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PhD thesis in Physics and Nanosciences, Curriculum Physics, XXXVI Cycle

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Summary of contents

Fabrication and characterization of plexcitonic hybrid systems for nanoscale heat-transfer measurements

Introduction

Nowadays heat management at the nanoscale is a crucial technological issue, due to the ever growing diffusion of nanodevices at all levels. Heat diffusion at the nanoscale is fundamentally different with respect to the analogous macroscale phenomenon. The exchange of thermal energy at the macroscale is effectively describe by the Fourier's law which is valid in the so-called "diffusive regime", where the mean free path of heat carriers is much smaller than the size of the considered systems. At the nanoscale this condition can be misapplied causing the breakdown of the Fourier's law. Depending on the composition, size and geometry of the considered systems many heat transport regimes can take place: from *ballistic* to *hydrodynamic* to *heat confinement* ones.

Within this framework, there is a growing need for reliable nanothermometry experimental investigations; however, performing such measurements is a particularly challenging task. This is due to many factors, like the broadband and short-wavelength nature of heat-carrying phonons, the difficulty in fabricating nanostructures and the finite heat capacity of any solid-state thermal probe, which can affect the thermodynamics of the system under scrutiny, introducing unwanted artifacts.

To perform nanothermometry measurements in a non-perturbative and reliable way, we propose nanothermometry devices where heating and sensing at the nanoscale are performed in the same system, employing light as a temperature readout method. Light has no thermal capacity making it a low-perturbative probe. The devices are characterized by three layers: heater layer, dielectric insulator and sensing layer. The heater layer has the role of converting an incident electromagnetic (EM) radiation into a localized increase of temperature, the dielectric layer separates the other two, avoiding any coupling between them and conducts heat from heaters to sensors, finally, the sensor layer is characterized by temperature-dependent optical properties enabling the temperature measurement through light.

The thesis describes the fabrication and the characterization of two different nanothermometry devices, exploiting plasmonic nanostructures (NS) as heaters and bidimensional (2D) semiconductors as sensors. The experimental outcomes and the perspectives of the project conclude the thesis.

Chapter 1: Plasmonic and excitonic systems for nanothermometry measurements

The first part of this chapter consists in a general picture of the various nanoscale heat conduction regimes including both theoretical and experimental literature. The second part presents the properties of plasmonic NS and 2D semiconductors explaining why these systems were chosen as heaters and sensors for our nanothermometry devices.

Noble metal NS are characterized by optical properties ruled by the Localized Surface Plasmon Resonace (LSPR): a phenomenon in which the oscillating electric field of an EM radiation of proper wavelength can excite the free electrons of the NS in a resonant way. The result of this process is an absorption of EM energy by the NS. In a second time, LSPR can decay following two pathways: the radiative and the non-radiative decay. The latter can be exploited to make NS effective nanometric heat sources after the excitation of LSPR by means of optical wavelengths.

2D Transition Metal DiChalogenides (TMDC) are low-dimensional systems characterized by a direct band gap. This fact makes them appealing materials for optoelectronics explaining the growing literature in the field. The direct nature of their band gap allows high photoluminescence (PL) yields. PL is a thermo-sensitive property since after an increase of temperature the wavelength of the emitted radiation redshifts with an almost linear thermal dependence. This property, together with the reduced heat capacity per unit area, makes 2D TMDC ideal nanometric thermosensors. In particular, the thesis focuses on monolayer (ML) MoS_2 and WS_2 obtained both by chemical and physical fabrication routes.

Chapter 2: Experimetal methods

This chapter describes the experimental techniques adopted to characterize the nanothermometry devices and their components: Raman spectroscopy, (Imaging) PL spectroscopy, (Imaging) spectroscopic ellipsometry and atomic-force microscopy.

Particular emphasis is given to the nanothermometry techniques: transient absorption spectroscopy (TAS), for the ultrafast time-scales, and Steady-State Fluorescence Nanothermometry (SSFN), for the steady-state regime.

SSFN is performed in a home-assembled setup in which a 532 nm laser radiation is adopted to excite the 2D TMDC PL, and a 785 nm laser radiation is adopted to launch LSPR modes. The evolution of the 2D TMDC PL spectra before and after LSPR excitation is assessed with microscopy functionality enabling the estimation of local temperature variations. The employed wavelengths are carefully chosen so that the radiation that excites the LSPR is not absorbed by the heater layer and the 785 nm laser radiation is not absorbed by the sensor layer, avoiding perturbations of the heat-generation and temperature-sensing processes.

