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Plasmonic Structures for Sensing and Emitting Devices

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Abstract. We report on the study of a plasmonic nanostructure that could be adopted as platform for emitting and sensing applications. Several devices have been prepared and characterized by atomic force microscopy (AFM) and Fourier transform micro-reflectance (FT- μ R) techniques. In addition, a modelling via finite-difference time-domain (FDTD) simulations have been developed in order to interpret the morphological shape and the optical response of the considered structures. Until now, remarkable performances as surface plasmon resonance (SPR) based optical sensor have been founded. Moreover, we are performing preliminary trials in order to establish a coupling between photoluminescence (PL) features of suitable emitters with respect to the plasmonic resonances.

1. Introduction

The interaction between light and matter is one of the most fundamental topics in physics.

In most cases, metals are just considered materials for realizing reflectors. However, there is a useful light–matter interaction involving metals that enables us to use metals in a more refined manner. Surface plasmons (SPs) are electromagnetic (E.M.) modes involving mobile surface charges, typically the conduction electrons in metals.

Such charges react to an external E.M. field oscillating in a coherent collective way, exhibiting a behavior of a vast ensemble of interacting particles. Under appropriate energy and momentum matching conditions, light interact with SPs and absorption and excitation processes can be observed.

SPs modes have greater momentum than light of the same frequency and, as a consequence, the E.M. fields associated with this oscillations cannot propagate away from the surface: the wave is evanescent and the field strength decays exponentially with increasing distance from the surface.

SPs modes on a planar metal surface are thus bound to that surface and guided by it, propagating until their energy is dissipated as heat in the metal.



From this point of view, plasmonics represents a way to squeeze electromagnetic fields below the diffraction limit at a metal-dielectric interface, with a consequential huge confinement of the corresponding E.M. energy [1-4].

Then, in order to realize a working device, the probes (in the case of sensing applications) or the fluorophores (in the case of emitting applications) must be placed in the near-field region of the contact surface between the metal and the dielectric, within the decay length (a few tens of nanometers) of the plasmonic mode [5].

To this aim, we planned a morphology able to ensure an optimal spatial positioning of the plasmonic resonator, with an accessible and large contact area between the metal and the external environment. These properties allow us to apply this structure both in sensing and emitting applications.

2. The Plasmonic Structure

We made use of a plasmonic surface consisting of a gold film embedded in a two-dimensional array of dielectric polymeric pillars [6-8].

Figure 1 illustrates the design of a single pillar structure and their regular repetition compose the plasmonic nanostructure. It is also visible the shape of the main plasmonic resonance field distribution (placed at a wavelength of ~ 820 nm) in the real space. The extension of the field toward the external environment is the key to make the plasmonic field usable for applied implementations.

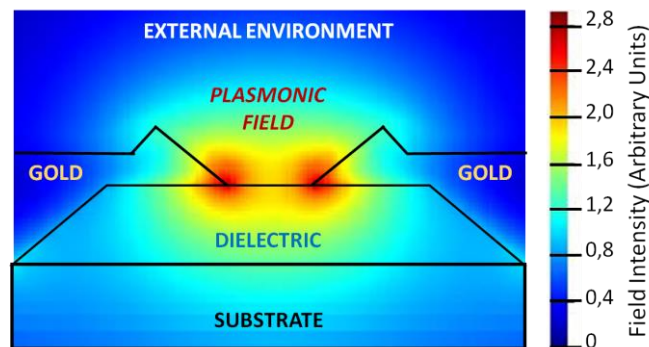


Figure 1. Electric field spatial distribution simulated using the finite-difference time-domain (FDTD) numerical analysis technique. The simulation is performed in the cross section of the pillars at the wavelength of the main spectral components of the plasmonic resonance (~ 820 nm). The superimposed scheme shows the various sections that compose the nanostructure.

Pillars are arranged in a triangular array in order to obtain a hexagonal lattice of plasmonic resonators (Fig. 2). With this particular configuration, we obtained an ordered series of localized resonators, circularly shaped and close enough to establish reciprocal coupling.

In this way, we have an E.M. network, confined at the surface of contact between the plasmonic nanostructure and the external environment, made of a combination of localized and travelling evanescent waves. Such a net is providing a high sensitivity on changes of the surrounding dielectric function that make the whole system perfect for sensing applications. Vice versa, thanks to its extensiveness, both in the surface plane and in the transversal one, the field mesh is favouring a good coupling with suitable fluorophores laid down on its top. Moreover, it should be possible to exploit the plasmonic field for pumping the fluorophores in order to sustain their photoluminescence (PL) features for emitting applications.

