Project title: **NAtuRal instability of semiConductors thIn SOlid films for sensing and photonic applications (NARCISO)**
Grant Agreement: 828890
Call identifier: H2020-FETOPEN-2018-2020/H2020-FETOPEN-2018-2019-2020-01
Start Date of Project: 01/03/2019
Duration: 36 months

Deliverable D6.5 – V1.0

Title: WHITE PAPER 1.

Leader partner	OTAB, all
Author(s)	Ye Zhou Persson, Marco Abbarchi, Monica Bollani
Estimated delivery	29/02/2020
Actual delivery	
Revised version	
Work Package	WP6 Communication, dissemination and exploitation activities
Tasks	6.5
Dissemination level	Public
Version	1.0

Contents

Contents 2
1. Introduction 3
2. Results 6
3. Dissemination 9

1. Introduction

Starting from the beginning of 2019 the European consortium NARCISO has been forged to work on the study, development and exploitation of the **NAtuRal instability of semiConductors thIn SOlid films for sensing and photonic applications (grant n°828890).** Its mission is to deliver reliable and scalable fabrication techniques of nano- and micro-structures over large scales to be exploited in several domains of application, such as nano-photonics (e.g. light filters for smart windows, light emitters), micro-electronics (e.g. electronic devices), micro-fluidic (e.g. water filters, bio-detectors for diagnostic). The consortium is composed by 5 academic groups and 1 non-academic partner, each of them leading their own research program on different aspects of NARCISO. The members of the consortium have been chosen in order to cover the needs of growth and fabrication, theoretical modeling, characterization, applicability and industrial scaling of the fabricated structures:

-1 CONSIGLIO NAZIONALE DELLE RICERCHE IT (lead. Dr. Monica Bollani, monica.bollani@ifn.cnr.it, http://www.ifn.cnr.it/home). Activity: device fabrication, , III-V integration on SiGe micro- and nano-structures, morphological-electrical and structural characterizations.

-2 UNIVERSITE D'AIX MARSEILLE FR (lead. Prof. Marco Abbarchi, marco.abbarchi@im2np.fr, http://www.im2np.fr/doct/abbarchi.html). Activity: solid state dewetting of SiGe, sol-gel dip-coating and nano-imprint lithography.

-3 TECHNISCHE UNIVERSITAET DRESDEN DE (lead. Prof. Axel Voigt, axel.voigt@tu-dresden.de, http://www.tu-dresden.de/). Activity: phase field simulations of solid state dewetting and particle diffusion.

-4 UNIVERSITE DE LAUSANNE CH (lead Prof. Pietro De Anna, pietro.deanna@unil.ch, www.pietrodeanna.org). Activity: microfluidic, filtering and sensing with nano-imprinted micro- and nano-structures.

-5 UNIVERSITA DEGLI STUDI DI FIRENZE IT (lead. Prof. Francesca Intonti, intonti@lens.unifi.it, http://www.lens.unifi.it/nanostructures/index.php). Activity: optical spectroscopy (near- and far-field) of dielectric micro- and nano-structures.

-6 OBDUCAT TECHNOLOGIES AB SE (lead Dr. Kristian Thulin, kristian.thulin@obducat.com, www.Obducat.com). Activity: scale up of nano-imprint lithography metal-oxides-based micro- and nano-structures.

1.1. Solid state dewetting.

There are many “tools” employed by the consortium NARCISO for building such kind of structures. At the basis there is solid state dewetting: a natural instability that leads thin films to break into tiny islands when perturbed. In analogy with a liquid dripping into droplets when surface and capillary forces dominate over gravitational ones, a solid film (e.g. of polymer, metal or semiconductor) breaks when heated up even well below the melting point the material in use. Exploiting this instability allows to transform a 2D flat payer in large arrays of 3D islands. In case of a simple flat layer of silicon or silicon-germanium alloys undergoing *spontaneous dewetting*, the organization of the islands will be quite poor, their size and shape dispersion being rather large reflecting the stochastic nature of this phenomenon (see Figure 1). The main advantage of this method with respect to other fabrication tools for micro-and nano-structures is that it does not depend on the extension of the substrate in use. As such, the nano-structures can be produced in a single fabrication step over arbitrary large wafers.

