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Laser irradiation induced tunable localized surface plasmon resonance of silver thin film

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ABSTRACT

Tunable localized surface plasmon resonance (LSPR) properties of silver thin films were realized by CO_2 laser irradiation. The effects of laser irradiation on the structure, morphology and optical property of the samples were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscopy (AFM), UV-VIS-NIR double beam spectrometer and Raman system, respectively. XRD patterns show that laser irradiation has the effects of improving grain growth and orientation of Ag thin films. With laser irradiation power increasing, the topography of as-irradiated silver thin films were observed to develop discontinuous nano-ellipsoid structure with a red-shift of the surface plasmon resonance wavelength in visible region. Both the various ellipsoid sizes and the states of aggregation of as-irradiated silver thin films contributed to increase significantly the sensitivity of surface enhanced Raman scattering (SERS). Additionally, the simulation result of Finite-Difference Time-Domain (FDTD) was proved to be in good agreement with that of the experiment.

1. Introduction

Surface plasmons have attracted lots of interests in recent years for their localized surface plasmon resonance (LSPR) properties [1,2]. When the resonance frequency of conduction electrons and incident light are matched, LSPR induced by collective electron charge oscillations in metallic nanoparticles (NPs) shows its strong confinement and enhancement of near-field amplitude [3–5]. It is indicated that LSPR has many potential applications, such as surface enhanced Raman scattering (SERS) [6,7], photothermal therapy [8,9], nonlinear optics [10], biological and chemical sensors [11–13], plasmon enhanced fluorescence [14,15] and other fields. In particular, SERS has attracted considerable attention due to its nondestructive and single molecular level sensitivity [16–18]. The efficiency and intensity of these applications largely depend on the LSPR wavelength which is not only determined by the size, shape and the surrounding medium of metallic NPs but also by metal materials [4,19–21]. It is demonstrated that strong tunable LSPR can be achieved by modifying these factors appropriately.

At present, researches on surface plasmon resonance mainly focus on noble metals which have the unique LSPR properties due to their strong resonant oscillations [2,9,22]. Among various noble metals, silver, gold and copper are mostly used in plasmonic applications because of their low optical loss. Gold has the advantage of being chemically stable but a higher cost compared with silver. Considering the cost of silver and gold, copper is applicable yet it is easily oxidized [23]. Therefore, silver (Ag) is a reasonable choice to research LSPR properties. Its fine LSPR tunability from visible to near-infrared wavelength can be realized by controlling the size and shapes of Ag NPs appropriately. However, it is still a challenge to fabricate desirable size and shapes of Ag NPs. For examples, electron beam irradiation technique shows slow and costly processes [24]; the arrangement of colloid monolayers has disadvantages about poor reproducibility [25]. Compared to these conventional methods, laser irradiation technique has been studied theoretically and experimentally for its unique advantages which make Ag thin films transformed into droplets with different shapes directly due to its good ductility [26,27]. These Ag samples with nanoparticle structures can be fast and easily prepared by this technique with flexible and low-cost process at the same time. To achieve the tunable LSPR properties, laser irradiation technique is

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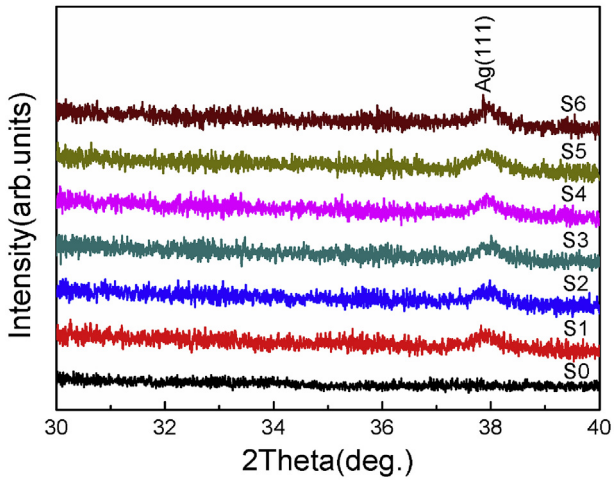

Fig. 1. The XRD patterns of the as-annealed and as-irradiated Ag thin films with various laser powers.

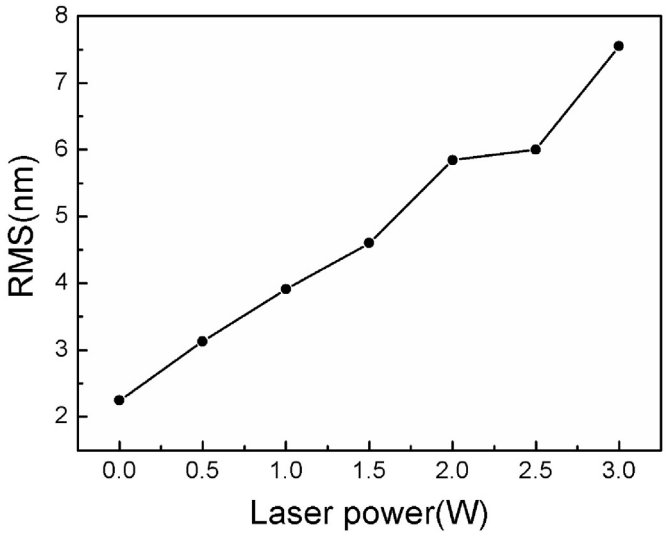

Fig. 3. Surface roughness of Ag thin films corresponding to gradually increased laser power.

applied to prepare Ag NPs with various sizes and gaps by changing certain parameters of the laser equipment such as laser wavelength, laser energy and scan rate and so on. Nevertheless, the practical application of laser irradiation technique is still worthy of deeper researches for its detailed influence on the sizes and shapes of NPs.