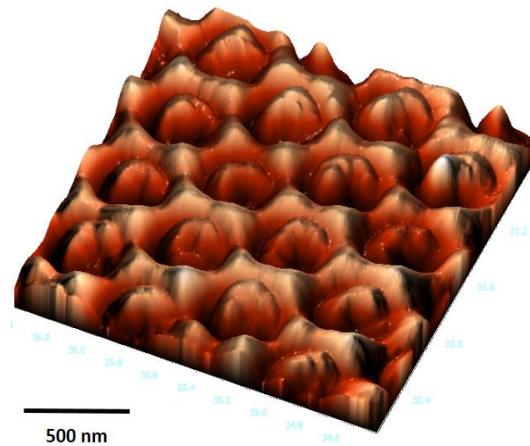


Figure 2. Three dimensional virtual image of the surface of the plasmonic structure obtained by an AFM measurement. The triangular array of pillars is well visible as the corresponding hexagonal lattice of plasmonic resonators.

3. Sensing Applications

The main feature of the optical response in the near infrared of the plasmonic surface can be interpreted in terms of plasmonic excitations localized at the contact edge among the head of the dielectric pillars, the gold slab and the free external surface.

Due to the high sensitivity of the plasmonic surface to refractive index n variations, any alteration in the chemical and physical composition of the external environment affect the spectral position of the plasmonic resonance.

The detection of such a refractive index change in the external environment is obtained by measuring the reflectance spectra with light incident from its substrate side, before and after the change (Fig. 3 shows an example).

The main resonance is shown as a reflectance minimum at ~ 820 nm.

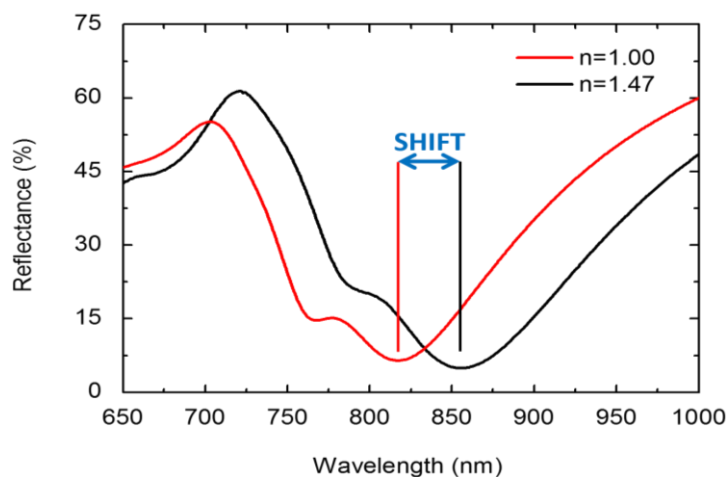


Figure 3. Reflectance spectrum between 650 and 1000 nm measured with TM polarized light at nearly normal incidence. In this particular case, the plasmonic resonance shift is due to the deposition of a thin (~ 10 nm) silicate layer (refractive index = 1.47) over the device surface.

Operatively, the plasmonic response can be evaluated as the ratio among reflectance spectra (Fig. 4-a). It has been shown that the numerical value of this ratio is directly proportional, at each

wavelength, to the spectral shift induced by the variations in the external environment refractive index n [9] and the consequent sigmoid-like function can be used to evaluate the corresponding refractive index variation signal amplitude. Several measurements with ethanol, sodium chloride, glycerol and polyelectrolytes were performed in order to prove the surface capability. Further experiments have been realized to apply the nanostructure for medical diagnostic purpose [9].

Moreover, a combined study of sol-gel synthesis and dip-coating method, enabled us to deposit well-controlled ultrathin silica layers on the plasmonic nanostructure. Such layers allow both surface protection and morphology preservation and, in addition, it has been proved that, for ultrathin silica thickness, they establish sensitivity gain in detecting refractive index changes (Fig. 4-b) [10].

