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Fabrication of 2D arrays of multi-component nanoparticles

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Abstract. The paper presents a study of a physical method for fabrication of two-dimensional (2D) arrays composed of multi-component nanoparticles on a dielectric substrate. The method consists of two steps. In the first one, thin films composed of different metals are deposited by a classical PLD technique by using targets consisting of sections of different materials. Thin films composed of mixtures of different metals, as gold, silver, nickel, cobalt, iron, platinum, are thus deposited on a quartz substrate. By changing the area of the different sections in the target, thin films with different concentration of the metals are produced. The films fabricated are then annealed by nanosecond laser pulses delivered by a Nd:YAG laser system operating at its third harmonic. The modification of the films is studied as a function of the parameters of the incident radiation, as number of pulses and laser pulse fluence. It is found that the laser annealing can lead to a decomposition of the film into a monolayer of nanoparticles with a narrow size distribution. The optical properties of the structures produced are analyzed on the basis of their transmission spectra. The structures can be used in surface enhanced Raman spectroscopy (SERS) and magneto-optics.

1. Introduction

Following the development of reliable methods of production of nanoparticles, the research efforts have lately been directed to exploring the possibilities of fabricating multicomponent nanostructures containing two or more nanometer-scale components, such as composites, alloys and multilayered particles [1–5]. Such structures have attracted much attention recently due to the synergistic properties induced by the interactions between the different components that may enhance some specific characteristics compared to single-material particles and even give rise to new properties [6–9]. Progress in nanomaterial synthesis has made it possible to mix uniformly nanoscale components in hybrid materials [10, 11]. A special interest has been devoted to the fabrication of multicomponent nanoparticles composed of noble and ferromagnetic metals with potential applications in catalysis, biophotonics and magneto-optics [12–15]. Ag/Co, Ag/Ni, and Au/Ni particles show well-expressed plasmon effects combined with magnetic properties [16]. The position of the plasmon absorption maximum of nanoparticles of an Au/Ag alloy can be tuned precisely in a wide spectral range by changing the ratio between the two metals. A linear dependence has been shown of the plasmon resonance wavelength on the composition of such nanoparticles [17]. This effect can be used to increase the efficiency of the surface-enhanced Raman spectroscopy, in photothermal cell therapy, and in bio-imaging based on such structures.

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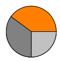
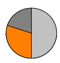
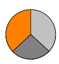
The fabrication of multi-component particles can make use of various techniques, the most popular among them being wet chemical synthesis, sonochemical synthesis, photochemical synthesis, sputter deposition, electroless plating, and electrochemical synthesis [8]. Depending on the specific conditions, particles of core–shell, random or separate structures can be produced [8, 18]. Multi-component materials can also be prepared via self-assembly of NPs from their binary colloidal mixtures [19–21]. Although highly productive, these synthesis techniques usually consist of several steps and require toxic reagents. In this respect, in addition of being flexible and inexpensive, the laser-treatment-based methods exhibit important advantages in the fabrication of nanoparticle arrays. E.g., the de-wetting instabilities produced by laser annealing may result in a homogeneous decomposition of thin metal films directly into 2D nanoparticle arrays [22–24]. The method can also be applied successfully for fabrication of alloyed and bimetallic structures [24–26]. Moreover, the characteristics of the nanostructures formed can be controlled by varying the laser fluence applied and the films' thickness and composition. Furthermore, by controlling appropriately the laser beam parameters, one can produce complex alloy structures with desirable 2D configurations.

In this article we report a study on a method of forming 2D arrays of multi-component nanoparticles using laser structuring of thin Au/Ag/Ni and Au/Fe_3O_4 films on a SiO_2 substrate. We found that laser annealing of the films leads to fabrication of 2D arrays composed by particles whose size, shape and density on the substrate surface depend on the processing parameters and the initial films' composition. The morphology, composition and optical spectra of the structures prepared are studied and discussed.