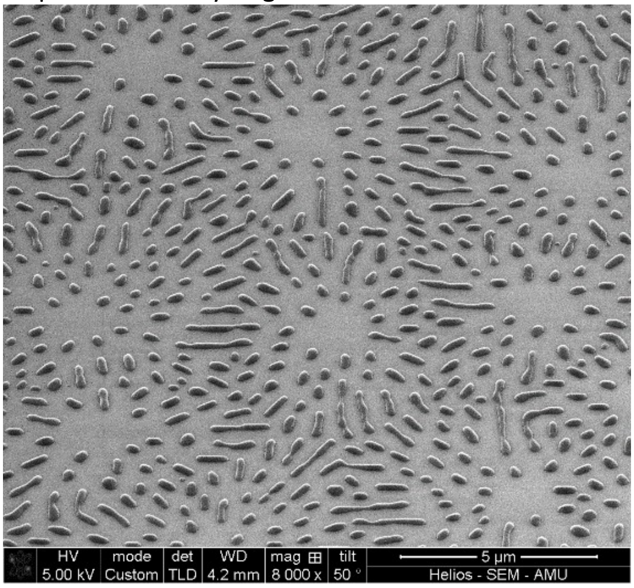

Figure 1 *Silicon islands on SiO_2 obtained via solid state dewetting of 12 nm of Si annealed at 800 C for one hour.*

However, for some application (e.g. structural color with SiGe-submicrometric antennas or for micro-electronics, owing to the mandatory need of spatial addressability of the devices), a precise ordering of the dewetted islands is preferable and in some case essential. For this reason, within the NARCISO consortium, the dewetting dynamic has been engineered by patterning the Si(Ge) layers before annealing: with an appropriate choice of pattern size and shape, solid state dewetting can deliver extremely complex nano-architectures with a high fidelity (Figure 2).

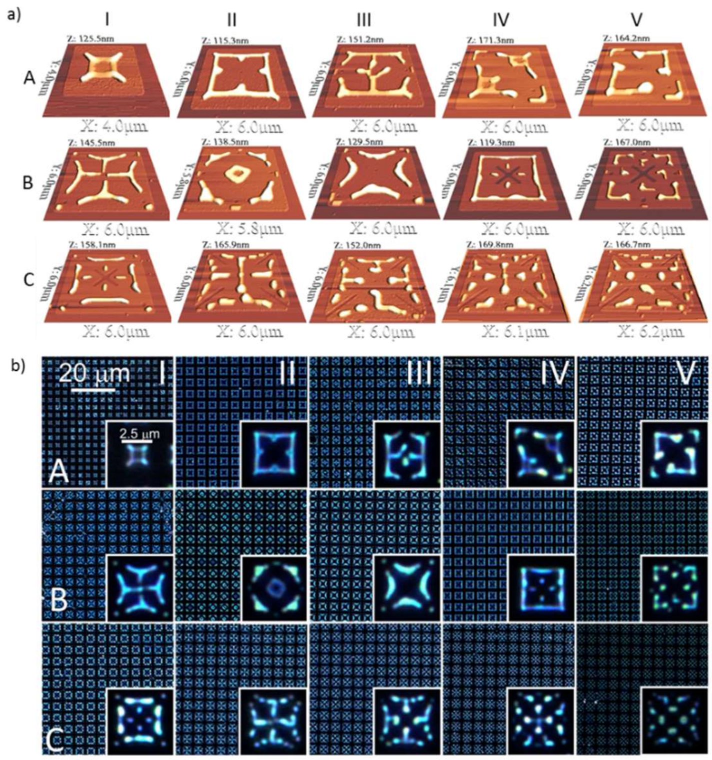

Figure 2 Structural and optical characterization of dewetted Si on SiO2. (a) 3D view of atomic force microscopy (AFM) images of patches annealed for 3 hours. (b) Optical dark-field microscopy images. From NAFFOUTI et al., SCI ADV 2017 eaao1472.

1.2. Phase field simulations.

A second essential element exploited in NARCISO are theoretical simulations based on a *phase field approach*. By making use of advanced mathematical methods and of supercomputers, the evolution of real structures evolving under solid state dewetting can be predicted *a priori* with great accuracy (Figure 3). The importance of the phase field method is that it provides a predictive representation of the expected experimental outcomes. As such, it can be used to optimize size and morphology of Si(Ge)-based micro- and nano-architectures towards a specific application.

