Vacuum 110 (2014) 94–101

Contents lists available at ScienceDirect

Vacuum

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

Structure and localized surface plasmon tuning of sputtered Au nano-islands through thermal annealing

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ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form
8 September 2014
Accepted 8 September 2014
Available online 21 September 2014

Keywords:
Localized surface plasmon resonance
Au nano-islands
Structure tuning
Refractive index sensitivity

ABSTRACT

Localized surface plasmon resonance of noble metallic nanoparticles has been widely used in the fabrication of various sensors. Turning the nanostructure of localized surface plasmon resonance is significant because the resonance induced localized surface plasmon resonance shift is found to be strongly dependent on the structural characteristics, and thus the performance of the sensors. A simple sputtering, annealing, re-sputtering, and re-annealing process was proposed to tune the structural and optical characteristics of Au nano-islands deposited on the glass substrate. It was found that the size and inter-particle distance of nano-islands depend on annealing time and temperature. High temperature annealing tended to increase the size and inter-islands distance of Au islands. Re-sputtering and re-annealing under different conditions made size and inter-particle distance further tuning possible. Investigations on the optical characteristics of Au nano-islands demonstrated that the surface plasmon resonance peak and the spectral bandwidth of islands were tunable from 510 nm to 620 nm and from 50 nm to approximately 400 nm, respectively. The refractive index sensitivity of Au nano-islands determined by the surface plasmon band position change in different surrounding medium was compared. 500 °C 5 h annealing increased the value of refractive index sensitivity to approximately 58 nm/RIU from 26 nm/RIU under 100 °C 5 h annealing. Besides, Au nano-islands with the same re-sputtering condition but different re-annealing conditions showed the maximum value when the re-annealing temperature is at 500 °C for 5 h. In addition, the refractive index sensitivity, surface plasmon band position, and figure of merit were dependent with each other. These results suggest that the scheme "sputtering, annealing, re-sputtering, and re-annealing" is an effective method to adjust the structure and increase the refractive index sensitivity of sputtered Au islands.

1. Introduction

Noble metallic (e.g., gold, silver, copper) nanostructures exhibit special optical and electronic properties, notably different from those of bulk materials [1,2,5], which are derived from excitation of localized surface plasmon resonance (LSPR) by electromagnetic radiation in the UV–vis spectral range. The LSPR phenomena are expressed as strong light scattering, the appearance of intense surface plasmon absorption bands, and enhancement of local electromagnetic fields near the metal surface [1–5]. Noble metal nanostructures supporting excitation of surface plasmon (SP) polarizations are of special interest in the rapidly developing nano-sensing technology. The refractive index sensitivity (RIS) of SP extinction bands to the dielectric properties of the surrounding medium have been studied as the fast speed and sensitive sensors applied in chemical and biological sensing [2,4].

The spectral properties of nanoparticles (NPs) are sensitive to the size, shape, neighboring distance, and the effective refractive index (RI) of the surrounding environment [1–3,6,7]. The size of NP determines plasmonic features including the ratio of absorption to scattering, the number of LSPR modes, and the peak position of an LSPR mode [1,2,5,8–10]. As the size of the particle becomes larger and larger, the energy levels will continue to split and finally merge into the quasi-continuous band structure for the bulk solid [1,2]. Shape factors such as sharp corners, edges or the specific geometry of a nanostructure can have a large effect on the plasmonic properties. For instance, the SP peak of the cubic nanostructures with sharp corners shifts to the red when compared to rounded structures of similar sizes, which is attributed to the reduced restoring force which caused the greater charge separation during the dipole

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http://dx.doi.org/10.1016/j.vacuum.2014.09.005
0042-207X/

oscillation [1,2]. In addition, the geometry of nanostructures also changes the position of the LSPR peak, number of resonances, and the scattering and absorption cross sections [1,2,8]. The distance between NPs influences the LSPR characteristics due to the electronic-field coupling between NPs during excitation [1,2,5,11–14]. The effect from surrounding RI is dependent on the electron transfer occurs between NPs and the adsorbents. Generally speaking, a red shift is expected if electron transfer occurs from NPs to the adsorbent, and a blue shift results from electron transfer from the adsorbent to NPs [15–18]. The sensing response of metallic nanostructures applied in LSPR sensors field is affected by the optical feature of nanostructure. It is important to broaden the scope of LSPR sensing by exploring electronically resonant adsorbates in biosensing event through biomolecules contain visible chromophores [19]. When these resonant molecules are adsorbed on the surface NPs, the induced LSPR shift is found to be strongly dependent on the spectral overlap between the electronic resonance of the adsorbates and the plasmon resonance of the NPs [20]. In the reference [21], a large red shift occurs when the LSPR of NP is located at a slightly longer wavelength than the molecular resonance wavelength of adsorbates. Hence, tuning the shapes, sizes, orientations, and inter-particle distance of nanostructures is significant for the development of LSPR sensors with a higher performance and wider application.

