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Near field properties of nanoparticle arrays fabricated by laser annealing of thin Au and Ag films

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ABSTRACT

In this work we show the properties of the electromagnetic field in the vicinity of a monolayer nanoparticle array on SiO_2 substrate. The nanoparticle array is produced by a simple experimental procedure, where thin gold and silver films are deposited on a substrate by pulsed laser deposition technique and they are annealed by nanosecond laser pulses. At certain conditions the laser annealing leads to a homogeneous decomposition of the film into nanoparticles with diameters in the range of few tens of nanometers. Using FDTD simulations the near field distribution in array structures taken from SEM images are obtained. The distribution shows presence on "hot spots" where the near field intensity is enhanced more than two orders of magnitude compared to the incident one. The existence of enhanced field intensity is assumed to be the main reason on enhancement of the Raman scattering signal obtained experimentally using the produced structures as active substrates.

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1. Introduction

The optical properties of metal nanostructures have attracted considerable attention recently. It is related to the efficient excitation of collective electron oscillations, plasmons, that define the particle response to external electromagnetic field. The resonant frequency of these oscillations usually falls in deep UV spectral region. For some metals (Au, Ag and Cu) the plasmon resonance is realized in the near UV or visible spectral range. This makes these metals good candidates for resonance plasmon excitation sources and for utilizing their properties in the region where commercially available coherent lights sources work. The efficient plasmon excitation in metal nanostructures shows a drastic enhancement of heir extinction coefficient, which in some cases exceeds by orders of magnitude those of commercially used organic dyes [1]. These unique properties are used in development of different techniques and systems imaging, diagnostics, therapy and catalysis applications [2].

The properties of the electromagnetic field in the near field zone around the nanosized metal structures irradiated electromagnetic field also exhibit unique features. It is demonstrated that the field in close vicinity of metal structure is localization and its intensity is enhanced by orders of magnitude compared to the incident one. Furthermore, the spatial characteristics of this field are defined by the size of the structure, not by the incident wavelength [3] which breaks the diffraction limit of the far field optics. Examples of applications of these properties are scanning near field optical microscope [4] or tip enhanced Raman spectroscopy [5] that have a resolution in nanometer scale.

One of the most important applications of the nanostructured metal surfaces is in surface-enhanced Raman spectroscopy (SERS), a technique for identification and structural characterization of substances [6,7]. The practical application of SERS is based on the signal enhancement which is several orders of magnitude higher compared to the normal Raman scattering (NR). Thus it allows measurements with very low analyte concentration at low laser intensity [8–10] which is one of the major limitations of NR scattering.

Among the different methods developed for fabrication of nanostructured surfaces are electron and ion beam lithography [11–13], direct laser 2D and 3D structuring [14–16], the use of enhanced near field around metal tip [17]. Femtosecond laser nanostructuring of silicon-based SERS substrates is also recently reported [18]. The nanostructuring of thin metal films by eximer laser pulses is introduced as a novel technique for the production of silver nanoparticles on SiO_2/Si and ITO/glass substrates by Henley et al. [19,20]. The fragmentation of the metal surface into nanosized droplets during the melting is due to of the poor

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wetting between substrate and liquid phase. The detailed picture of the optical properties in the near field zone of such structures is still lacking.

In this paper we investigate the near field properties of nanomodified thin gold and silver films on a SiO_2 substrate. We define experimental conditions that ensure thin film modifications with close to uniform spatial characteristics in a wide area. The near field properties are studied on the basis of Finite Difference Time Domain (FDTD) simulation at parameters close to practical applications. It is shown that the produced substrates can be used as active substrates for SERS analysis. The enhancement of the Raman signal is explained by the electric field distribution and the optical near field enhancement in the vicinity of produced nanostructures. The near field mapping presented could be used as a basic for designing applications on these easily produced structures in the field of sensors and near field optics.

2. Simulation model

The description of the properties of the electromagnetic field in the near field zone of the produced structures is made by Finite Difference Time Domain Simulation [21]. This technique is a numerical algorithm for solving of Maxwell's equation and it allows the solution of electromagnetic distributions for complex geometries and inhomogeneous systems. In this work the simulations are made for system that consists of gold nanoparticles placed on glass substrate. The structure of the nanoparticle array is taken from SEM image of the fabricated surfaces. The simulated system is divided in to elementary cells, where the electric and magnetic field components are calculated at each time step [21]. The dielectric function of the gold particles as the input parameters are taken from [22,23]. The incident irradiation is a plane wave at wavelength of 532 or 785 nm, which corresponds to a standard Raman spectroscopy system. The dielectric function of the substrate is taken from Palik [24]. The electric field intensity which is an input parameter for FDTD simulation is assumed to be 1 $(V/m)^2$ in all simulations.

