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Optical and structural characterization of silver islands films on glass substrates

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A B S T R A C T

Metal island films (MIFs) of Ag on glass substrates were fabricated by the e-beam evaporation technique. The dependence of the surface plasmon (SP) absorption properties on the deposition mass thickness and substrate temperature was quantified. The structural and optical characterization of the MIFs, obtained using spectrometry, grazing-incidence small-angle X-ray scattering (GISAXS) and atomic force microscopy (AFM) evidences the evolution of SP characteristics depending on the fabrication parameters: the red shift of the absorption peaks with the increase of deposition thickness accompanied by peak widening and the blue-shift of peaks with the increase of deposition temperature followed by the peak narrowing. These findings were explained by the differences in the concentration, shape and size of the obtained silver islands.

1. Introduction

Metal island films (MIFs) consist of the metal clusters deposited on a substrate surface and represent one of the most basic cases of nanostructured matter. They can be obtained by thin film evaporation, when the deposited mass thickness is in the range of few nanometres and the film growth is characterized by the formation of islands. MIFs show unique optical properties due to the surface plasmon (SP) resonance of the clusters. The SP properties of MIFs can be tailored by two step evaporation of metal compounds [1], coating of MIF with dielectric film [2] or modifying the deposition conditions in order to influence the geometrical arrangement of the clusters [3]. Due to this capacity to tailor the optical properties, MIFs are used in multiple linear and non-linear optical applications: polarisers [4,5], data storage [6], chemical and biological sensing [7], second harmonic generation [8] or surface enhanced spectroscopy [9].

In order to tailor the SP properties of MIFs for applied purposes, it is necessary to understand the connection between the deposition conditions and the geometrical structure of the MIF. In addition it is required to establish a physical model that correlates the observed physical structure of the MIF and its optical properties. In the present study we focus on the properties of silver MIFs deposited by e-beam evaporation on glass substrates. The influence of two fabrication parameters (substrate temperature and deposited Ag mass thickness) in the MIF optical behaviour is analysed. MIFs are characterized with grazing-incidence small-angle X-ray scattering (GISAXS), atomic force microscopy (AFM) and optical spectroscopy in UV–VIS–NIR range. The structural and optical characterization of the samples shows that the evolution of SP characteristics with the fabrication parameters is explained by the differences in the concentration, shape and size of the islands.

2. Experimental

MIFs were prepared by the e-beam deposition of silver onto 1 mm thick BK7 glass substrates. Prior to deposition substrates were cleaned with the Balzers substrate cleaning liquid nr. 2, wiped with cotton cloth and puffed with dry air. The deposition was done in a Varian 3117 evaporator under pressure of 1.33×10^{-5} mbar. The film thickness was controlled by quartz crystal monitoring. Silver was deposited in three different mass thicknesses (3 nm, 7 nm and 12 nm) and at three different substrate temperatures: 25 °C, 120 °C and 215 °C. Deposition rates determined from mass thickness increment with time were $\sim$0.5 nm/s. Over the silver layer a protective capping layer of 13 nm SiO_2 was deposited in the same deposition run, in all cases.

The SP absorption (A) properties of the samples were studied using optical spectroscopy in the 300–1100 nm spectral range. In order to do this, transmission (T) and reflection (R) measurements were performed using a Perkin–Elmer spectrometer Lambda 25.

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Absorption was then calculated according to the formula: $A = 1 - T - R$.

GISAXS measurements were performed at the Austrian SAXS beam line [10] at the Synchrotron ELETTRA, Trieste, Italy. GISAXS setup data were: X-ray photon energy was 8 keV (i.e. wavelength $\lambda = 0.154$ nm); energy resolution ($\Delta E/E$) was $\leq 2.5 \times 10^{-3}$ and focal spot size FWHM was (4×0.15) mm^2.

The absolute value of the scattering wave vector $\mathbf{q}$ equals $q = 4\pi \sin\theta/\lambda$, where 2θ is the X-ray scattering angle. The GISAXS intensity curves are obtained from the scattering pattern recorded by a two-dimensional charge-coupled device (CCD) detector with image sizes of 1024×1024 pixels. The detector to sample distance was $L = 1.5$ m. A motorized Al beam absorber was positioned perpendicular to the sample surface to reduce the transmitted and specularly reflected beams. The samples were mounted on a stepper-motor-controlled tilting stage with a step resolution of 0.001° and measured at the chosen grazing angles. GISAXS for each sample was measured at critical angle and also at a slightly larger angle.

Atomic force microscopy was performed with a Dimension 3100 (Digital Instruments) instrument in the tapping mode. The radius of the tip was ≤10 nm. Lateral accuracy was typically within 1%. AFM was used for the island morphology characterization as a complementary method to GISAXS.

3. Results

Fig. 1 a) shows optical absorption in the case of films of different thicknesses deposited at 25 °C and Fig. 1 b) shows the case of 3 nm thick films deposited at different temperatures. These are typical spectroscopic results obtained for all samples. They are characterized by an absorption peak related to the SP resonance. Two main effects are observed: i) red shift and widening of the absorption peaks with the increase of deposition thickness and ii) blue-shift and narrowing of absorption peaks with the increase of deposition temperature.

