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Characterization of Ag nanostructures fabricated by laser-induced dewetting of thin films

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ABSTRACT

The paper presents results on laser nanostructuring of Ag thin films. The thin films are deposited on glass substrates by pulsed laser deposition technology. The as fabricated films are then annealed by nanosecond laser pulses delivered by Nd:YAG laser system operated at $\lambda = 355$ nm. The film modification is studied as a function of the film thickness and the parameters of the laser irradiation as pulse number and laser fluence. In order to estimate the influence of the environment on the characteristics of the fabricated structures the Ag films are annealed in different surrounding media: water, air and vacuum. It is found that at certain conditions the laser treatment may lead to decomposition of the films into a monolayer of nanoparticles with narrow size distribution. The optical properties of the fabricated nanostructures are investigated on the basis of transmission spectra taken by optical spectrometer. In the measured spectra plasmon resonance band is observed as its shape and position vary depending on the processing conditions. The fabricated structures are covered with Rhodamine 6G and tested as active substrates for Surface Enhanced Raman Spectroscopy (SERS).

1. Introduction

Metal nanoparticle array still attracting widespread attention due to their unique properties and functionalities compared to their bulk counterparts. The main interest towards these structures is related to their specific optical properties. When nanostructure of noble metal, as gold and silver, is illuminated by electromagnetic radiation it exhibits strong extinction peak in the ultraviolet–visible (UV–vis) range of the spectrum [1,2]. This optical phenomenon is known as surface plasmon resonance (SPR) and is caused by the coherent oscillation of the conduction electrons in the nanostructure. Among the majority of applications utilizing this effect are chemical sensors [3], biological sensors [4], photovoltaic devices [5], light emitting diodes [6] and surface enhanced Raman spectroscopy [7]. Besides the SPR based applications, metal nanostructures are important in catalysis for nanowire and nanofiber growth [8], making and enhancing spintronic materials [9], improving light emitting characteristics of polymer semiconductors [10] and use as magnetic materials [11]. The electromagnetic field (EM) in the near field zone around the metal nanostructures also shows specific properties when electromagnetic wave irradiates the system at resonance conditions. The intensity of the EM field is greatly enhanced and localized in close vicinity of the nanostructure. The enhanced EM field could be few orders of magnitude stronger compared to the incident one and it has evanescent behaviour – it decreases rapidly with the distance from the metal surface [12,13]. Therefore, the spatial characteristics of this field are defined by the structure size, but not by the incident wavelength [14]. This unique property breaks the diffraction limit of the far field optics and is used in development of systems for surface analysis as scanning near-field optical microscopy [15] that has a resolution in nanometer scale.

The enormous enhancement of the EM field intensity in the metal nanostructures is used in one of their most important applications – surface enhanced Raman spectroscopy (SERS) [7,16]. This is a technique used for detection and analysis of broad range of materials [17] as explosives, drugs, water and food pollutions, soil, viruses and bacteria, and DNA. The high sensitivity of SERS allows detection of even single molecule [18]. The key principle of signal enhancement in SERS is development of high intensity of the near field that may excite efficiently the analyzed substance. However, the strong dependences of the near field properties on

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the characteristics of the nanostructure, incident irradiation and environment, often cause difficulties in fabrication of reliable and reproducible systems with application in SERS.

Furthermore, fabrication of metal nanoparticle arrays with desirable parameters on a substrate is still a significant challenge. Electron-beam lithography offers high resolution, uniformity, and repeatability for array fabrication, but it usually includes slow and costly processes. Another commonly known method to fabricate a metal nanostructure film on a glass substrate is the immobilization of colloid monolayers through organic linkage [19]. These monolayers are often nonuniform with many agglomerates of nanoparticles and it is difficult to control the density of deposited nanoparticles that leads to poor reproducibility. As an alternative of common fabrication methods laser-induced dewetting of thin films deposited on oxide substrates show some advantages. In this technique the laser processing of the sample may result in decomposition of the thin metal film directly into 2D nanoparticle arrays [20–23]. These studies show that the properties of the formed nanoparticle arrays depend on both the properties of the deposited films and the characteristics of the heating process. Furthermore, the size of the particles and the interparticle distance can be controlled by the film thickness and the parameters of the laser irradiation. Advantages of this technique are also relatively fast and easy sample preparation, flexible and cost-effective fabrication process, high purity and formation of nanoparticle monolayer. Main drawbacks of the laser-assisted method are related to inhomogeneity of the processed area due to the mode structure of the laser beam. Furthermore, the efficient practical application of this method needs better understanding of the influence of the different processing conditions on the characteristics of the nanoparticle arrays. Therefore, the nanostructures produced by this method require more detailed study to optimize their functionality for various applications.

