

Magneto-optical Properties of Core–Shell Magneto-plasmonic Au– $Co_xFe_3 - xO_4$ Nanowires

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ABSTRACT: The magneto-optical properties of Au–Co_xFe_{3-x}O₄ core–shell nanowires embedded in porous alumina membranes are studied. The structures were obtained by depositing Co_xFe_{3-x}O₄ on the pore walls of alumina membranes by atomic layer deposition and filling the resulting nanotube with gold by electrodeposition. The effect of plasmon resonance excitation on the magneto-optical activity is clearly observed as a modification of the spectral line shape of the Kerr rotation signal.



In the past few years, nanoparticles formed by more than one compound have attracted much attention because of their additional functionalities resulting from combining materials with different properties. Nanoparticles made from noble metals and magnetic materials are an example of these composite nanoparticles; these nanostructures present at the same time plasmon resonances and magnetic properties and have potential applications in areas such as biomedicine and nanophotonics.¹⁻⁴ Moreover, they exhibit enhanced magnetooptical (MO) activity in the spectral region of the surface plasmon resonance, whose spectral position can be tuned by modifying the nanoparticles' structural and/or compositional parameters, being, therefore, well suited to develop novel MO nanodevices and sensors.⁵⁻⁷ These structures have been obtained either by chemical synthesis or by combining thin film deposition processes and lithography. In this work, we present a new approach to fabricating these systems using atomic layer deposition (ALD) and electrodeposition. The structures (core-shell nanowires) were obtained by first depositing the shell material on the pore walls of alumina membranes by conformal ALD⁸ and filling the remaining space with the core material by electrodeposition. As the core element, we have used a typical plasmonic material, gold, and for the shell component, we have used a low absorption magnetic material, Co-ferrite, which has higher magneto-optical activity than other iron oxides used in previous work.⁵

Self-ordered alumina membranes have been fabricated using a two-step anodization process in oxalic acid electrolyte.¹⁰ This results in a membrane with a hexagonal arrangement of pores with a 40 nm diameter and a 100 nm interpore distance. Pores are widened by chemical etching of up to 75 nm in order to facilitate the ALD process. These membranes were used as templates for the subsequent growth of nanotube arrays (Figure 1). The cobalt ferrite nanotubes were grown by a combination



Figure 1. Sketches of the samples showing the porous alumina membrane and the core-shell nanowire structure.

of the ALD processes for Co_3O_4 and Fe_2O_3 , which use cobaltocene and ferrocene as metal–organic precursors, respectively, and ozone as an oxidizing agent.^{11,12} The process was carried out at 250 °C, and the composition was controlled by the relative number of cobaltocene to ferrocene exposures. In this way, hexagonal arrays of long nanotubes were obtained with outer diameters of 75 nm and shell thicknesses ranging from 2.5 to 20 nm. To improve the magnetic properties of the nanotubes, the structures were annealed at 550 °C in air for 3 h, with a preannealing step of 1 h at 120 °C. Subsequently, the

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tubes were filled with gold by electrodeposition. For that purpose, a thin Au contact layer was first deposited on one side of the membranes. Then the membranes were turned over, and the growth of Au inside the nanotubes proceeded with a gold sulfite—thiosulphate solution. This solution improves the growth inside the pores without affecting the alumina membrane or the cobalt ferrite (pH 7), even after long depositions. Finally, the gold contact layer and the top cobalt ferrite layer were removed by chemically assisted mechanical polishing.

As an example of the resulting structures, we present in Figure 2a,b two planar views, after polishing, of two



Figure 2. (a) SEM images of a sample with a 7.5 nm shell thickness and detail of a Au wire with the ferrite shell after alumina removal. (b) SEM image of a sample with a 20 nm shell thickness and a zone where pores have not been filled with Au. (c) TEM image with corresponding SAED for a sample with a shell thickness of 15 nm. (d) Reflectivity spectra at normal incidence of the samples displayed in a and b and for a 15-nm-shell hollow tube.

representative samples with different ferrite shell thicknesses. As can be observed, in samples with wall thicknesses larger than 10 nm, as for the sample with the thickest ferrite shell (Figure 2b), some of the pores appear without gold. This is due to the closing of some pores of the alumina membrane during ferrite deposition, which prevents the growth of the Au wires in that pore. In Figure 2a, we also include a cross section of the sample after the removal of the alumina template where the Au core and the ferrite shell are clearly visible. In addition, as proof of the gold-cobalt ferrite core-shell nanostructure, a TEM image with corresponding selected area electron diffraction (SAED) is presented in Figure 2c (shell thickness 15 nm). Rings originating from polycrystalline cobalt ferrite could be indexed in addition to the diffraction peaks for FCC gold. Also, in Figure 2d we present reflectivity spectra at normal incidence of the samples in Figure 2a,b and of a hollow 15 nm ferrite shell. As can be observed, the spectra display a peak in the 580-600 nm region. This peak can be related to the excitation of the localized surface plasmon resonance (LSPR) of the Au nanowires perpendicular to the wire axis because the reflectivity from a hollow 15 nm ferrite shell is featureless. It must be noted

that the intensity of this peak decreases as the Au radius is decreased.

