Optical Materials 83 (2018) 212–219

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

The influence of dielectric environment on the localized surface plasmon resonance of silver-based composite thin films

Ruijin Hong[a,b], Wen Shao[a], Wenfeng Sun[a], Cao Deng[a], Chunxian Tao[a], Dawei Zhang[a,*]

[a] Engineering Research Center of Optical Instrument and System, Ministry of Education and Shanghai Key Lab of Modern Optical System, University of Shanghai for Science and Technology, No.516 Jungong Road, Shanghai 200093, China

[b] State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

ARTICLE INFO

Keywords:
LSPR
Plasmonic materials
Optical absorption
Raman scattering
FDTD

ABSTRACT

Ag-based thin films with different topography were prepared by annealing process and laser irradiation, respectively. The tunability of localized surface plasmon resonance (LSPR) was realized by adjusting the cover layer thickness of ITO or TiO_2. The effect of dielectric environment of Ag-based composite thin films on structure, surface morphology and optical property was investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscopy (AFM), UV-VIS-NIR double beam spectrometer and Raman system, respectively. With the thickness of dielectric layer increasing, the topography of as-irradiated Ag-based thin films became smoother while the as-annealed Ag-based thin films had a rougher surface. LSPR absorption of both ITO/Ag and TiO_2/Ag bilayers showed red shift with the thickness of dielectric layer increasing. The electromagnetic field coupling between dielectric layers and Ag thin films contributed to increase significantly the sensitivity of surface enhanced Raman scattering (SERS). Additionally, the result of finite-difference time-domain (FDTD) simulation was in good agreement with that of the experiment.

1. Introduction

Localized surface plasmon resonance (LSPR) induced by collective electron charge oscillations in metallic nanoparticles (NPs) has the strong confinement and enhancement of near-field amplitude, which will occur when the resonance frequency of conduction electrons matches with the frequency of incident light [1,2]. LSPR has attracted a lot of attentions in recent years for its plentiful potential applications, such as surface enhanced Raman scattering (SERS) [3,4], biological sensors [5,6], plasmon enhanced fluorescence [7], photothermal therapy [8], nonlinear optics [9] and other photonics and optoelectronics devices [10]. To achieve the high intensity and efficiency of the above applications, it is of great significance to tune and extend the plasmon resonance wavelength. The tunable LSPR wavelength, which has been reported in various matrices like configurations of multilayers [11] and core-shell nanoparticles [12], is not only determined by the size, shape and composition of metal materials but also by the surrounding medium of metallic NPs [13,14]. It has been proved that strong tunable LSPR wavelength can be achieved by adjusting these factors appropriately [15].

Recently, a majority of researches focus on noble metals which have the unique LSPR properties for strong resonant oscillations to study surface plasmon resonance [16–18]. As a noble metal, silver (Ag) has been focused on for years because of its strong resonance absorption, low optical loss and low-cost fabrication. The size, shapes and surrounding medium of Ag thin film can be controlled appropriately to achieve the fine tunable LSPR. Nonetheless, the preparation of desirable size and shapes of Ag NPs and the difference of various surrounding mediums of Ag thin films are still worth exploring. On the one hand, laser irradiation technique has been studied theoretically and experimentally in recent years [19,20] to prepare the Ag thin films with various shapes. On the other hand, the effect of surrounding medium on Ag thin film, which can be structured through dielectric/metal bilayer, is of great importance to research about its LSPR tunability, plasmonic coupling and LSPR stability [21,22]. The dielectric/metal bilayer structure, such as indium tin oxide (ITO)/Ag, has been studied for years [23]. However, as a non-conductive material, TiO_2/Ag bilayer compared with ITO/Ag bilayer on LSPR property has little reports. In addition, the plasmonic coupling between the two materials and Ag thin films with different topography also needs an integrated study.

In this paper, we deposited ITO and TiO_2 layers as the dielectric layer upon Ag thin films which were fabricated by annealing process and laser irradiation to research the structure, morphology and optical properties of Ag-based composite thin films. LSPR wavelength of these

* Corresponding author.
E-mail address: dwzhang@usst.edu.cn (D. Zhang).

https://doi.org/10.1016/j.optmat.2018.06.019
Received 6 May 2018; Received in revised form 7 June 2018; Accepted 11 June 2018

bilayers was tuned in visible region with various thicknesses of dielectric layers, and the comparison of LSPR coupling between ITO/Ag and TiO_2/Ag bilayers was studied. Furthermore, the stability of LSPR wavelength in bilayer structures, which has a practical application in sensor devices, was discussed by air exposure with different days. Raman scattering properties of these bilayers were also investigated along with the simulation of finite-difference time-domain (FDTD) to figure out the electric field distribution of all samples.

2. Experiment

Prior to deposition, fused quartz substrates were ultrasonically cleaned in acetone, ethanol and deionized water for 20 min respectively and then dried with a flow of nitrogen. Ag thin films with a thickness of 15 nm were deposited on the substrates by electron beam evaporation with a base pressure of the chamber less than 4.0×10^{-4} Pa. The as-deposited Ag thin films were subsequently annealed in situ in the same vacuum chamber with the temperature of 100 °C for 30 min. After annealing process, laser irradiation with a continuous wave CO_2 laser source with the wavelength of 10.6 μm was applied in the experiment. The laser parameters were as follow: laser beam power was set as 3 W, the beam diameter was 0.1 mm, and the scan speed was set at 50 mm/s. Following the laser irradiation, ITO and TiO_2 layers with the thicknesses of 10, 20 and 30 nm were deposited upon as-irradiated Ag thin films by electron beam evaporation, respectively (ITO/as-irradiated Ag (ITO/as-ir Ag) and TiO_2/as-irradiated Ag (TiO_2/as-ir Ag)). The chamber was evacuated to a base pressure of less than 8.0×10^{-4} Pa. For comparison, Ag thin film without being irradiated was also used in the study (ITO/as-annealed Ag (ITO/as-an Ag) and TiO_2/as-annealed Ag (TiO_2/as-an Ag)). The thicknesses of all thin films were monitored by a quartz crystal microbalance. To better understand the whole process, a schematic of the experiment is shown in Fig. 1.

