Magnetic and optical properties of nanocorrugated Co films

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Nanostructured Co films were prepared on the top of a polymethyl methacrylate (PMMA) colloidal crystals by magnetron sputtering. Optical reflectance spectra were studied in the range of near UV, IR, and visible light for p- and s-polarizations. Valleys were observed in the spectra and their positions scaled with the PMMA sphere diameter. Both the surface plasmon resonance and the dipole resonance of single Co nanocaps should be considered to explain the obtained results. Magneto-optic measurements showed the qualitative change of the magnetization curve and the enhancement of magneto-optic rotation at wavelength $\lambda = 632$ nm in comparison with the control Co film. © *2010 American Institute of Physics*. [doi:10.1063/1.3372634]

The main idea of quickly developing plasmonics is to enhance and manipulate optical phenomena at the nanoscale dimension by plasmonic mechanisms.[1] Since the extraordinary optical transmission through optically opaque metallic films perforated by a two-dimensional array of subwavelength holes has been discovered[2] and explained by the coupling of surface plasmon resonance (SPR) with the incident light, the periodic nanostructures are considered to be promising materials with a controlled optical response. The investigation has been focused on the systems based on noble metals due to the low absorption losses of the surface plasmons in these metals. The influence of SPR on the optical properties of magnetic materials are studied much less so far. Recently the enhancement of magneto-optic effects by resonant scattering of the light in nanostructured magnetic materials has been predicted theoretically.[3,4] Besides, some works are devoted to the experimental study of SPR effect on the optical transmission through a subwavelength hole array in magnetic films[5–7] and on magneto-optical effect in magnetic periodic nanostructures.[5,7,8] Therefore, the further investigation of SPR effects in the magnetic nanofabricated materials is required. Metallic films deposited on the surface of a colloidal crystal are considered to be very perspective material for plasmonics.[8–10] Moreover, in the case of magnetic coating the material seems to be interesting for magnetic memory applications or as a material with a noncomplanar distribution of magnetization.[11]

In this paper we report on the study of SPR effects on the optical properties of Co films deposited on the surface of PMMA colloidal crystals. The investigations of reflection spectra carried out separately for s- and p-polarization of the incident light and for different film thicknesses allowed to distinguish the effects of the propagating and localized surface plasmons. The measurements of the magnetization curves demonstrated the increase of the magneto-optic rotation of the nanocorrugated film in comparison with the control flat Co film. Magnetic force microscopy (MFM) investigations of the magnetization distribution in the samples were carried out to explain the peculiarities of the magnetization curves.

The initial colloidal crystals of PMMA were prepared in the following way. PMMA particles were synthesized during three to five hours by polymerization of MMA monomer in the water solution in the presence the potassium peroxodisulfate (0.08 wt %).[12] A particle suspension was carefully dried in a chamber at room temperature. Thus, the 100–300 μm film of colloidal crystal was obtained on the hydrophobized glass as a substrate. Depending on the polymerization time the particle diameter was 250–350 nm for different samples. The preliminary measurements of the colloidal crystals reflection spectra demonstrated the existence of peaks typical for photonic crystals. Characterization of the colloidal crystal was made by scanning electron microscopy (SEM) (Fig. 1). The SEM images showed that PMMA particles are densely packed in a hexagonal structure. The main defects in the structure are single particles upon the surface of the colloidal crystal, vacancies in the upper layer and the boundaries between crystallites with different orientations of the crystal axes.