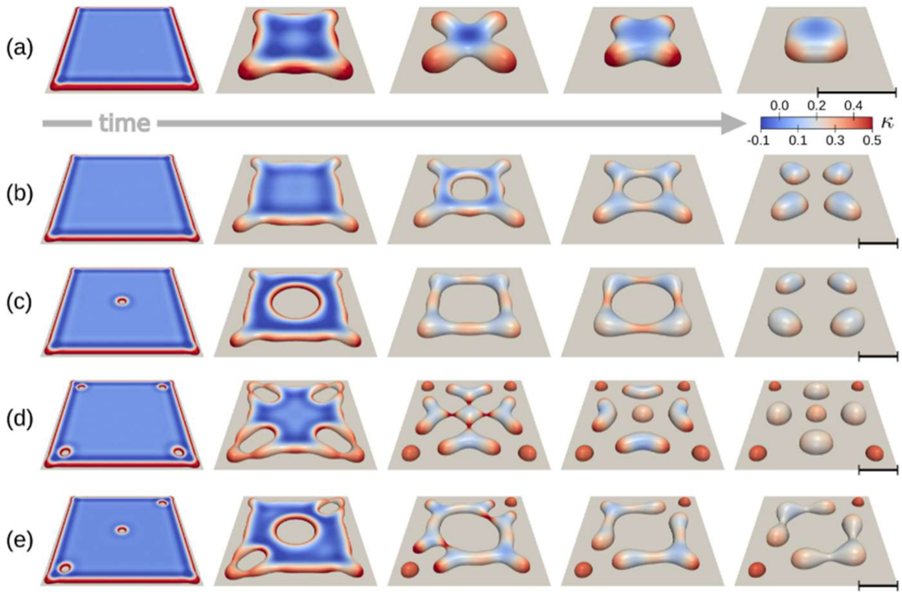

Figure 3: Phase field simulations of square silicon patches on SiO2 with etched holes. (a) Evolution with time of a squared patch with an aspect ratio of 1:40, corresponding to Fig. 2D. (b) Evolution of a squared patch with an aspect ratio R = 1:80. (c) Evolution of a squared patch with a central hole, as in Fig. 2 (A-II). (d) Evolution of a squared patch with four holes at the corners, as in Fig. 2 (B-I). (e) Evolution of a squared patch with three holes on the diagonal, as in Fig. 2 (A-V). Representative steps of the evolution are selected for each simulation. From NAFFOUTI et al., SCI ADV 2017 eaao1472.3

1.3. Nano-imprint lithography.

A last key tool of NARCISO is *sol-gel dip-coating and nano-imprint lithography*(Soft-NIL) used to transfer the morphology of the dewetted nano-architectures on arbitrary substrates using different materials. In fact, only few materials can undergo **solid state** dewetting. Within NARCISO we are using the technologically-relevant silicon and germanium. However, there are many limitations associated with the technique in use and also to these materials (e.g. the substrate used for dewetting is not transparent, nor flexible or stretchable, to name a few). It is thus of the utmost importance extending the exploitation of these structures by adding new functions. The approach we are using is based on (1) the deposition of a liquid chemical solution containing the precursors (e.g. metal oxides such as SiO_2 or TiO_2) on a substrate (e.g. semiconductor, metal, glass, plastic), (2) printing the liquid solution with a polymer mould, (3) densifying the solution providing mechanically strong and chemically stable nano-architectures (see Figure 4).

The main idea of NARCISO is first, using solid state dewetting of SiGe to fabricate the master mould over large areas and second, replicate disordered and ordered nano-architectures on other substrates and different materials via soft-NIL, thus adjusting their composition, porosity, refractive index, absorption and functionality (e.g. embedding light emitters or surfactants to detect a specific molecule). The importance of this idea is twofold: (i) the use of solid state dewetting can provide hard-masters over large scales (note that, generally speaking, the most severe limit of NIL is the cost of the master), (ii) using the soft-NIL approach can provide, in a single step, hard materials (e.g. most kind of metal oxides: Titania, Alumina, Silica, Yttria-Zirconia, to name a few) eventually featuring a refractive index (e.g. 2.4 for TiO_2) much larger than that one of most polymers conventionally used for NIL.