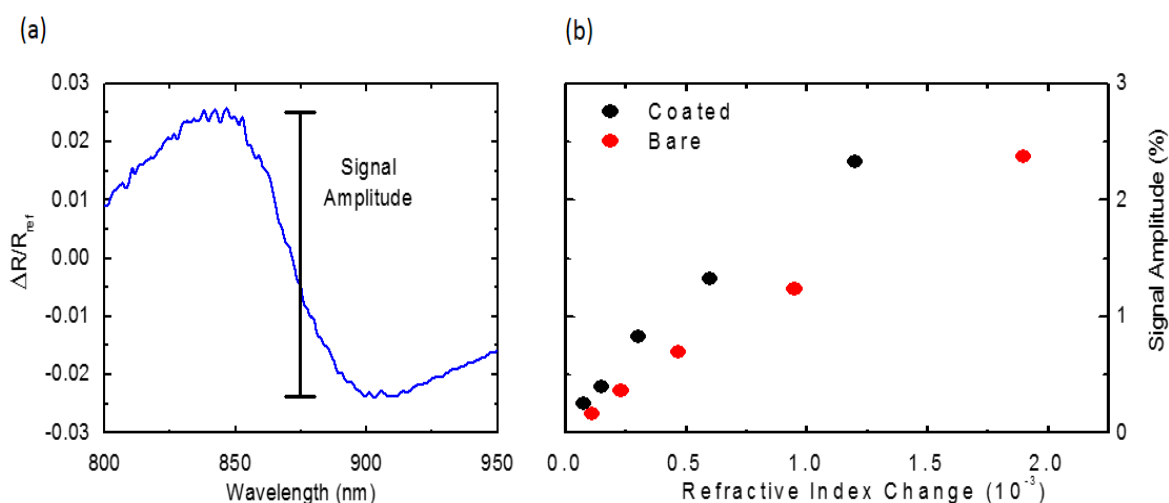


Figure 4. (a) Ratio of two reflectance measurements. ΔR is equal to the difference between the reflectance spectrum after the refractive index change (in this example a mixture of milli-Q water and ethanol at 3%) and the reflectance reference spectrum, R_{ref} , before the refractive index modification (milli-Q water only). (b) Plasmonic response to several ethanol solutions with different concentrations for the bare (black circles) and the ultrathin silica coated (red circles) surface. The plot displays the amplitude changes in reflectance referred to the signal shown in (a). Errors are very small (the maximum error for the refractive index change is 2×10^{-5} and the maximum error for the signal amplitude is 0.05%) and the corresponding error bars would not be clearly visible in the picture.

4. Emitting Applications

Plasmonic-photonic coupled devices, promoting the interaction between surface plasmons based devices and luminescent media, are very promising for nano-photonic applications [3].

In principle, the high electromagnetic density of the plasmonic field should be able to feed the fluorescence emission of suitable layers deposited within the field extension.

In this way, we realized preliminary trials in order to promote the coupling between PL emission of a standard fluorophore (rhodamine R6G) with respect to the plasmonic resonance exhibited by our nanostructure.

Until now, we focused our attention on the existence of a useful way to deposit the emitters on the nanostructure. We paid particular attention to avoid photoluminescence quenching effects due to metal absorption (gold in our specific case) when a fluorophore, is in close proximity with it.

Therefore, we coated the nanostructured surface with a thin film layer, ~ 10 nm in thickness, made of silica (SiO_2). Such *white-gauge* carries out the task of avoid the direct contact between gold and rhodamine. Anyway, its tiny width ensures a positioning of rhodamine within the plasmonic field penetration depth. The result is an efficient attachment platform for fluorophore molecules.

Consequently, we deposited the rhodamine by post-grafting on both the surfaces, the bare and the coated, and proved the quenching induced by the gold-R6G direct contact on the fluorophore PL emission together with the benefit introduced in the system by the silica coating.

The PL results are reported in figure 5.

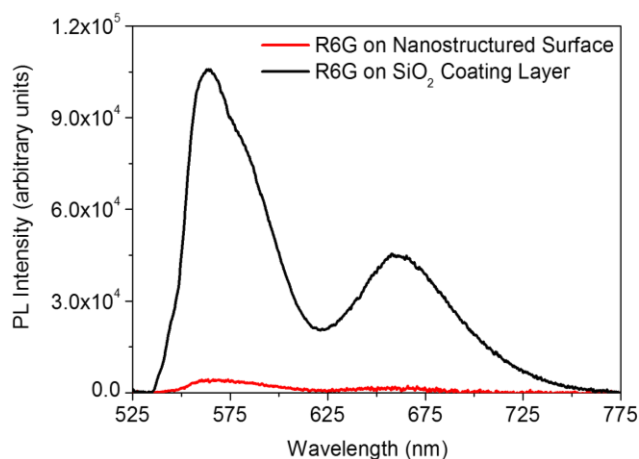


Figure 5. Photoluminescence signal of rhodamine (R6G) dropped off by post-grafting directly on the nanostructured surface (red line) and on the silicate coating layer (black line). The effect of quenching on the PL intensity emission, induced by the gold when it is in contact with the fluorophore, is well-rendered. Both the systems were excited with a laser source at the pumping wavelength of 532 nm.

5. Conclusions

In summary, we developed a platform consisting in a plasmonic nano-structured surface based on a gold film embedding a two-dimensional array of polymeric pillars, able to be adopted as platform for emitting and sensing applications. Numerous devices have been realized and characterized by atomic force microscopy, Fourier transform micro-reflectance and spectroscopic ellipsometry techniques.

Significant performance as surface plasmon resonance based optical sensor, for both biological and medical diagnostic applications, have been proved. In addition, we realized encouraging attempts to verify the likely occurrence of a coupling between photoluminescence emission of a standard fluorophore (rhodamine) with the plasmonic resonance supported by our nanostructure.

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