2. Experimental

The multi-component films were prepared by on-axis pulsed laser deposition. The targets consisted of sections of different metal foils (see table 1), namely, Au, Ag and Ni of 99.99 % purity. By changing the area of the different sections in the rotating target, thin films with different compositions were obtained. An Nd:YAG laser system operating at the wavelength of 355 nm at a pulse repetition rate of 10 Hz and a pulse duration of 15 ns was used to ablate material from the rotating target. The laser fluence on the target was 1,2 J/cm^2. The films were deposited in a vacuum chamber at an ambient pressure of about 10^{-3} Pa for a deposition time of three minutes. The thickness of the bimetallic films thus produced was about 80 nm as measured by AFM.

Table 1. Composition of the thin films studied. The target structure is shown schematically.

	Ni, %	Au, %	Ag, %	Fe_3O_4, %	
Sample 1	35	40	25	-	
Sample 2	20	30	50	-	
Sample 3	26	37	37	-	
Sample 4	-	50	-	50	

The laser treatment of the as-deposited films was performed using the laser system dscribed above. The films were annealed by five laser pulses in the fluence range from 60 mJ/cm^2 to 130 mJ/cm^2 in order to investigate the influence of the processing conditions on the thin film modifications observed. The composition of the films and structures produced after the laser treatments were analyzed by EDX (Quantax 200 Bruker). The morphology of the nanostructures fabricated was studied by SEM (LYRA Tescan). The optical properties of the samples were analyzed on the basis of the transmission spectra taken by an optical spectrometer (Ocean Optics HR 4000). The films' composition was measured at ten points within the 5 mm × 5 mm central area. The EDX analysis showed a change of the atomic percentage of the materials of up to 5 %.

3. Results and discussion

Multi-component samples with different metal ratio were obtained by varying the areas containing the different metals in the target. Table 1 describes the samples with different concentrations used in this study. The table also shows the structure of the target corresponding to the different film compositions. The composition of each sample was confirmed by EDX analysis of the as-deposited thin films. The morphology of the annealed films was observed by SEM. Figure 1 shows SEM images of Au/Ag/Ni (a – c) and Au/Fe_3O_4 (d) films annealed by five laser pulses at different laser fluences.

The structural changes of the films were followed in the fluence range from 60 mJ/cm^2 to 130 mJ/cm^2. At the lowest fluence, only slight changes of the surface relief were observed without decomposition of the film being evident (figure 1a). Annealing of the same alloy at a higher laser fluence (F = 90 mJ/cm^2) results in a nanoparticle array containing particles with a nearly uniform size and density on the substrate surface, as can be seen in figure 1b. Laser treatment at F = 130 mJ/cm^2 leads to the formation of nanoparticles with a larger size and a lower film's density (figure 1c) compared to the structure fabricated at F = 90 mJ/cm^2 due to agglomeration. This effect is expressed even more strongly in the case of sample 4, as evidenced by the absence of material in the close vicinity

