Enhancement of the magneto-optical activity via surface plasmon resonance on Au-Co nanocomposite thin films

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ABSTRACT

Appropriately designed metallic nanoparticle arrays and thin films are suitable platforms for sensing applications based on their optical, magneto-optical (MO) and magneto-transport properties. For example most current biosensing schemes based on optical excitation of surface plasmon resonance (SPR) are "passive", i.e., they are based on changes in the optical properties at the sensor surface -typically gold- when a biological specimen to be detected is bound to it and SPR is excited. We have shown that it is possible to enhance the sensitivity of these thin films by combining Au with other materials that exhibit changes under suitable external modulation hence developing "active" plasmonic surfaces. In such scenario, optimal combination of materials can exhibit enhanced optical as well as electrical transport properties. Here, such physical properties, i.e. optical and electric transport, have been investigated in Au-Co nanocomposite thin films after modifying growth parameters such as growth temperature and relative Au:Co concentration. We found that suitable combinations of these two materials can exhibit enhanced MO effects and in some cases also substantial magneto-resistance, the latter of interest for sensing magnetic media. Thus, here we have applied theoretical models to simulate the optical properties in the nanocluster-matrix aggregation and compared with the experimental optical data. Correlation between the nanocomposite films' microstructure, morphology, optical, MO enhancement and magneto-transport is discussed.

Keywords: surface plasmon resonace, magneto-optical Kerr efffect, plasmonics, magneto-transport

1 INTRODUCTION

Gold-cobalt is an interesting metallic binary system where no actual alloying occurs[1] and where the microstructure and composition can be tuned, particularly in thin film form, in order to exploit properties of greatest benefit for sensing applications. In this system one of the constituents, i.e. gold, can sustain sharp surface plasmon resonances (SPR) when optically excited while the other constituent while also susceptible of SPR excitation although considerably damped due to stonger optical absorption, also exhibits magnetic and MO response that can be modulated with modest external magnetic fields. Suitable compositions of these two materials can be tailored in thin film geometry to also favor antiferromagnetic coupling between Co regions such that giant magneto-resistance can also be observed. Our preliminary work with this sytem indicates that correlation between these optical and magneto-transport phenomena warrants further study.

With respect to optical properties, surface plasmon polaritons (SPPs) are surface electromagnetic waves that propagate at the interface between a metal and a dielectric. These evanescent waves excited at the boundary of the metal and the external medium are very sensitive to any dielectric change at this interface. Thus, optical sensors, based on SPPs at planar gold surfaces, are fast becoming a preferred method in many bio-sensing applications. Nonetheless, in order to improve sensitivity it is highly desirable to develop "active" plasmonic systems such that some optical property can be modulated under application of an external field. Transition metals alone such as Fe, Ni and Co exhibit MO effects accessible at relatively low fields, but their absorption coefficients are higher than those of Au and therefore their SPPs are over-damped. Thus, composite noble-metal/ferromagnetic-metal sensing elements can overcome the high absorption problem while exhibiting high MO activity. In fact, we as well as other researchers have observed that carefully tailored multilayer films of Co and Au do exhibit enhanced MO activity related to SPPs excitation.[2] In order to explore less stringent materials designs, we have considered here the possibility of using nano-composite Au-Co films. Codeposition of these two metals can yield different nanocluster-matrix aggregates depending on their relative concentration and the growth temperature, and thus their properties, i.e magneto-plasmonic, magneto-transport, etc. can be optimized.

Correlation between magneto-trasnport properties and optical properties can thus be investigated to establish possible composition and microstructure parameters that can enhance/optimize both, optical and magneto-transport properties in Au-Co nano-composite thin films.

2 EXPERIMENT SETUP

The Au-Co nano-composite films were prepared using DC magnetron sputtering codeposition in an ultra-high vacuum chamber with base pressure in the low 10^{-9} Torr

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regime. Before growth, soda lime glass substrates were UHV annealed at 600 ℃ for 30 minutes. Sputtering deposition was carried out simultaneously from high purity (99.99 %) Au and Co targets at 5×10^{-3} Torr Ar pressure. 50 nm thick films were deposited at temperatures ranging from room temperature (RT) up to 600 ℃ in order to explore the dependence of the microstructure with the growth temperature. The Co concentration was varied from 5% to 60% by controlling the DC voltage applied to the Co and Au targets during co-deposition. All samples were capped with 3 nm Au films deposited at RT to prevent oxidation of Co.