The structure of NPs can be tuned by the techniques include both the top-down technique, such as electron-beam lithography (EBL) [22] and the bottom-up fabrication methods, such as colloidal lithography (CL) [23–25]. These methods have become the popular selection in making metallic NPs with various structures. However, EBL requires costly instrumentation, and is hard to control due to machine difference. In addition, CL includes colloidal fabrication and self-assembly process which are hard to realize, and the production rate is very limited. Hence, a more easily controllable, efficient, and economic method for making and tuning nanostructure has yet to be developed.

In our recent research, a simple procedure of Au sputtering was developed to deposited nano-islands on the transparent glass substrate [29,30]. Through controlling the sputtering conditions such as current or time and thermal annealing treatment, Au nano-islands films with different morphology, size, and optical characteristics have been obtained and utilized to fabricate LSPR gas sensors. A rapid response of the LSPR sensor to the volatile organic chemicals was realized, which demonstrated a potential application in the field of sensor-loaded robot for the fast speed environment gases detection.

In this work, a simple method based on Au sputtering, annealing, re-sputtering, and re-annealing was proposed to tune the size, density, inter-particle distance, and the SP bandwidth and position of Au nano-islands. The sensing performance of Au nano-islands films was evaluated by the RIS and figure of merit (FOM) characteristics, according to the spectral changes induced by the bulk RI change in the surrounding medium. The nano-islands film annealed at 500 °C showed higher RIS, and the nano-islands film under the re-sputtering and re-annealing process realized the RIS further improvement when the re-annealing temperature was 500 °C. Furthermore, RIS, SP band position, and FOM of Au nano-islands films were verified to be dependent on each other.

2. Experimental section

2.1. Au nano-islands fabrication

Cleaned and dried borosilicate glass substrates were processed in a plasma cleaner (PDC-001, HARRICK) in argon atmosphere (110 V, 10.2 W) for 5 min. After that, the substrates were immersed in a 1:15 (volume ratio) solution of 3-aminopropyl triethoxysilane (APTES) (Shin-Etsu Chemical) in ethanol for 3 h, and then rinsed thoroughly with ethanol to remove physically adsorbed APTES molecules. Au was deposited on glass substrate using a quick coater (SC-701HMC, Sanyu Denshi, Japan). Thermal anneal treatment was carried out in air atmosphere at a serial of temperatures varying from 100 °C to 600 °C in a muffle furnace (ISUZU SSTS-13K, ISUZU Seisakusho co., Ltd). Beginning of the heating was taken as zero time for the kinetics. A stationary temperature of 500 °C was reached within about 20 min, and maintained constant within ±5 °C for the desired time. The heating rate was approximately 25 °C min^{-1}. The substrates after annealing were left to cool till room temperature before use.

2.2. Atomic force microscopy, scanning electron microscopy, and UV–vis spectroscopy

Scanning electron microscopy was performed using a scanning electron microscopy (SEM, SU8000, Hitachi). Atomic force microscopy (AFM, Nanoscope IIIa, Digital Instrument) was utilized to analyze the morphology characteristics of Au nano-islands operated in a tapping mode. The transmittance spectra of Au nano-island films were obtained by an UV–vis spectrophotometer (UV1800, Shimadzu), in which the scanning range was set from 400 to 1000 nm, and the wavelength resolution was 0.5 nm, using air as baseline. Au islands samples were inserted into a 1 cm path plastic cuvette, while a matched cuvette with the same bare glass slide in the same cuvette served as a reference. Hence, the spectra obtained are only related with the optical characteristics of Au nano-islands.

2.3. Evaluation of RIS

The bulk RIS is one of the commonly used methods to assess the sensing performance of noble metallic NP sensors [27]. The extinction spectra of Au nano-islands films in water–glycerol mixtures of varying glycerol volume ratios were compared. With the increase in the volume percentage of glycerol, plasmon peak of Au nano-islands film shifted toward the red direction. The refractive index of the liquid mixture was calculated according to the Lorentz–Lorenz equation as shown in reference [31]:

$$\frac{n_{12}^2-1}{n_{12}^2+2}=\varphi_1\frac{n_1^2-1}{n_1^2+2}+\varphi_2\frac{n_2^2-1}{n_2^2+2} \quad (1)$$

where n_{12} is the refractive index of the liquid mixture, n_1 and n_2 are the indexes of water (1.333) and glycerol (1.475), respectively, and φ_1 and φ_2 are the volume fractions of the two components. The calculated refractive index of the liquid mixture as a function of the volume percentage of glycerol are approximately 1.340 (5%), 1.347 (10%), 1.357 (15%), and 1.361 (20%).

3. Results and discussion

3.1. Morphology of Au nano-islands on glass

T. Karakouz and coworkers' research show that as-prepared Au nano-islands (10 nm in thickness on glass) show a marked change when the heating temperature reaches at about 200 °C, while a surface plasmon band appears when the heating temperature reaches around 300 °C [33]. In light of this result, the annealing temperature was initially set at 300 °C in this work to investigate the dependence of morphology of islands on the annealing time. The morphological parameters of Au islands deposited on glass under different processing conditions are shown in Table 1. Au