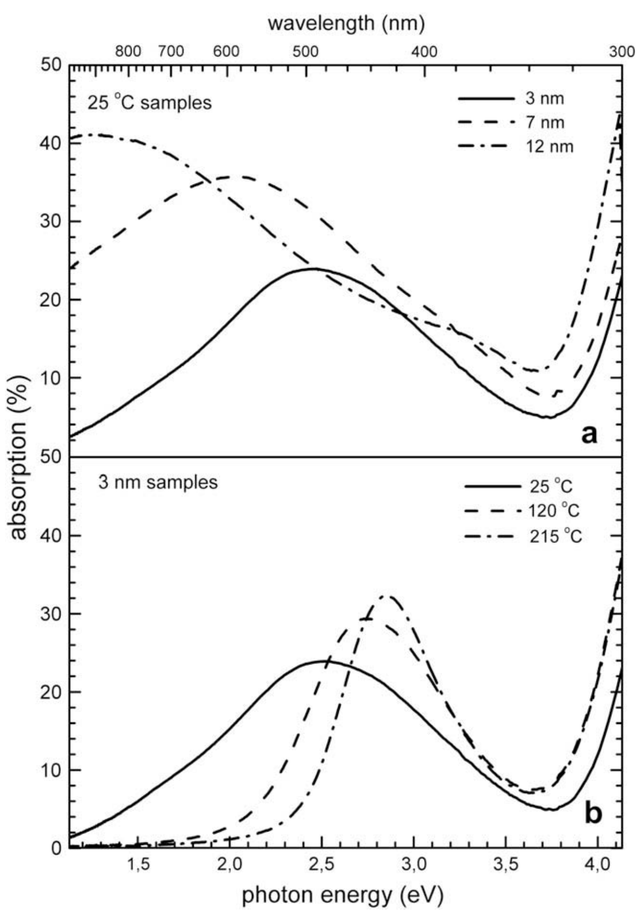

Fig. 1. (a) The evolution of SP absorption properties at 25 °C for different Ag deposited mass thickness and (b) the evolution of SP absorption properties in case of 3 nm deposited Ag at different substrate temperature (denoted at the figure).

Fig. 2 depicts 2D GISAXS scattering patterns of the samples. In all cases well-defined areas of maximum intensities at both sides of the beam stop can be observed. The scattered intensity concentrates more and more towards the origin of the reciprocal space as the deposited Ag thickness increases (see Fig. 2 from left to the right) as well as the deposition temperature increases (see Fig. 2 from top to the bottom). This reveals the growth of island sizes in all real-space directions as it is expected [11] and this assumption will be proved later in this section. In each pattern in Fig. 2 two maxima situated parallel to the q_y axis are separated by the partly seen (partly screened by the beam stop) specular rod at $q_y = 0$ nm^{-1}. This interference effect arises because there is a preferential nearest neighbour centre-to-centre distance (D) between the islands [11]. This intensity is oscillating in z direction due to interference effects in the SiO_2 capping layer.

The island size analysis was performed using a simplified approach. D was determined by direct extraction from the position of the intensity maximum q_m using the "Bragg" law ($D = 2\pi/q_m$). In order to determine the average vertical and lateral size of the silver islands, 1D vertical (i.e. perpendicular to the sample surface at q_m) and horizontal cuts (i.e. parallel to the sample surface at q_m) of a 2D GISAXS patterns were done, respectively. When the Guinier's approximation [12,13] is applied to the vertical and horizontal cut data the respective island sizes are estimated. The obtained vertical and horizontal island's average sizes clearly show the trend of growing with both the deposition thickness and deposition temperature. The GISAXS characterization results are presented in Table 1.

For a more precise determination of the island sizes and inter-particle distances, only the direct modelling of the data is adequate. It should include reflection–refraction effects, the coupling between interference function and the island's form factor which greatly increases the complexity of the analysis [11,14,15].

Fig. 3 presents AFM micrographs of all obtained samples. It was observed that the lateral size of the islands shows an increase with the increase of deposition thickness as well as with the substrate temperature. Results for all samples are also presented in the Table 1. Good agreement of AFM and GISAXS results is obtained in the average inter-particle distance data.

Table 1 depicts the characterization results, obtained by spectroscopy, AFM and GISAXS, for all samples.

4. Discussion

The most evident trends of the geometrical properties of the clusters with the deposition parameters are the increase of the inter-particle distance and sizes in all directions with the deposited mass thickness. Such trends are explained by the typical growth mechanism of metal films [16] that starts with a nucleation process gives place to small clusters and as the amount of deposited metal increases, the clusters start to coalesce and form bigger islands. A secondary trend, observable from the structural characterization, is an increase of the particle size, together with an increase of the inter-particle distance, as the deposition temperature increases. The formation of larger, more spherical and more separated islands, also reported in [17], is connected to the higher energy available to the Ag atoms arriving on a hotter substrate.