The surface morphology of the samples was characterized with scanning electron microscopy (SEM, Hitachi 4700 Scanning Electron Microscope with Energy-Dispersive X-Ray Spectroscopy). In addition, the microstructure of the samples was investigated using scanning transmission electron microscopy (STEM) in an aberration corrected VG Microscopes HB501UX operated at 100 kV. Selected specimens for STEM observations were prepared by conventional thinning, grinding, dimpling and Ar ion milling. Principal component analysis (PCA) was applied to the EELS images to remove random noise.

The optical response of the Au-Co nanocomposite films was investigated using a variable angle spectroscopic ellipsometer in the spectral range from 1.4 to 3 eV. The optical and MO response of the multilayers under SPP excitation were investigated in the Kretschmann configuration using p-polarized He-Ne laser radiation (λ=632.8 nm). In this configuration, the glass substrate is coupled to a semi-cylindrical glass prism by a matching refractive index liquid. A Si amplified photodetector preceded by a p-oriented polarizer was used to detect intensity variations in the reflected radiation. The transverse MOKE was also investigated by applying an alternating magnetic field H=30 mT (60 Hz) in the plane of the sample and perpendicular to the incidence plane, intense enough to saturate the Co films with in-plane magnetization. The MO signal, i.e. the intensity variation of the p-polarized reflected light at the modulation frequency, was investigated, detected, and analyzed in this transverse geometry using lock-in techniques. The magneto-resistance measurement was measured with four point measurement using transverse configuration.

3 RESULTS AND DISCUSSION

3.1 Morphology and microstructure

As above mentioned, Co and Au do not form a binary alloy, and therefore, two separate phases co-exist in the films[1], i.e. a matrix with a cluster distribution. The size distribution of the various clusters is critical to the optical, MO and magneto-transport behavior. In order to investigate the surface morphology and the film composition we have used SEM and STEM.

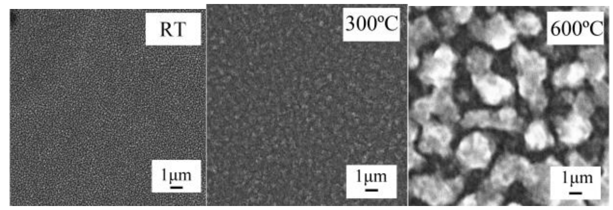

Figure 1: SEM image for 50 nm Co:Au films with concentration ratio of 50:50 and grown at RT, 300 ℃ and 600 ℃

Figure 1 shows SEM images for films with Co:Au concentration ratio of 50:50 and deposited at temperatures ranging from RT to 600 ℃. While at RT the surface exhibits low roughness, it gradually increases with the deposition temperature becoming significantly rougher at 600 ℃ and exhibiting separate three-dimensional grains with no specific orientation. The average diameter of the observed clusters is 150 nm, 500 nm and 2.5 micron for the samples grown at RT, 300 and 600 ℃ respectively.

Our concurrent studies using transmission electron microscopy coupled with scanning electron energy loss spectroscopy (STEM/EELS)[2] are discussed elsewhere. Namely they evidenced a very homogeneous distribution of Co in the films deposited at RT while strong segregation occurs where Co grains embedded in Au in both the perpendicular and lateral direction for the samples grown at 600 ℃.

We interpreted these results by noting that when heating the substrate above 200 ℃ an irreversible transformation from amorphous to a metastable FCC crystalline phase occurred in the Co-Au thin films, that subsequently decomposed into equilibrium phases above 275 ℃, leading clearly to segregated micro-structure.

Our findings can be understood considering that at lower temperature, the adatoms freeze in sites close to their points of impingement on the surface, and form close packed "crystalline" particles, while as the surface mobility increases at higher temperatures, atoms diffuse for longer distance such that they can form separate phases. We also note that the two randomly mixed components do not form clusters of the same size because of the different diffusion energies of the two atomic species. Thus, there is a balance between the random cluster distribution and their ability to fill the available space in the film that can be tailored by modifying the deposition conditions.

In the present case, our data indicates that at RT, the lowest substrate temperature tried, an amorphous metastable structure can exist that separates into distinct aggregate phases at higher deposition temperature. Thus, optimal optical and magneto-transport behavior is observed for samples deposited at 300 ^{o}C and the discussion below will center mainly on these samples.