Figure 4 Schematic representation of the successive steps involved in the soft-NIL/sol-gel processing. The controlled environment was performed using a computer-piloted set of mass flow controllers delivering air at a constant flow and temperature, and at humidity adjusted between 2 and 98% with 2% error. The xerogel layer/substrate sample stands on a heating plate (not-shown) in the chamber to increase slightly the temperature if required. From BOTTEIN et al., Nanoscale 10, 1420 (2018).

2. Results

During the first year of activity the consortium has been working in order to validate several goals, either preliminary or advanced. Several of these results have been published as open access and presented in a conference or workshop (see the following section 3. Dissemination), whereas many others are only preliminary and need to be validated before publication.

2.1 Simulations. Phase-field (PF) simulations of solid-state dewetting have been performed. They allowed for reproducing the key features observed in experiments, unveiling the driving forces at play. Particular attention has been devoted to simulating the dewetting of stripes resulting in ultra-long nanowires (see also 2.4) and assessing the role of surface-energy anisotropy in the process. The optimization of the PF simulations of surface diffusion, including strong anisotropy and realistic surface-energy density, has been necessary. Moreover, the classical PF model of surface diffusion has been coupled to elasticity. This allowed the investigation of dewetting in the presence of misfit strain and allowed for explaining the onset of spinodal dewetting of SiGe thin films deposited on SOI. The PF model of surface diffusion has also been improved, namely through the development of the so-called Degenerate Cahn-Hilliard model, allowing for simulations with high accuracy and relatively limited computational costs and a better description of interfaces in the presence of both isotropic and anisotropic surface energies.
Furthermore, theoretical tools have been developed to analyze the outcome of the dewetting process as resulting from experiments. An image analysis framework characterizing the topology and global properties of the patterns such as the so-called Betti Numbers, Minkowski functionals, and hyperuniformity has been developed (arXiv preprint arXiv:1912.02952).

2.2 Flexible photonics with dielectric structures: Within the first year, CNR, AMU and TUD have been working on several aspects of solid state dewetting. Firstly, the process has been extended over 2 inches, which represents a record of SiGe nano-structures (this result has been published in January 2020) while a new generation of samples has been already implemented on 4 inches (result not yet published). Secondly, in order to overcome the limitations of solid state dewetting (implemented on rigid and non-transparent samples), the islands have been released and transported within a polymer slice providing a stretchable, flexible and transparent support (see Figure 5 and 6).

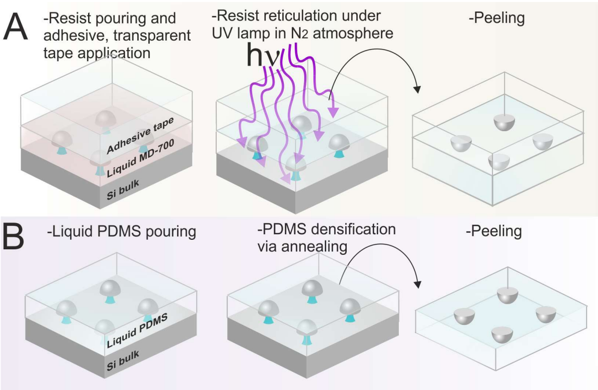

Figure 5 Schematic representation of two alternative transfer processes for removing the islands from the original support embedding them in a plastic support. From BENALI et al., 2020 J. Phys. Photonics 2515 ab6713.

2.3
2.3
2.3

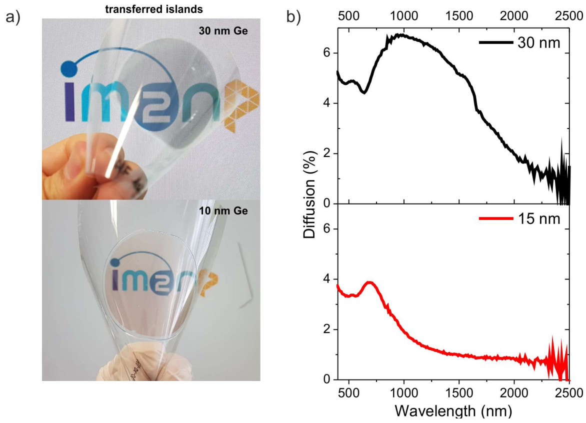

Figure 6: Ge islands transported in a polymer slice after dewetting over 2 Inches wafers. For sufficiently small islands a structural color emerges (a) bottom panel). From BENALI et al., 2020 J. Phys. Photonics 2515 ab6713.