The Co film was deposited on the surface of PMMA colloidal crystal by using magnetron sputtering. Thus, 30 and 60 nm thick Co films were prepared. As the thickness of the film was sufficiently less than the diameter of the particles, the film became corrugated in two dimensions. It is necessary to note, that thicknesses 30 and 60 nm are the thick-

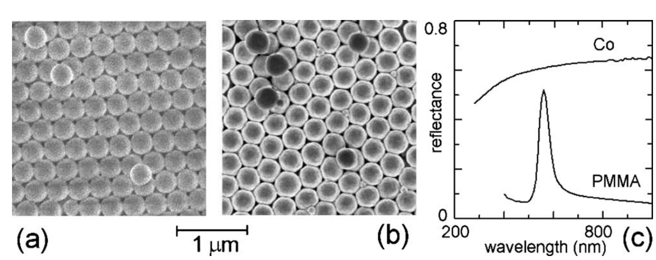

FIG. 1. SEM images of the PMMA colloidal crystal: (a) before deposition of the Co film, (b) after deposition of the film. The single particles are seen on the surface in both cases. (c) Reflection coefficient of the initial PMMA colloidal crystal (particle size 290 nm) and reflection coefficient of the control Co film (thickness 30 nm) for 45° of incident angle for s-polarizations.

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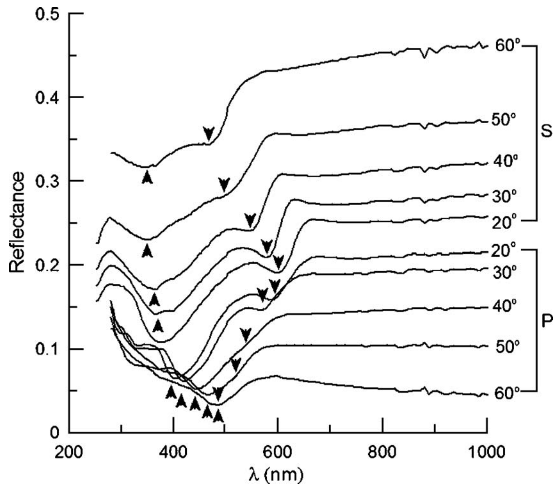

FIG. 2. Measured optical reflectance spectra of 30 nm thick nanocorrugated Co film (particle size of initial PMMA colloidal crystal is 290 nm) for s- and p-polarization of the incident light and for different angles of the light incidence. Down arrows indicate minima due to propagative surface plasmon mode; up arrows indicate minima due to localized dipole modes.

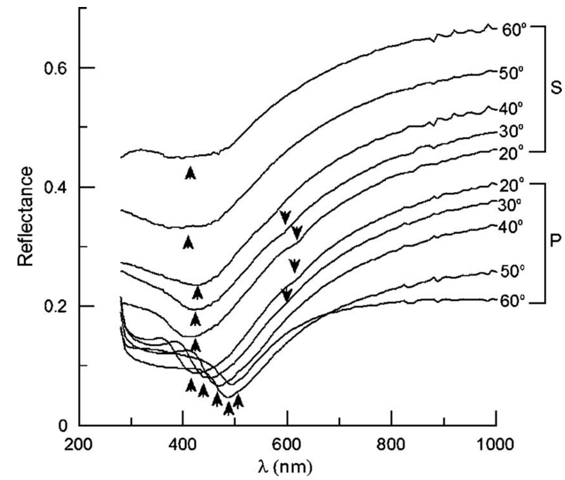

FIG. 3. Measured optical reflectance spectra of 60 nm thick nanocorrugated Co film (particle size of initial PMMA colloidal crystal is 290 nm) for s- and p-polarization of the incident light and for different incident angles. Up arrows indicate minima due to localized dipole mode; down arrows indicate remnant minima due to propagative surface plasmon mode.

nesses of the control flat Co films on Si substrate prepared in the same process. The actual average thickness of the obtained Co nanocorrugated film is smaller (as surface area of hemisphere/surface area of circle=2) and may be nonuniform. The optical reflection spectra of the nanocorrugated Co films, control Co films, and initial colloidal crystals were obtained at room temperature by using high pressure xenon lamp, diffraction spectrometer and precision silicon photodiodes designed as detector for 200–1100 nm wavelength range.

The mirror reflection spectra for the 30 nm Co film deposited on the surface of the colloidal crystal with particle diameter of 290 nm are represented in Fig. 2. The measurements were performed in the angle range from 20° to 60° (measured from the structure surface normal) both for s-(TE) and p-(TM) polarizations.