3.2 Optical and magneto-optical characterization

The optical constants for the Au-Co composite films were measured with ellipsometry in the spectral range from 1.4 to 3 eV. Figure 2 shows the refractive index (n) and absorption coefficient (k) for some selected films deposited at 300 ^{o}C, along with the bulk values for Au and Co. Effective medium simulations were performed in order to understand the optical mechanisms taking part in the nanocomposite films. Two different models, namely Bruggeman and Maxwell-Garnett approximations were tested[3]. In the Bruggeman approximation, no distinction is made between the matrix material and the nano-cluster material. Thus, this approximation should be used to treat systems where no clear assignment of which component is the matrix material and which is the host can be done. On the other hand, in the Maxwell-Garnet approximation the matrix material determines the choice of the reference dielectric tensor as this one is taken equal to that of the matrix. Thus, it is more appropriate to treat systems using this formalism when adequate assignment of the matrix material is possible.

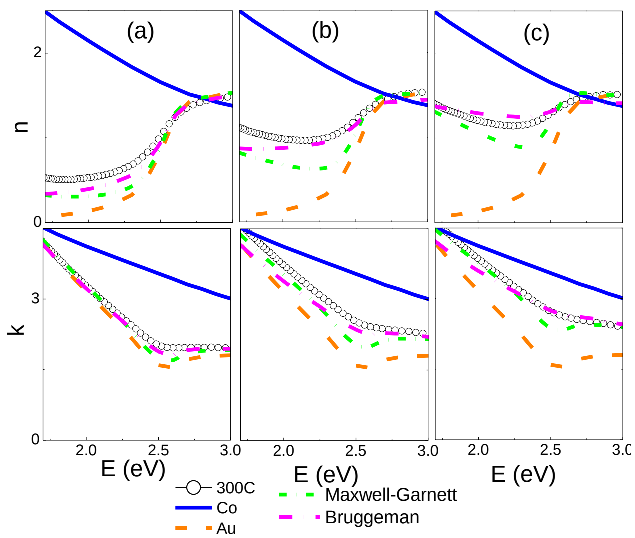

Figure 2: Optical constants (Upper Column: n, Lower Column: k) for Co:Au nano-composite films with composition ratio of (a) 10:90, (b) 30:70 and (c) 50:50. The optical constants of bulk Co and Au are plotted for comparison, along with the optical constants for nano-composite films with identical concentrations calculated using Maxwell-Garnett and Bruggeman effective medium approximations.

Good agreement is found between the experimental values measured in Au-Co films grown at 300 ℃ and the Bruggeman model for all compositions studied, indicating a good segregation of Co and a homogeneous distribution in the Au matrix for this growth temperature.

Reflectivity measurements in the Kretschmann configuration as a function of incident angle for the various Au-Co films with different Co concentration and grown at 300 ℃ is shown in Figure 3 along with simulations using a transfer matrix formalism and the experimental optical constants.

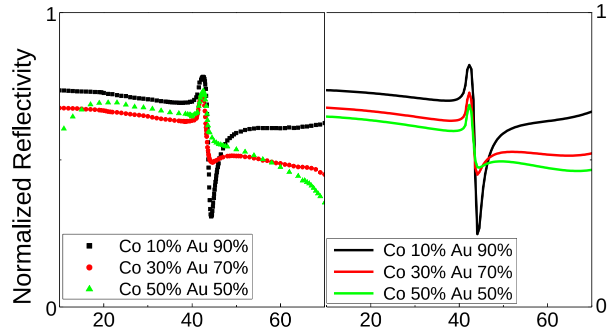

Figure 3: Angular dependence of the reflectivity in the Kretschmann configuration for Co-Au nano-composite films grown at 300 ℃ with concentration ratios of 10:90, 30:70 and 50:50. Experimental data are shown on the left column whereas simulations are shown on the right column.

Both the theoretical calculations and the experimental data in Figure 3 show that as the Au concentration decreases the reflectivity minimum shifts to higher values of incident angle. As expected, the nano-composite films do not exhibit as sharp reflectivity minimum as compared to pure Au films due to the higher absorption of Co. Thus, we notice that the minimum in reflectivity "broadens" when the Co concentration is increased, consistent with the stronger absorption of Co.

We also note that the experimental reflectivity curves and thus the SPP excitation in the nano-composite films also depend on their microstructures. Simulations carried out using experimental optical constants agree well with the experimental data for all the samples deposited at 300 ℃. We expect that optimal excitation of SPP in these nano-composite films should lead to enhanced MO effects, since these depend on the actual electromagnetic fields near the magnetic components[4].