Chapter 3: Nanofabrication and characterization of arrays of plasmonic nanostructures

This chapter is devoted to the description of the lithographic techniques adopted to fabricate the arrays of plasmonic NS employed as heaters in the nanothermometry devices. The geometry and the spatial distribution of the NS were carefully designed in order to match the LSPR wavelength with the one of the 785 nm laser. Two top-down routes were employed to obtain two different devices: Electron-Beam Lithography (EBL) and Thermal Scanning-Probe Lithography (t-SPL). Fabrication recipes were specially adapted to work also on the insulating, optically transparent substrates required for the nanothermometry measurements.

In particular, t-SPL was performed on glass substrates coated with an ad-hoc designed ultrathin film of Transparent Conductive Oxide (TCO). This way, it was possible to reproduce the peak performances that this technique shows on Si (the standard lithographic substrate) also on glass [1].

This upgraded lithographic recipe was successfully exploited also to directly decorate exfoliated 2D TMDC flakes with plasmonic NS without damaging this delicate substrate [2].

Chapter 4: Nanothermometry devices and measurements

Starting from the two arrays of plasmonic NS fabricated via EBL and t-SPL, two nanothermometry devices were assembled, noted as *Device 1* and *Device 2* respectively.

In order to obtain the Device 1, the heater layer fabricated through EBL was coated with 200 nm of Al_2O_3 (which constitutes the dielectric spacer) and then by flakes of ML WS_2. The flakes were grown via Chemical-Vapour Deposition (CVD) and then transferred on Al_2O_3 through a semi-dry transfer process. With this device it was possible to perform TAS measurements thanks to the wide area (0.5 mm X 0.5 mm) decorated with plasmonic NS. After that, SSFN measurements were conducted. It was not possible to detect any measurable thermo-induced variation of WS_2 PL because of the thickness of the dielectric spacer.

Device 2 was assembled by depositing three layers of 2D materials on the plasmonic NS fabricated via t-SPL: a layer of CVD-grown ML WS_2 sandwiched between two layers of ML Hexagonal Boron Nitride (hBN). The first hBN layer acts as dielectric spacer between heaters and sensors while the second one protects WS_2 from oxidation and reduces heat dissipation via convection. SSFN measurements were conducted and a thermo-induced spectral shift of WS_2 PL was detected. WS_2 PL spectra of Device 2 were measured at different temperatures in order to obtain the thermometric calibration of the PL spectral position. This way it was possible to estimate the temperature increase in the sensor layer after the non-radiative decay of LSPR of the heater layer as (36 ± 3)°C in the adopted experimental conditions [3].

Conclusions and future perspectives

Two nanothermometry devices made by a heater layer of plasmonic NS, a dielectric spacer and a thermometer layer of ML TMDC were fabricated through different lithographic approaches and optically characterized in order to perform nanothermometry measurements. With one of the two it was effectively possible to detect a thermo-induced optical signal which was converted in a temperature estimation after a thermometric calibration of the system.

This experiment was the proof-of-concept that it is possible to measure a temperature variation at the nanoscale, where the heating and the sensing is performed in the same device employing two different kind of nanostructures.

This platform will be exploited to assess the effect of the fluence of the adopted lasers on the thermodynamics of the systems. By changing the thickness and the composition of the dielectric spacer, heat conduction properties of different ultrathin films will be assessed. After the steady-state thermal characterizations, the systems will be also analyzed through ultrafast techniques in order to unveil the details of the transient processes.

[1] L. Ramò, M. C. Giordano, G. Ferrando, P. Canepa, F. Telesio, L. Repetto, F. B. de Mongeot, M. Canepa and F. Bisio, *Thermal Scanning-Probe Lithography for Broadband On-Demand Plasmonic Nanostructures on Transparent Substrates*, ACS Applied Nano Materials, 6, (19) 18623–18631 (2023) (https://pubs.acs.org/doi/10.1021/acsanm.3c04398)

[2] L.Ramò, E.Peci, M. Magnozzi, E. Spotorno, V. Venturino, M. Sygletou, M.C. Giordano, G. Zambito, F. Telesio, Z. Milosz, M. Canepa, F. Bisio *Non-invasive deterministic plasmonic nanostructures lithography on 2D transition metal dichalcogenides*, (submitted to ACS Applied materials & Interfaces)

[3] L.Ramò, V. Venturino, D. Convertino, C. Coletti, M. Canepa and F. Bisio, *Steady-state nanothermometry of plasmonic photothermal effect through monolayer WS_2 photoluminescence,* (in preparation)