The crystal structure of the samples were analyzed by X-ray diffraction (XRD) using a Rigaku MiniFlex600 system with Cu kα radiation (λ = 0.15408 nm). The surface morphology and roughness were characterized by scanning electron microscope (SEM) (S-4800, Hitachi) and atomic force microscopy (AFM) (XE-100, Park System) with the scanning area of 3 μm × 3 μm. The optical absorption of the samples was measured with an UV-VIS-NIR double beam spectrophotometer (Lambda 1050, Perkins Elmer). Raman scattering spectra were examined using a confocal microprobe Raman system (inVia Raman Microscope, Renishaw) with 633 nm laser. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Structural properties

Fig. 2 shows the XRD patterns of all samples prepared by electron beam evaporation. In both Fig. 2(a) and (b), there is only one diffraction peak at around 38.184° (2θ), which is corresponding to the (111) crystallographic plane of Ag (JCPDS: 04–0783). No other grain growth can be observed during the deposition of dielectric layers. With the thickness of dielectric layer increasing in each bilayer, the intensity of the diffraction peak has a slight decrease because of the protection of dielectric layers [24]. For ITO/as-ir Ag (in Fig. 2(a)) and TiO_2/as-ir Ag (in Fig. 2(b)) bilayers, the XRD intensity of as-irradiated Ag is respectively stronger than that of as-annealed Ag in ITO/as-an Ag and TiO_2/as-an Ag bilayers. It indicates the preferential orientation of Ag grains along the (111) crystallographic direction by laser irradiation. When ITO and TiO_2 are at the same thickness in bilayers, such as the wine lines (with the thickness of dielectric layer for 30 nm) in Fig. 2(a) and (b), the diffraction peaks are almost indistinguishable in XRD intensity. These results reveal that the dielectric layers have no obvious effect on the grain growth of Ag thin films.

3.2. Surface morphology

Fig. 3 shows the representative AFM images of Ag thin films and ITO/Ag bilayer structures with different ITO thicknesses. The morphology of as-annealed Ag thin film presents disorders (in Fig. 3(a)). After laser irradiation, the thin film was transformed into orderly spheroidal or ellipsoidal structures (in Fig. 3(e)). According to Fig. 3(a)-(d) and (e)-(h), the changes in morphology are closely related to the thickness of ITO layer. For as-annealed Ag thin film, with the ITO thickness increasing, it grows from small and sharp islands into rough and undulate accumulated island structures. At the same time, the surface of as-irradiated Ag thin film becomes relatively smooth during the deposition of ITO layer. As shown in Fig. 4, the values of the root mean square (RMS) surface roughness of the two groups are 2.477, 2.243, 2.263, 2.440 nm (ITO/as-an Ag) and 5.762, 5.501, 5.464, 5.415 nm (ITO/as-ir Ag), respectively, which are in accord with the surface morphology. The RMS values of TiO_2/Ag bilayer are shown in Fig. 4 as well, they are 2.477, 2.586, 2599, 2.697 nm and 5.762, 5.557, 5.477, 5.320 nm for TiO_2/as-an Ag and TiO_2/as-ir Ag, respectively.

Fig. 5 shows the representative SEM images of Ag thin films and ITO/Ag bilayer structures with increased ITO thicknesses. Comparing Fig. 5(a) and (e), it is obvious that laser irradiation makes as-annealed Ag thin films broken into defined particles. With increased ITO thickness, as shown from Fig. 5(b)–(d), morphology on as-annealed Ag thin film grows into accumulated island with bulky NPs. While the surface of as-irradiated Ag thin films shows almost unchanged with the deposition of dielectric layer between Ag NPs (as shown in Fig. 5(f)–(h)). The SEM results reflect the uniformity with AFM images.

Laser energy is transferred to Ag thin films by laser irradiation and this thermal energy causes the films breakup into droplets with certain nanosize solid metallic particles [19,20]. In the experiment, this breakup results in the as-annealed Ag thin films readily transformed into Ag NPs with ellipsoidal structures. For ITO/as-an Ag bilayer structure, the increased thickness of ITO layer causes the higher grain size, broadened height distribution and low valleys which result in an increasing RMS of Ag thin film [25]. Whereas the deposition of ITO

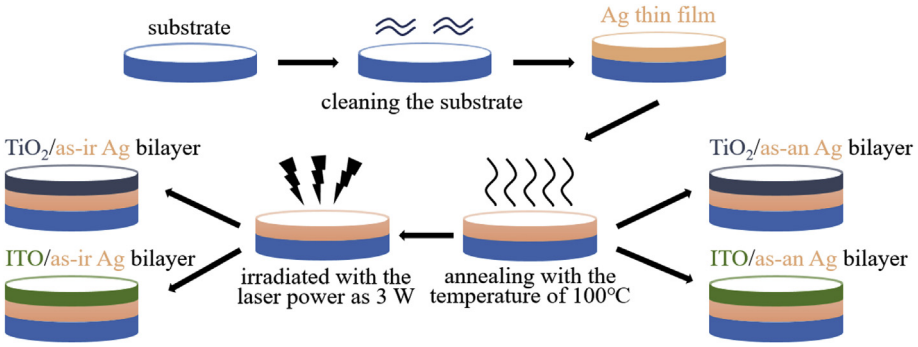

Fig. 1. A schematic diagram of the experiment process.