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2D photonic gratings from thermal imprinting of ITO-based films

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ABSTRACT

A nanocomposite system based on titania-bound indium tin oxide (ITO) nanoparticles has been developed as directly patternable material for the realization of two dimensional (2D) plasmonic gratings through nanoimprint lithography. An optical and electrical characterization of the ITO-based films has been performed. The imprinting process has been optimized in order to obtain a faithful negative replication of an array of nanopyramids on a hard master, in terms of period and depth of the structures. The morphology of the fabricated 2D gratings has been characterized with Atomic Force and Scanning Electron Microscopy. Experimental measurements and theoretical simulations of the far-field properties of the "naked" photonic grating, before coupling with an emitter or depositing a thin metal film on top, have been carried out for incident light in the 300–1500 nm wavelength range. A good qualitative agreement for transmittance data has been obtained. Simulated data for reflectance properly reproduce the experimental result only at long wavelengths, in the near-infrared region. Suggestions for further model implementations are proposed. The plasmonic architecture will be eventually designed and realized by applying the suitable metal coating.

1. Introduction

The optical properties of dielectric periodic nanostructures covered with thin metal layers presently attract the interest of much research, for they can exhibit strong optical responses at certain wavelengths associated with surface plasmon excitations [1].

The coupling of 2D photonic gratings with an emitter in the near-field has demonstrated to generate an elevated localization of the electric field, as light can be coupled more efficiently, leading to a higher field enhancement, with respect to 1D sinusoidal architectures. Multiple surface plasmon polaritons can be excited using one incident wavelength λ of given polarization angle, along a direction on the plane of the grating, and varying the azimuthal angle φ [2].

2D photonic gratings can be fabricated through a wide range of nanofabrication techniques, but double exposure interference lithography and soft nanoimprint lithography (s-NIL) on commercial polymeric resists [3,4] are most typically used for a fast realization of large-area 2D square lattice geometries.

Engineering functional materials suitable for direct patterning with lithographic techniques provides the possibility to take advantage of a range of properties not accessible with commercial polymeric resists, such as enhanced stability, electrical conductivity, porosity, and allows for fast and cost effective fabrication procedures.

In particular, organic–inorganic nanocomposite systems conveniently combine mechanical, thermal and chemical stability of inorganics, with simple processing and functionality of organics, for a given lithographic process and a specific final application.

A nanocomposite material based on titania-bound indium tin oxide (ITO) nanoparticles has been developed as patternable coating for the realization of two dimensional (2D) plasmonic gratings. ITO is a widespread used, transparent to visible light and conducting oxide material for optoelectronic devices, that was demonstrated as plasmonic material itself for wavelengths longer than 1.3 μm [5,6].

2D hexagonal lattice photonic gratings on ITO-based films have been fabricated through nanoimprint lithography (NIL), which is a low cost, high throughput and high resolution patterning technique, suitable for imprinting or embossing of functional structures, that can directly be employed for photonic devices.

An optical and electrical characterization of the nanocomposite ITO-based films has been performed. The imprinting process has been optimized in order to obtain a negative replication of the periodic nanometric surface pattern on a stamp. In this paper, only the study of the "naked" photonic grating is proposed, before its coupling in the near-field with an emitter or before depositing a thin metal film on top. Experimental measurements and theoretical simulations [7] of the far-field properties of the 2D ITO-based photonic grating, reflectivity and transmittance, have been carried out

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in the 300–1500 nm range. Comparisons among collected and simulated data have been performed, and suggestions for further model implementations are proposed. The plasmonic architecture will be produced by applying a proper metal coating.

2. Experimental

The solution has been prepared according to the following procedure. Titanium isopropoxide (Sigma–Aldrich) diluted in methoxy ethanol (Sigma–Aldrich) has been introduced in a ITO nanoparticle solution in toluene (In_2O_3:SnO_2 = 90:10 wt.%, 30 wt.% concentration, diameter of 20–30 nm, ShangHai HuZheng Nano Tech Co.), in a ITO:TiO_2 = 9:1 weight ratio. An epoxide monomer has been added in order to increase the viscosity of the solution, and to control the rheological properties of the film. TiO_2 works as a photocatalytic component under UV exposure, to promote organic species elimination and film densification in combination with a hard baking. Such curing treatments on patterned films can be required for specific applications, for instance, to take advantage of the increased refractive index and conductivity that they determine, or to transform the patterned structures into a totally inorganic material.

Films can be deposited by spin coating on silica glass substrates without adhesion problems, and thickness can be varied within the 500 nm–1.4 μm range modifying spinning rate. After deposition and post-application bakings at temperatures in the 60–100 °C range, films look uniform but present an elevated porosity degree due to the high loading of the 20–30 nm diameter nanoparticles. A 4 nm RMS roughness was estimated by AFM analysis.

