Sujet de Thèse

C(PN)^2

La Centrale de Proximité en Nanotechnologies de Paris Nord

"Optimizing the multifunctionality of polymer-based composite thin films by using an innovative confinement technique"

Scientific Area: Nanomaterials and Nanolithography, Functional properties: piezoelectricity, ferromagnetism.

Host Laboratory: Laboratoire des Sciences des Procédés et des Matériaux, CNRS UPR-3407, Axe MINOS
Université Paris Nord, 99 Avenue J.-B. Clément, F-93430 Villetaneuse.

PhD supervision: Director: Silvana MERCONE, silvana.mercone@sorbonne-paris-nord.fr

Short Context: The realization of a device with simultaneous strong electric and magnetic order at room temperature would be a milestone for modern electronics and multifunctional materials. These systems offer potential for new generations of sensors, filter, and field-tuneable dielectric devices. In this framework, the poly(vinylidene fluoride) (PVDF) is one of the most challenging and interesting organic materials for the development of advanced applications due to its high dielectric constant, piezo-, pyro-, and ferroelectric (FE) effects. One of the major advantages of using ferroelectric polymer-based devices is the solution compatibility of the polymer and, thus, the easy and simple elaboration process that it offers for deposition of uniform thin films. The ability to fabricate composite devices in a shorter number of fabrication steps, without post-treatment and with less energy input is expected to be a key contribution in driving their commercialization and further increase the prospects of sustainable energy methods.

Current Issues: One exiting developing area in this framework is the incorporation of additives into piezoelectric polymers. Previous studies, including ours, showed possibilities of maximizing the amount of β phase (FE) in composite thin films based on PVDF (thickness lower than 100 nm) but also put in evidence the on-going presence of the non-piezoelectric α phase melted with the predominant β one. The unwished α phase is still present although the inclusion of magnetostrictive nanoparticles (base on Cobalt) is supposed to enhance the piezoelectric properties of the polymer. We recently show that optimizing the dispersion of the nano-inclusions by functionalizing the nano-inclusions surface can help in restoring a part of the piezoelectric film response. Recent papers showed that there is a promising possibility, which is the film nanostructuring. The confinement of PVDF-based structures seems to be selective for polar ferroelectric micro- and nano-domains and, thus, enhances the piezoelectric properties of the polymer-based nanostructures. Besides, the dispersion and organization of the nano-inclusions by nanostructuring the hybrid film is also going to be selective for the magnetic properties of these latter. Last but not least, the capability of micro-/nanopatterning a large surface of the polymer-based composite thin film is, so far, mandatory to ensure high-density integration of the multifunctional "cells" per unit area and, thus, open the way to a new multifunctional nanotechnology.

PhD Main goals:

(Confinement) In order to keep in mind the future electromagnetic-based applications, a nano-patterning of the optimized hybrid structures obtained will be achieved by a specific nano-photo-lithography based technique (see Figure 1) that can overcome chemical processing limits observed in literature. This optical technique has been developed at C(PN)^2 and optimized on organic-based films.The PhD student will systematically study and analyse all the issues that this technique may bring up, in order to further reduce the size of the nanostructures on a large surfaces.

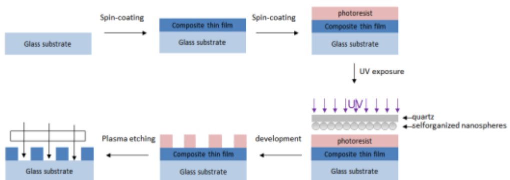

Figure 1: *Fabrication process: Nanosphere Photolithography combined with plasma etching (USPN-clean room)*

(Peculiar characterization) We will combine together the use of standard XRD and IR spectroscopy with Raman one and non-destructive local microscopy in order to fully understand the effect of the hybrid interphase as well as of the nano-confinement on the multifunctionalities of the PVDF and copolymer based composite systems. It is obvious that this work to optimize nanostructuring of single and two-phase material will be associated with a study of the physical (electromagnetic) and structural properties of the hybrid, polymer and / or inorganic material as a function of the change in morphology and distribution of nanostructures. This will be possible in a collaborative environment via the easy access to several characterizations techniques like AFM, IR, Raman spectroscopy, X-ray diffraction, magnetometry, and PFM (LSPM and LabeX SEAM). In addition, the macroscopic orientation of these confined crystals should also be oriented in the direction of the (magnetic or electric) fields. GI-SAXS and GI-WAXS (Grazing Incidence Wide or Small Angle X-Ray Scattering) are ideal techniques to probe the lamellae orientation in the confining domains (An established collaboration ready to host the PhD student is already onset between S. Mercone at LSPM and S. Roland at ENSAM on this aspect).