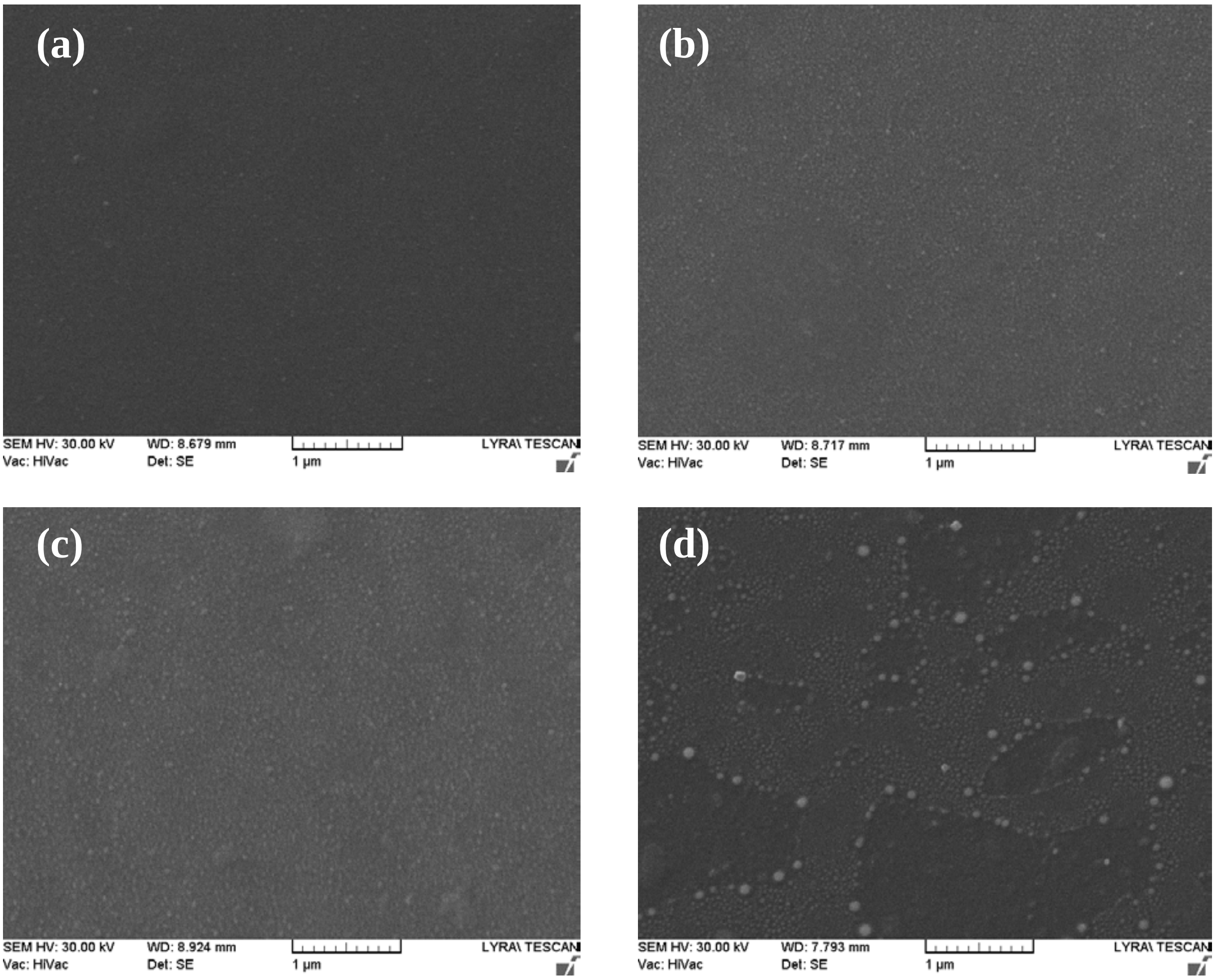


Figure 1. SEM images of multi-component films after treatment by five laser pulses. Sample 3 is annealed at (a) F = 60 mJ/cm^2, (b) F = 90 mJ/cm^2, (c) F = 130 mJ/cm^2 and sample 4 at (d) F = 90 mJ/cm^2.

of the big particles (figure 1d). At laser fluences over 130 mJ/cm^2, a process of film removal off the substrate begins. Since the goal of the study was to define the conditions for formation of a nanoparticle monolayer, we focused our attention on the above-mentioned processing window. It should be mentioned that in the cases of all samples presented in table 1, the laser annealing led to a decomposition of the thin film into a nanoparticle array in the given fluence window. The change of the content of metals in the Au/Ag/Ni films did not influence significantly the characteristics of the structures produced under the same processing conditions.

The fabrication of multi-component nanoparticles containing noble metals presupposes the presence of a surface plasmon resonance in their optical spectrum. In order to determine the specific optical properties of the fabricated structures, we studied their dependence on the processing parameters. Figure 2a presents the optical transmission spectra of a Au/Fe_3O_4 film (sample 4) annealed by five laser pulses at different laser fluences. The well-expressed minima located at 566 nm, 554 nm and 551 nm for the nanostructures fabricated at F = 60 mJ/cm^2, F = 90 mJ/cm^2, F = 130 mJ/cm^2, respectively, are related to plasmon excitation in the nanoparticle array. It is seen that increasing the laser fluence results in a blue-shift of the resonance wavelength. Figure 2a shows also that no plasmon resonance behavior is observed in the spectrum of the unannealed Au/Fe_3O_4 film.