In this paper, we proposed a cost-effective technique, CO_2 laser irradiation, to achieve fine LSPR tunability of Ag thin film. This CO_2 laser with long wavelength, different from the short-wave lasers which are commonly used to prepare Ag NPs in previous experiments, only has the thermal transmission when irradiates Ag thin films. The LSPR absorption peaks of the Ag thin films were tuned by varying the laser irradiation power. The influences of laser irradiation power on the structure, optical absorption and Raman scattering properties of Ag thin films were investigated in the paper. Also, the simulation method of Finite-Difference Time-Domain (FDTD) was employed to figure out the electric field distribution of Ag thin films.

2. Experiment

Ag thin films with a thickness of 15 nm were deposited on fused quartz substrates by electron beam evaporation at room temperature. The thickness of thin films was monitored by a quartz crystal microbalance. After finishing the deposition process, the as-deposited thin films were annealed in situ in the same vacuum chamber with the temperatures of 100 °C for 30 min. These as-annealed Ag thin films were irradiated by a continuous wave CO_2

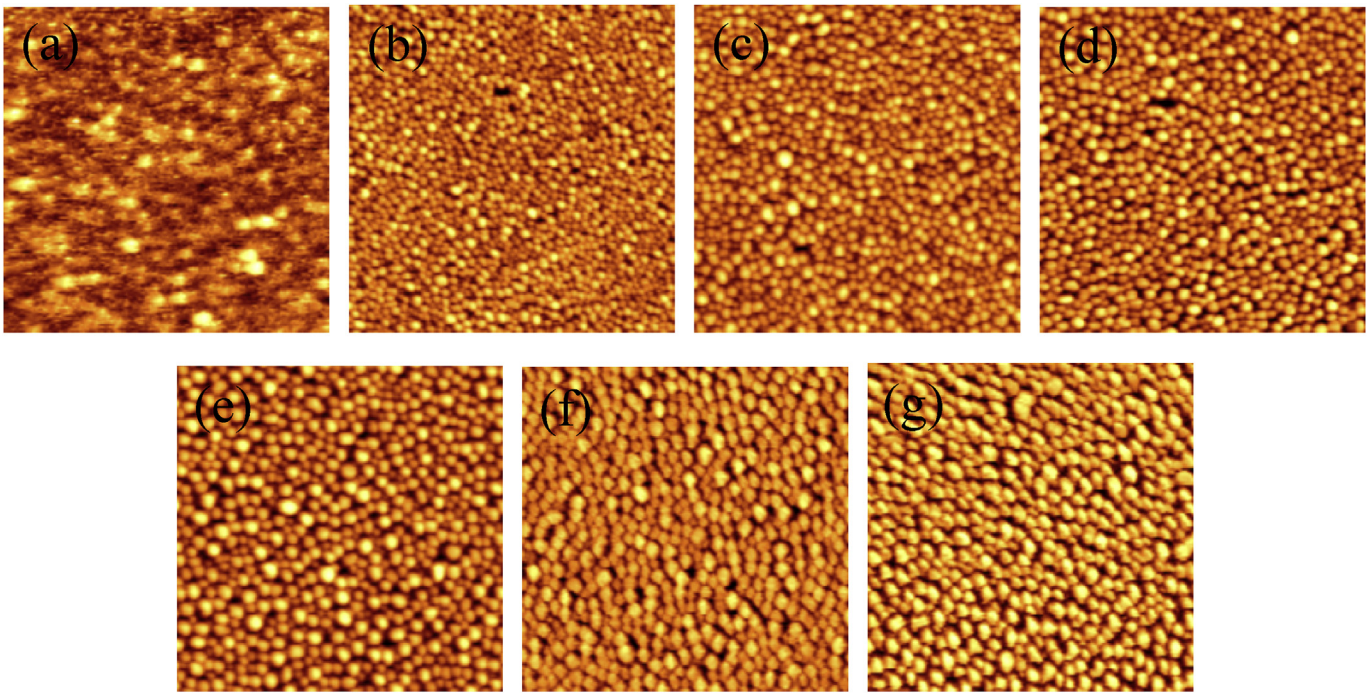

Fig. 2. AFM images of Ag thin films irradiated with laser powers of (a) 0 W, (b) 0.5 W, (c) 1 W, (d) 1.5 W, (e) 2 W, (f) 2.5 W and (g) 3 W.