For photonic grating fabrication, films have been deposited on ITO-coated sodalime substrates (30–60 Ω nominal resistance, Sigma–Aldrich) at 5000 rpm for 60 s, resulting in a thickness of about 600 nm. The ITO coating of the commercial slide has been characterized in terms of thickness and refractive index by spectroscopic ellipsometry, resulting in a 28 nm thick layer with $n = 1.7326$ and $k = 0.0431$ at 633 nm. After deposition of the nanocomposite ITO-based film, a decrease in conductivity of about 45% with respect to the commercial substrate conductivity has been measured using a digital multimeter (NI2100, Nimex). The conductivity is not appreciably altered after the imprint process and the post application bake.

The nanoimprint process has been optimized in terms of imprinting time, temperature and pressure, to obtain the negative transfer of a 2D hexagonal array of nanostructures.

Transmission spectra of films deposited on fused silica slides have been collected in the 300–1500 nm range using a UV–vis spectrophotometer (Jasco V-570), equipped with an integrating sphere, with a resolution of 2 nm. Refractive index and thickness of the samples have been measured using a Variable Angle Spectroscopic Ellipsometer (VASE, J.A. Woollam Co.). The same apparatus has been exploited to record the far-field transmittance and reflectance curves of the photonic grating for p-polarized incident light. Images of the realized photonic gratings have been acquired by Atomic Force Microscopy (AFM, NT MDT Solver Pro) using a NSG 01 probe (NT MDT) and Scanning Electron Microscopy (SEM, Leo Gemini 1530 FEG SEM).

Simulations of the transmittance and reflectance of the investigated system have been done by a Finite Element Method (FEM) analysis software (COMSOL Multiphysics) by building specific models of the investigated structures.

3. Results and discussion

The refractive index and extinction coefficient of films deposited on fused silica slides are reported as a function of the wavelength in the plot of Fig. 1, in which samples of different thickness have been taken into consideration to evaluate the dispersion. Experimental data have been fitted in Effective Medium Approximation (EMA) considering an ITO layer, where IR absorption due to free carriers and UV absorption of interband transitions are modelled with Lorentz oscillators, and a Cauchy layer.

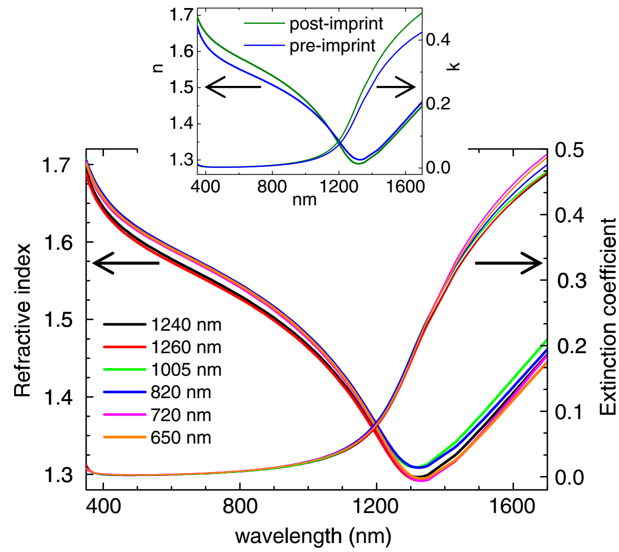

Fig. 1. Refractive index and extinction coefficient measured by spectroscopic ellipsometry for films of variable thickness as a function of λ. The inset reports a comparison between the optical constants for a film before and after the imprinting process.

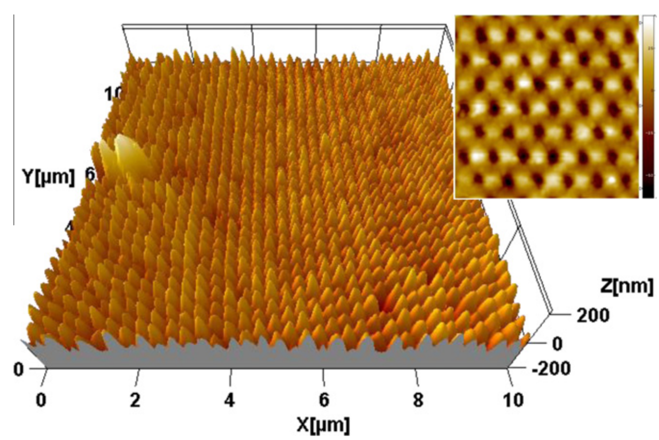

Fig. 2. 3D AFM image of the patterned ITO-based film. Depth of 132 nm and period of 300 nm along the corresponding X′ and Y′ directions defined for the master. On top, 2D image of a zoomed 2 × 2 μm^2 area.

The nanocomposite ITO-based material is characterized by a thermosetting behaviour. Films of elevated initial thickness, with respect to the pattern dimensions, have been employed to favour the squeeze flow of the viscous material driven by the pressure exerted on the master. The structure has been first moulded and then heated to induce crosslinking, before stamp demoulding from the hardened surface relief. The pattern of Fig. 2 has been obtained pressing the film under a nickel mould (NIL Technology, Denmark) containing periodic surface relief nanopyramids (Fig. 3) at a constant force of 3 kN at room temperature for 20 min. Then, temperature has been raised at 12 °C/min up to 125 °C at constant pressure, and kept at 125 °C for 2 min (curing step), registering a pressure peak of 3.5 kN. The removal of the stamp has been carried