2.3Disordered hyperuniform structures: Another relevant aspect that is central in NARCISO is the fabrication of disordered nano-structures with a configuration that is known as "hyperuniform". This is a special class of disordered materials where hidden correlations in the relative position of the objects bring novel functionalities. Experimental results have been reproduced theoretically by phase field simulations demonstrating for the first time that SiGe-based micro- and nano-architectures obtained via dewetting can provide hyperuniform structures. This is a very important result: de facto we can now exploit this original class of correlated-disordered material in SiGe and in metal oxide for photonic and electronic devices, and micro-fluidic. The actual size of the sample is limited for the moment to 2 cm x 2 cm and it will now expand to 4 inches wafers, once determined the best size and shape of the structures for a specific application. These results have been recently submitted for publication and an example of the spinodal hyperuniform structures is shown in figure 7.

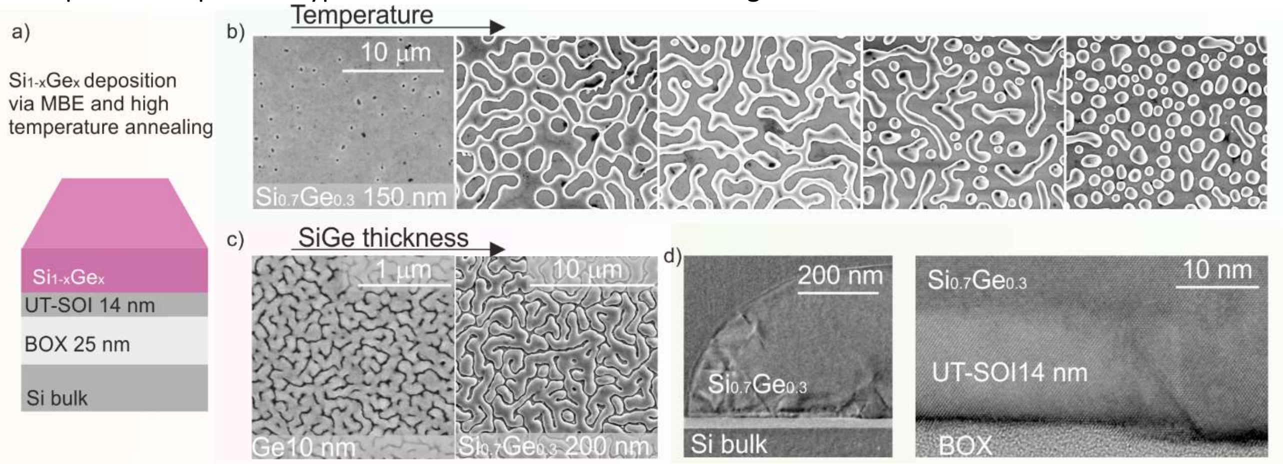

Figure 7: Spinodal solid-state dewetting. a) Scheme of the system under investigation: ultra-thin silicon on insulator substrates (14 nm thick Si on 25 nm thick SiO2, buried oxide, BOX) followed by epitaxial deposition of Si 1−x Ge x alloys and high temperature annealing in a molecular beam reactor (MBE). b) Scanning electron micro-graphs (SEM) displaying the morphological evolution (from the edge of the sample, left panel, towards its center, right panel) of 150 nm Si0.7Ge0.3 on UT-SOI after 4 hours annealing at 800 ◦C. c) Left panel: transmission electron micro-graph (TEM) of a dewetted island. Right panel: high-resolution TEM highlighting the interface between the BOX, some pristine UT-SOI and the Si0.7Ge0.3.