The following distinguished features are found. First, the reflection spectra look like neither the spectrum of a flat Co film nor the spectrum of an initial colloidal crystal (Fig. 1). It lost a monotonic character which is typical for a flat Co film and has two minima, let us define them as long-wave (lw) and short-wave (sw) minima. The lw-minimum blueshifted with the increase of the angle of light incidence in the same manner for s- and p-polarizations. On the contrary the sw-minimum redshifted for p-polarization and almost did not shift for s-polarization. The sw- and lw-minima come together for p-polarization at 60°. In order to interpret the above results, the optical reflectance spectra were measured for the 60 nm thick Co film deposited on the same colloidal crystals (Fig. 3). As for the sw-minimum it remained similar to 30 nm thick Co films while the lw-minimum almost disappeared. Only small remnants of lw-minimum were visible for small angles of incidence. One more "control knob" in the experiment was the size of the colloidal particles which determined the period of the structure. It was obtained, that the reflection spectra were scaled with a particle diameter (Fig. 4).

Let us try to elucidate the physical mechanisms which can lead to such reflection spectra. The angle dependence of the lw-minima and its scaling with the structure period are the fingerprints of the excitation of propagating plasmon. The propagation plasmons can be exited both by s- and p-polarization of the light because the film is corrugated in two directions. The disappearance of lw-minima for 60 nm thick film indicated that the SPR occur at the metal/dielectric interface. The SPR is excited under the matching condition of $k_0 \sin\theta \pm nG_x \pm mG_y = k_{SP}$ where k_0 is the wavevector of light incident at angle θ, G_x, and G_y are Bragg vectors of the structure, n and m are integers, and k_{SP} is surface plasmon wavevector. Unfortunately we could not calculate surface plasmon dispersion relation for such a complex periodic structure. Let us use the dispersion relation for surface plasmon on metal-dielectric interface $k_{SP} = (\omega/c)\sqrt{\varepsilon_m\varepsilon_d/(\varepsilon_m+\varepsilon_d)}$ for estimation. For the visible light the permittivity of PMMA is approximately 2.25.[13] In its turn ε_m can be estimated in Drude approximation with plasma frequency $\omega_p = 1.48\times10^{16}$ s^{-1} for Co.[14] In this approxima-

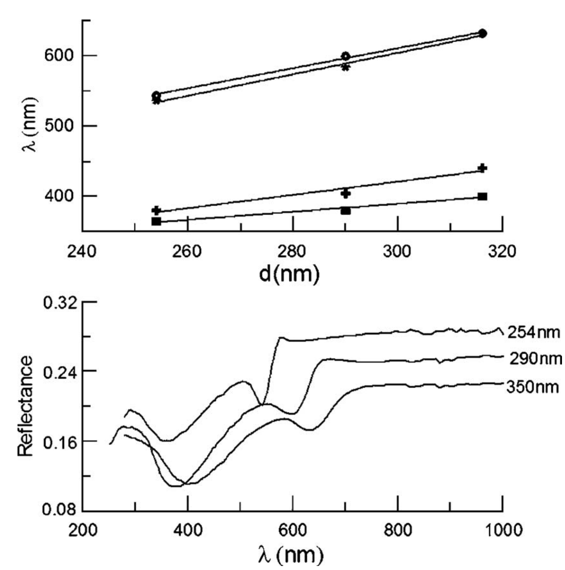

FIG. 4. Scaling of the reflectance spectrum of nanocorrugated films with the diameter of the particles of the colloidal crystal. Upper graph is the positions of lw and sw reflectance minima for the samples with different diameters (Co thickness is 30 nm) for the incident angle 20°: Circles and squares—s-polarization, stars and crosses—p-polarization. The bottom graph is the reflectance spectra for s-polarized light with the angle of incidence 20°.

tion the wavelength of an incident light when SPR occurs is 300 nm for the incident angle equal to 60° and 360 nm for 20° while the experimentally measured values were 440 and 590 nm, so the observed SPR corresponded to slower plasmons. We think that in the case of the nanostructured Co film propagating plasmons can be slowed down due to two-dimensional corrugated shape of the film which increases the actual way passed by the plasmons. Another reason is the appearance of band gap for SP in the case of the periodic structure and splitting of the dispersion curve.