To address the phenomenon of LSPR excitation, it is convenient to refer to the spatial distribution of the intensity of the electromagnetic field (EMF) when the structure is under linearly (*x*-direction) polarized illumination at normal incidence. In Figure 3, we present numerical calculations



Figure 3. FDTD simulation of the spatial distribution of the intensity of the electromagnetic field (normalized to the incoming field) when the system is illuminated by a linearly polarized (*x*-direction) plane wave under normal incidence. In a-c, we show the in-plane (x-y plane) distribution 20 nm from the surface of the system for a 20-nm-thick ferrite shell: (a) gold-filled pores in resonance at 600 nm wavelength, (b) void pores at 600 nm, and (c) gold-filled pores out of resonance at a 450 nm wavelength. (d) Cross section (x-z plane, y = 0) of the gold-filled pores at resonance. The surface is indicated by a dashed line at z = 100 nm, and the horizontal continuous line represents the depth for a-c.

using FDTD software (Lumerical) of such a spatial distribution for a 20 nm ferrite shell system in different situations. In Figure 3a, the pores are filled with gold and the wavelength is 600 nm, allowing plasmon excitation. The field is calculated in the sample plane (x-y plane) 20 nm from the surface. The field pattern shows a high localization of the EMF and presents the typical shape of the dipolar excitation along the polarization direction. In Figure 3b, the same situation is considered, but the pores are now empty. The absence of EMF localization when compared to the previous situation is evident. In Figure 3c, we show the calculated EMF with the pores filled with gold, but for a wavelength at which no resonance is excited (450 nm). Here, the effect of the nonresonant situation is again clear. In Figure 3d, we present, for completeness, a cross section of the x-zplane for a gold-filled system in resonance. The dipolar excitation and the penetration of the EMF along the wires is, again, that of a localized surface plasmon resonance.

The MO characterization of the samples has been carried out by means of Kerr (reflection) spectroscopy in the polar configuration. The sample, placed inside an electromagnet that applies a magnetic field perpendicular to its surface and large enough to ensure magnetic saturation (1.2 T), is illuminated at normal incidence by a monochromatic beam coming from a Xe lamp followed by a monochromator. By modulating the beam polarization with a photoelastic modulator and recovering the reflected intensity with a photomultiplier using a lock-in technique, both the Kerr rotation and ellipticity for each wavelength are determined.¹³

No MO signal was obtained from nanowires with a Coferrite shell thickness below 15 nm, which indicates that there might be a threshold for the onset of ferromagnetism, or at least MO activity, on a macroscopic level for this material. For ferrite layer thicknesses of 15 nm and above, the MO signal is detected in the Kerr rotational spectra as can be seen in Figure 4 for the



Figure 4. Kerr rotational spectra of $Au-Co_xFe_{3} - {}_xO_4$ core-shell nanowires with 15 and 20 nm shell thicknesses, hollow-core 15 nm shell tubes, and a 40-nm-thick $CoFe_2O_4$ film. (For the sake of clarity, the Kerr rotation of the hollow system and the film appear with the sign reversed, and for the film, the Kerr rotation has also been divided by 2). (Inset) Numerical simulations of the Kerr rotational spectra of Au-Co-ferrite core-shell nanowires with 15 and 20 nm shell thicknesses.

15- and 20-nm-thick ferrite wires. The spectra are characterized by an S-like feature located in the spectral region where the LSPR of the gold nanowire takes place, with its intensity increasing as the amount of Co-ferrite is increased. Although this feature is related to the excitation of the LSPR of the Au nanowires, its shape results from a combination of the wavelength dependence of the MO properties of both Coferrite and the LSPR excitation.¹⁴ This is clearly seen in the Kerr rotation of a 40-nm-thick Co-ferrite film grown using the same deposition conditions as for the Co-ferrite of the coreshell nanowires, depicted in Figure 4. It must be noted that the hollow-core system (measured for the 15-nm-shell sample) presents the same spectral shape as the thin film but with a different intensity because of the difference in the amount of MO active material. Contrary to the Au-filled core-shell structures, the continuous film and the hollow-core spectra have two peaks related to transitions between electronic levels of Co²⁺ ions located on tetrahedral sites (peak at 700 nm) and

intervalence charge-transfer transition between the Co²⁺ and Fe³⁺ ions on octahedral sites (peak at 550 nm).¹⁵ As can be observed, plasmon excitation induces a strong modification of the shape of the MO spectra, presenting a marked feature at the location of the plasmon resonance of the gold wire. For example, in the inset of Figure 4 we present numerical simulations of the MO activity for the 15- and 20-nm-thick ferrite shell structures using a scattering matrix method (SMM) adapted to consider MO effects.¹⁶ The optical and MO constants of the Co-ferrite shell were obtained from ellipsometric and polar Kerr measurements of the 40-nmthick ferrite laver, whereas the optical constants of Au were obtained from ellipsometric measurement of a Au thick film and those of alumina were obtained from ref 17. The shape of the simulated spectra is similar to the experimental ones but the intensity is much higher, a fact that could be partially attributed to the reduced concentration of core-shell wires in the samples because of the closing of the pores, although the experimental values are still much smaller than the expected ones. The origin of this reduction is still unclear and deserves further investigations that are beyond the scope of this work.

In conclusion, the MO properties of Au–Co-ferrite core– shell nanowires obtained by depositing Co-ferrite on the pore walls of alumina membranes by ALD and filling the remaining space with Au by electrodeposition are studied. The effect of plasmon resonance excitation on the MO activity is clearly observed. The spectral line shape of the Kerr rotation corresponding to the hollow-core ferrite tubes, which is very close to that of the bare ferrite film, gets modified from a twopeaked curve to a marked s-like shape in the region of the plasmon excitation of the gold wire.

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Notes

The authors declare no competing financial interest.

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