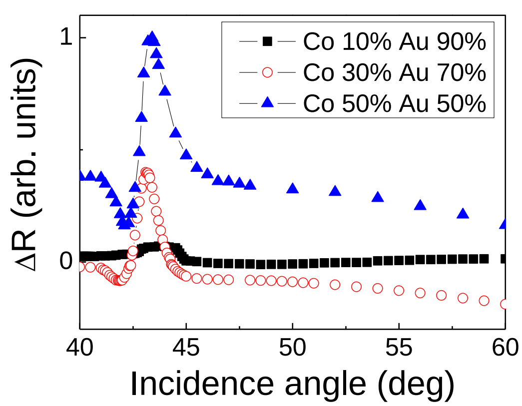

Figure 4: Angular dependence of the magneto-optical Kerr effect in the transverse configuration ΔR=R(H+)-R(H-) for nano-composite films grown at 300 ℃ with different Co concentrations.

The curves shown in Figure 4 illustrate the transverse MO Kerr effect measured in the Kretschmann configuration for the composite films, given by the magnetic field induced change of the reflectivity between the two opposite external magnetic field orientations ΔR=R(H+)-R(H-). Figure 4 shows ΔR for the films grown at the optimum temperature 300 ℃ and with different Co concentration ratios. Higher MO response is obtained for the films exhibiting a higher concentration of Co. We also notice that unlike the field-independent reflectivity, the field modulated reflectivity keeps a narrow angular resolution at resonance, which is of interest in the design of magneto-plasmonic sensors for field-modulated sensing schemes.

4 MAGNETORESISTANCE

The definition of magneto-resistance (MR) is given by $MR=(R(H)-R(H_0))/R(H_0)$, where R(H) and $R(H_0)$ are the resistivities when a magnetic field is applied and when no magnetic field is applied respectively. All measurements were done at RT in the transverse configuration with magnetic field applied parallel to the film surface and perpendicular to the current. As shown in Figure 5, the samples tested revealed a negative MR effect with an increase in resistance when the magnetic field applied increases, with anisotropic magneto resistance (AMR) values comparable to those observed in Co-Au multilayers[5]. The 300 ℃ grown films exhibit a balance between segregation of Co in Au and percolation phenomena. When a current is imposed in the nanocomposite film, the current will converge into Au through the neighboring Co due to the high conductivity of Au. With a saturated magnetic field, the moments of Co are aligned and the spin-polarized conduction electrons are injected from magnetized Co into Au grains.

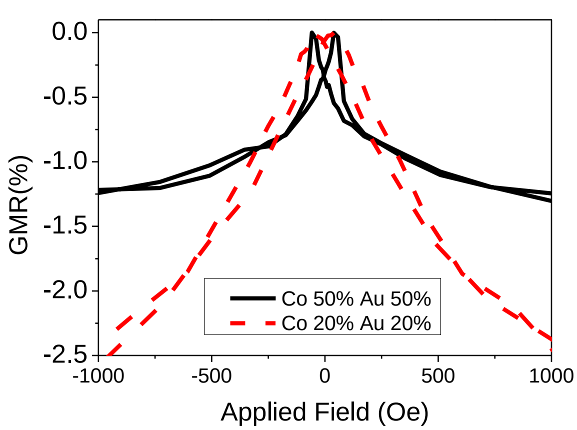

Figure 5: Magneto-resistance versus magnetic field for transverse configuration for Au-Co nanocomposite film grown at 300 ℃. Modify the leyend, only one for each curve is needed.

The observed curves are typical of the AMR effect, arising from the ferromagnetic coupling of adjacent magnetic moments between neighboring clusters, hinting at cluster separations similar to the interlayer separation in Au-Co multilayers (MLs) that also exhibit AMR.[5] Remarkably, a considerable change in the shape of the MR curve is observed for Co 20% and Au 80%, which suggests that the inter-cluster separation may fall in the Au thickness range where a perpendicular anisotropy has been reported in Au-Co MLs.[6] Further studies to exploit experimental conditions leading to similar behavior than that observed in magnetron-sputtered Co/Au MLs that exhibit a low-field GMR effect[5] and the correlation between optical and magneto-transport properties are in progress.

5 CONCLUSIONS

Au-Co nanocomposite films were prepared using co-deposition from Au and Co targets at different substrate temperatures. Samples grown at 300 ℃, which exhibit segregate nano-cluster microstructure and smooth surface capable of SPP propagation also exhibit enhanced MO effects when SPR is excited. We also note that the SPR-enhanced MO activity also increases with increasing Co concentration consistent with the presence of more magnetic material in the films, while the angular resolution of the field-dependent change of the reflectivity at resonance is somewhat insensitive to the amount of Co present. Our preliminary results on magneto-transport properties indicate that there is strong correlation between composition and electrical transport and further studies to fully explain this dependence and possible correlation with magneto-optical properties in these nano-composite films are in progress.

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