The sw-minima did not disappear in the case of a thick film and demonstrated a different behavior for s- and p-polarizations of incident light. The following qualitative explanation can be suggested. There are single PMMA particles covered by Co nanocaps on the colloidal crystal surface (Fig. 1). They have two eigenmodes of the dipole oscillations—with the dipole lying in the plane of the system or with the dipole perpendicular to the plane of the system. Generally, this oscillation will have different frequencies. The s-polarized incident radiation will excite only a parallel dipole oscillation independently on the incident angle. Indeed the position of the sw-minima measured in experiment did not depend on the incident angle for s-polarized light. As for p-polarized incident radiation it will excite parallel dipole oscillation at small incident angles, so the positions of minima in spectrum for p- and s-polarizations are close for 20°. On the contrary, at tangent incident angles the p-polarized incident radiation will excite a perpendicular dipole oscillation with a different frequency. With the increase of the incident angle of p-polarization the amplitude of the parallel dipole mode will decrease while the amplitude of the perpendicular mode will increase. If the resonances width is comparable with the distance between them one will observe only one minimum in the reflection spectrum, but its position will depend on the incident angle. So, while the lw-minima in the reflectance spectrum are caused by the excitation of the propagating plasmon, the sw-minima are caused due to localized dipole resonances.

The magnetic properties of the nanocorrugated Co films were also studied. The magnetization curve was investigated by the measurement of longitudinal magneto-optic Kerr effect (Fig. 5) with the use of He-Ne laser $\lambda = 632$ nm. Two main facts should be mentioned. First, the magnetization curve of 30 nm nanostructured Co film is similar to that of magnetic nanoparticles with the vortex distribution of magnetization.[15] This was verified by MFM measurements. Both the contact surface and exchange interaction between Co nanocaps increases in the case of 60 nm film and the hexagonal vortex lattice become frustrated in this case. Therefore the ground state of 60 nm film is the mixture of vortices and single domain states. The second fact is that all measured nanocorrugated 30 nm Co films had a higher coefficient of the magneto-optical rotation in saturation for $\lambda = 632$ nm than the corresponding control flat Co films deposited in the same process.

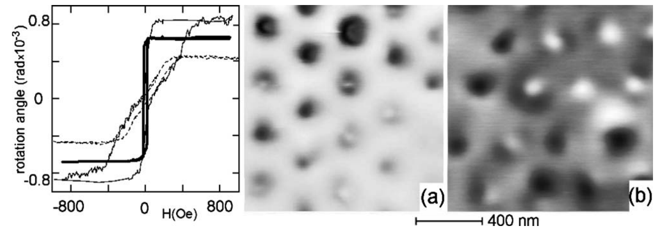

FIG. 5. Magnetization curves of the nanocorrugated Co films (thin line for 30 nm film, dashed line for 60 nm film), PMMA particle diameter 290 nm. Thick line is a magnetization curve of the flat 30 nm Co film. (a) MFM image of the 30 nm sample at H=0, magnetization states of Co hemispheres looks like magnetic vortex. (b) MFM image of the 60 nm sample, both vortices and single domain states are visible.

In conclusion, it was found that the reflectance spectra of the Co films deposited on colloidal PMMA crystal have two minima in the visible region. The position of minima was redshifted with increasing a size of the colloidal particle. The optical spectra are different for s- and p-polarization and accounted for by both the excitation of the SPR on the Co/PMMA interface and the dipole resonances of single Co nanocaps. The observed rise of the magneto-optic rotation for $\lambda = 632$ nm indicates that the nanocorrugated Co films can be perspective as a magnetoplasmonic material but some additional investigation should be done in this way.

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