In this article we study nanomodification of thin Ag films deposited on glass substrates. We show that laser processing of the thin film may results in its decomposition into array of particles with narrow size distribution. It is investigated the influence of the processing parameters – number of applied laser pulses and laser fluence on the characteristics of the structures. It is found that the parameters of the formed nanoparticle array – particle size and interparticle distance depend significantly on the environment of the sample during the annealing process. The morphology and optical spectra of the produced structures are studied and discussed. The Ag nanostructures are tested as active substrates for surface enhanced Raman spectroscopy (SERS).

2. Experimental

The fabrication of Ag nanostructures on glass substrate consists of two steps. The first one is deposition of thin Ag film on glass substrate by classical pulsed laser deposition (PLD) technique. Nanosecond laser pulses delivered by Nd:YAG laser system operating at wavelength of 355 nm are used to ablate the Ag target (purity of 99.99%) material. The films are deposited on 15 mm × 30 mm glass substrates. The substrate and the target are placed in vacuum chamber as the deposition process is carried out at ambient pressure of $\sim 10^{-3}$ Pa. The delivered laser pulses have duration of 15 ns and the repetition rate is 10 Hz. The Ag films are deposited at laser fluence of 1.5 J/cm^2. The deposition time is 180 or 240 s in the different cases. The film thickness is about ~80 nm or ~100 nm depending on the deposition time.

The next fabrication step is annealing of the as-deposited films by laser pulses. The thin films are processed using the same laser system applied in the deposition process. Laser annealing is performed at different laser parameters (number of the applied pulses and laser fluence) in order to investigate their influence on the Ag film modifications. The surface morphology and the optical properties of the fabricated structures are studied as a function of surroundings during the annealing process. For this examination Ag films are processed by laser radiation with same parameters but in different environment: vacuum, air or water. The thin film modifications on the substrate surface are studied by scanning electron microscopy (SEM). The optical properties of the fabricated structures are examined on the basis of transmission spectra taken by HR 4000 spectrometer (Ocean Optics). Micro-Raman system (InVia Renishaw) operated at excitation wavelength of 514 nm is used to examine the SERS ability of the obtained samples. The SERS measurements are carried out for a standard dye Rhodamine 6G as accumulation time of 5 s is used.

3. Results and discussion

The process of nanostructure fabrication starts with the deposition of thin Ag film on the glass substrate. The transparent substrates are coloured in yellow-grey after the deposition of the silver films. The laser treatment of the films results in colourful yellow spot in the irradiated area which is indication for presence of Ag nanoparticles. Morphological changes of the films used in this study are meanly investigated in the fluence range ~200–300 mJ/cm^2. At processing with laser fluence below the lower value of this window the decomposition of the films is incomplete regardless of the number of the applied laser pulses. Energies higher than the aforementioned window lead to ablation of the film material from the substrate. This fluence range actually defines the conditions for formation of nanoparticle monolayer on the substrate which is a requirement for most applications of the proposed structures.

The transformation of the thin film into nanoparticle array depends on the structure of the as-deposited film and its interaction with the substrate [20,21]. In the case of pulsed laser deposition of Ag on insulator substrate it is demonstrated that the film grows according to the Volmer–Weber growth mode [24]. In accordance with this mode, the deposited atoms initially form domains that further form a thin film. In practice the deposited metal films have usually polycrystalline structure as well expressed domains are observed [25]. When a thin film is irradiated by nanosecond laser pulses with sufficiently high laser fluence it melts. Defects in the film such as domain boundary triple points, pinholes and gas bubbles play a role of seeds for formation of voids that rapidly grow, resulting in decomposition of the thin film. In the case of very thin metal film (1–100 nm) the system liquid metal film on oxide substrate is unstable as the system droplet–substrate has lower surface energy than the film–substrate one [26]. Thus, when the film temperature exceeds the melting point of the metal film it may transforms into defined particles (droplets) with different shapes – from cap to sphere, depending on the dewetting in the system liquid metal–substrate. The equilibrium film morphology is governed by the relative magnitudes of the three interfacial energies: film–substrate interfacial energy, film–environment interfacial energy and substrate–environment interfacial energy. In the case of metal films the dewetting is driven by reducing the energies of the interfaces metal film–environment and metal film–substrate. Since Ag is among the metals that poorly wet glass substrates after thermal annealing a thin film of this metal readily transforms into array of nanoparticles.

Fig. 1 represents SEM images of nanoparticle arrays fabricated by laser-induced dewetting of Ag films deposited on glass substrates. The films with initial thickness of 100 nm are annealed by laser pulses in atmospheric conditions. In order to investigate the influence of the processing parameters on the observed thin film modifications the Ag samples are irradiated by different number of laser pulses (1, 2 or 5) and with two laser fluences: 240 mJ/cm^2

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