politecnico di Torino'', while fabrication and morphological characterization has been optimized and performed by our group here in Genova.

3 Hybrid 2D-3D heterostructures for photovoltaic junctions

Starting from the idea of exploiting novel 2D materials for photovoltaic devices, part of my activity focused on a first implementation of 2D MoS_2 on standard Silicon substrates. More specifically, few-nm thick MoS_2 films are being deposited by Ion Beam Sputtering (IBS) techniques on p-doped Silicon substrates to create hybrid 2D-3D junctions. Such deposition approach allows to obtain macroscopically extended samples, with areas in the order of cm^2. These extended junctions are then electrically characterized while being controllably illuminated, to detect photo-induced effects. Preliminary results show a promising photovoltaic behavior that justify a deeper characterization and optimization of the system.

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. Ferrando, G.; Gardella, M.; Zambito, G. *et al.*, ''*Flat-optics hybrid MoS_2/polymer films for photochemical conversion*'', Nanoscale, 2023,15, 1953-1961

3. Marcucci, N.; Giordano, M. C.; Zambito, G. *et al.*, "*Spectral tuning of Bloch Surface Wave resonances by light-controlled optical anisotropy*" Nanophotonics, vol. 12, no. 6, 2023, pp. 1091-1104.
4. Giordano, M. C.; Pham, D.; Ferrando, G.; Si , Hieu N.; Ha, C.; Mai, T. H.; Zambito, G. *et al.*; *''Self-organized plasmonic nanoelectrodes for photoelectrochemical energy storage*'', *Under review*

ATTENDED COURSES: Nanophotonics & nanofabrication

CONFERENCE PRESENTATIONS

- ''Nanomanipulation Workshop'', Krakow, May 2023 (Oral presentation)
- ''Nanoseries 2023'', Madrid, June 2023 (Oral presentation)
- ''MNE23'', Berlin, September 2023 (Poster)