3. Experimental details

All metal films are produced by pulsed laser deposition on SiO_2 substrate by XeCl eximer laser at $\lambda = 308$ nm, and pulse duration of $\tau = 30$ ns. The gold and silver targets are with purity of 99.99%. The films are deposited at laser fluence of $F = 1.5$ J/cm^2, at ambient pressure of 4×10^{-3} Pa and room temperature of the substrate. The deposition rate of 15 nm/min is estimated at the presented conditions. The thickness of the thin films used in the presented work is 60 nm. Using the same eximer laser the films are then annealed in vacuum. The laser annealing is performed at laser fluencies varied in the range of 100 –300 mJ/cm^2 and fixed number of pulses $N_p = 20$.

The surfaces morphology of the samples is examined by field-emission scanning electron microscope (FEI). Renishaw InVia Micro-Raman system operated at 785 nm excitation, and Hitachi Micro-Raman system operated at 532 nm is used to characterize the SERS properties of fabricated nanostructures. SERS measurements are carried out for Rodamine 6G (R6G) dissolved in ethanol.

4. Results and discussion

The absorption of the laser energy at the process of thin films annealing leads to its heating. At certain fluence the thin film is transformed to a discontinuous structure consisted of small particles. The seeds of these transformations are the boundaries of the grains that compose the polycrystalline thin film. With the increase of the incident energy the small metal islands become in liquid phase. The shape of the formed particles at this stage is governed by the value of the surface energies at the interfaces and at equilibrium state the ratio between surface area to volume is minimal. For the system considered in this work, gold and silver on glass,

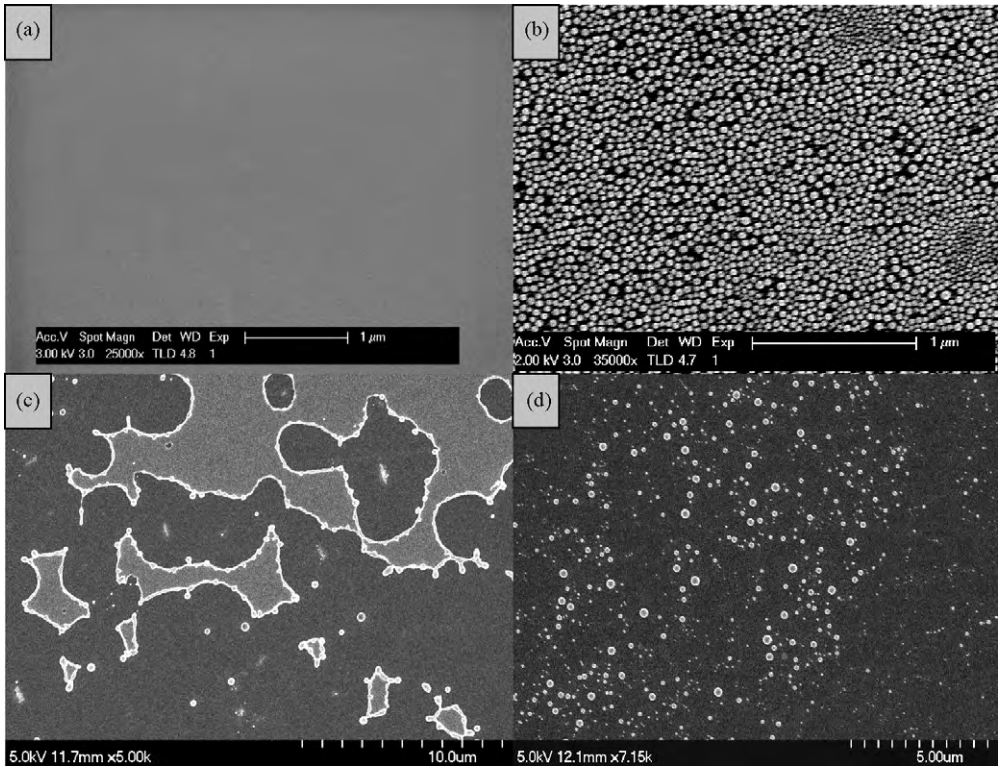

Fig. 1. SEM images of Au films with thickness $d \sim 60$ nm annealed at fixed number of pulses $Np = 10$ (a) shows the case of as deposited film, (b) annealed at $F = 130$ mJ/cm^2, (c) $F = 200$ mJ/cm^2, (d) $F = 300$ mJ/cm^2.

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