2.4 Ultra-long nanowires used as field effect transistor: A very important result that has been published in December 2019 within the NARCISO consortium is the formation of ultra-long nano-wires via solid state dewetting (see BOLLANI et al., Nat. Comm. 10, 5632 (2019). In this work we demonstrated for the first time the relevance of the dewetting approach for the fabrication of a realistic electronic device. We synthesized arrays of parallel monocrystalline, silicon-based nano-wires with a record length of 0.75 mm and complex, connected circuits (figure 8). Using these wires, we fabricated field-effect transistors showing state-of-the-art electronic figures of merit (trans-conductance and electron mobility). These remarkable properties have been reached without any optimization accounting for the ease of implementation of electronic devices on our platform (figure 9). Another relevant aspect shown in our work is the remarkable agreement between phase field simulations and experiments: for the first time a real-scale phase field simulation, successfully takes into account the facets of the monocrystalline structures.

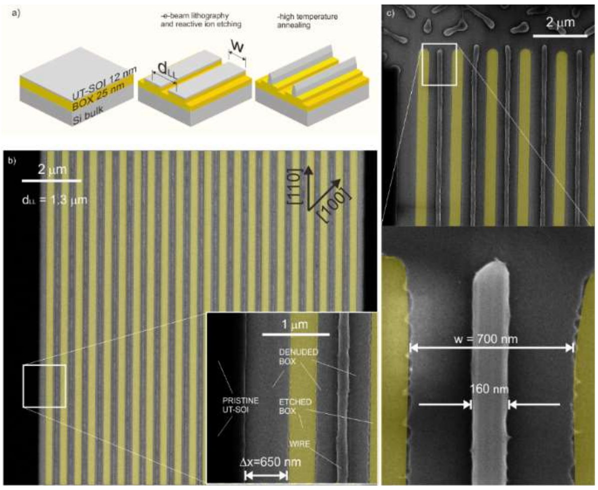

Figure 8 Ultra-long nano-wires formation. A) Scheme of the sample fabrication. B) Scanning electron microscope (SEM) image of 21 parallel nano-wires of length 0.75 mm. c) Top panel: detail of the extremity of the wires.

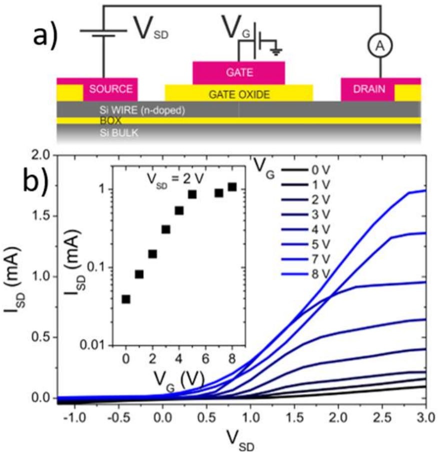

Figure 9 Electrical properties of parallel wires. a) Scheme of the field effect transistor (FET) wires device. b) Electrical transport characteristics (S-D current versus S-D voltage curves recorded at different G voltage).

2.5 Microfluidic. Within the framework of NARCISO, the UNIL partner combines optical time-lapse video-microscopy and image processing to study transport and filtration of colloid and bacterial behavior at pore (via Lagrangian statistics) and macroscopic (via breakthrough curves and deposition profiles) scales. This is done by using novel microfluidics obtained by both, exploiting geometries derived from de-wetted processes and printed into classical PDMS chips, and using de-wetted surfaces made of different materials. The use of such novel devices is allowing us to tune, on the one hand, the physical structure of the filter and, on the other hand, the physico-chemical interaction between transported colloids/bacteria and the solid matrix of the filter. In the past few months we: i) advanced in defining the diagnostic quantities of interest and successfully testing new methods to measure them, and ii) testing the fabrication of novel microfluidics based on de-wetted surfaces.