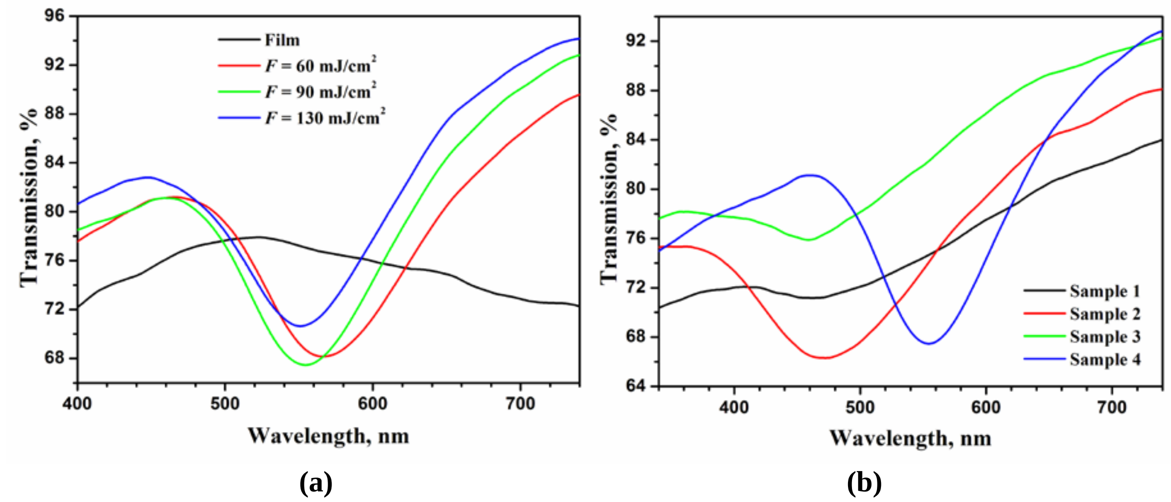


Figure 2. Optical transmission spectra of (a) Au/Fe_3O_4 film (sample 4) annealed by five laser pulses at different laser fluences and (b) multi-component nanostructures fabricated at F = 90 mJ/cm^2, N = 5 at different compositions.

The optical properties of the multi-component nanostructures depend not only on the laser treatment but also on the material's composition. Figure 2b shows the optical transmission spectra of the structures of the samples used in this study (see table 1). The nanostructures with different structural composition were fabricated by five laser pulses at a laser fluence of 90 mJ/cm^2. Plasmon excitation effect is observed in the optical spectrum of each alloy described in table 1. For the Au/Fe_3O_4 nanostructure, a well-expressed SPR minimum is located at 554 nm. In the case of the Au/Ag/Ni alloy, the resonance wavelength varies in the range 459 – 472 nm as a function of the metal content ratio. The SPR depths (with respect to the out-of-resonance level) here are lower compared to the case of the Au/Fe_3O_4 mixture. The influence of the material's composition on the plasmon band characteristics is realized through the change of the dielectric function of the system. Inclusion of Ni leads to an increase of the imaginary part of the dielectric function [24], which is related to a rise in the absorption of the incident radiation. This leads to a dampening of the plasmon minimum. It should be mentioned that the absence of two minima in the transmission spectra of the alloyed samples that would correspond to two single-metal particles also confirms the fact that the fabricated structures are composed by particles of a multi-component material [26].

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4. Conclusions

We proposed and demonstrated a technique for fabrication of 2D arrays of Au/Ag/Ni and Au/Fe_3O_4 nanoparticles. The method is based on laser annealing of multi-component thin films deposited by PLD. Under certain conditions, the annealing leads to a decomposition of the films into a monolayer of nanoparticles. The EDX and the optical properties analyses confirm that the particles consist of a mixture of the initial metals used in the deposition process. Treatment of the Au/Ag/Ni film by five laser pulses at a laser fluence of 90 mJ/cm^2 results in the formation of a 2D array composed of nanoparticles with a nearly uniform size and density on the substrate surface. Processing at $F = 60$ mJ/cm^2 does not result in a clear film decomposition and formation of a monolayer of nanoparticles. Surface plasmon resonance is observed in the optical transmission spectra of the fabricated nanostructures depending on the processing conditions. In the case of laser annealing of the Au/Fe_3O_4 film, changing the laser fluence from 60 mJ/cm^2 to 130 mJ/cm^2 results in a blue-shift of the plasmon band position from 566 nm to 551 nm. The material's composition is also found to affect the SPR. The resonance wavelength of the Au/Ag/Ni alloy varies in the range 459 nm – 472 nm as the ratio of the metals' content is varied.

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