2.6 Direct measurement of the local density of states (LDOS) of nanoresonators: Within the first year, UNIFI has been working on the spectroscopic characterization of light confined in nanoresonators. In fact, in order to address the collective optical behavior of complex nano-architectures implemented via solid state dewetting it is essential to understand first the spectroscopic characteristics of a single dewetted structure. By investigating optically active coupled systems showing mode overlap, we experimentally demonstrate that their LDOS is characterized by a strong non-Lorentzian lineshapes. The observed Fano-like LDOS represents a distinctive hallmark that allowed us to directly relate the spectrum locally collected by the near-field probe of a scanning-near-field-optical microscope (SNOM) with the electric LDOS of the investigated system (figure 10). In this way we proved that the hyperspectral imaging of the photoluminescence (PL) signal of emitter embedded in nanoresonators is a direct tool for mapping the LDOS with a deep-subwavelength spatial resolution of the order of 130 nm

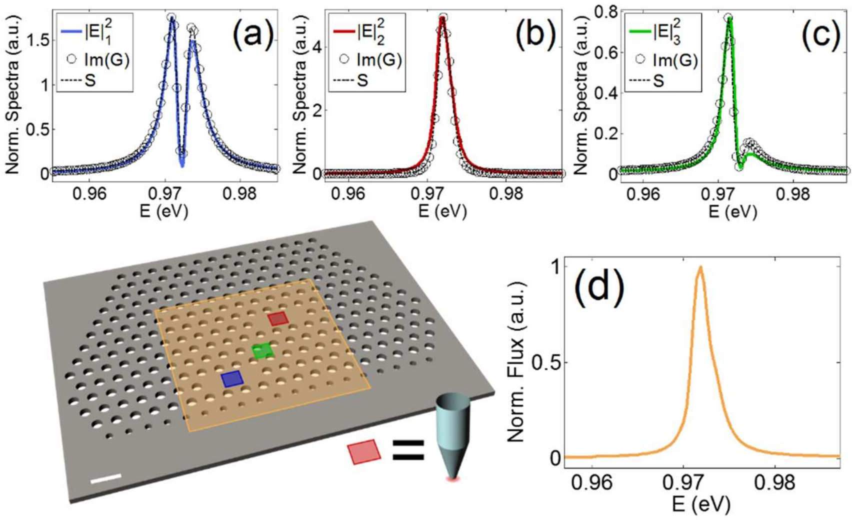

Figure 10 The sketch shows the scheme of the simulated system with three small sensors (0.3x0.3 □m2, they are in air 30 nm over the sample, simulating the SNOM tip) for calculating the near field PL spectra in (a)-(c) and the big orange sensor (3x3 □m2) for calculating the far field PL spectrum in (d). In the sketch the white scale bar is 500 nm. In (a)-(c) the simulated PL (|E|^2) is in full lines with the same color scheme of the sensors, the LDOS calculated by the Green's function in black circles and the LDOS calculated by the net flux of S in black dashed lines

3. Dissemination

During the first year of the project, the NARCISO network has published some scientific papers. All publications are open access, therefore accessible to anyone who wants to read them. The same list of publications is updated on the project website, at the link:
https://www2.mi.ifn.cnr.it/narciso/publications.html

NARCISO's network has also participated at several international conferences, by invitation or as oral presentations, in order to promote the results obtained during the first year of the project. The complete list is available at:
https://www2.mi.ifn.cnr.it/narciso/conferences.html

Our studies related to dewetting instability of semiconductor thin films have been also presented for 6 months at the exhibition "**Broken Nature**" (http://www.brokennature.org/) (March 2020-September 2019). Broken Nature has been a thematic exhibition from which the XXII International Exhibition took its name. This exhibition has been an in-depth exploration of the strands that connect humans to the natural environment that have been intensely compromised, if not entirely severed, over the years. By casting a wide net on architecture and design projects, Broken Nature underlined the concept of restorative design, highlighting objects and concepts at all scales that reconsider human beings' relationship with their environments – including both natural and social ecosystems.

Finally, dissemination towards the general public has been performed by participating to **Meet Me Tonight**, an event organized by the EU to put in contact EU citizens of all ages with the world of research (http://www.meetmetonight.it/meetmetonight-programma-milano/). Two other FET projects, microSPIRE (766955) http://www.microspire-h2020.eu/project/ and PROCHIP (801336) https://pro-chip.eu/ participated to the Meet Me Tonight event together with the NARCISO team.

The NARCISO and microSPIRE events used 3D goggles to visualize crystal structures in a “virtual reality” environment and a small optical set up to show the application of single photon detectors. An example of a 3D video showing dislocations in a Ge crystal is visible at: https://youtu.be/QxRh-2ygP-8.