Applied Surface Science xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Optimization of nanocomposite Au/TiO_2 thin films towards LSPR optical-sensing

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ARTICLE INFO

Article history:
Received 12 May 2017
Received in revised form 19 August 2017
Accepted 19 September 2017
Available online xxx

Keywords:
Plasmonics
Au nanoparticle
LSPR
Magnetron sputtering
Surface plasma activation
Titanium dioxide

ABSTRACT

Nanomaterials based on Localized Surface Plasmon Resonance (LSPR) phenomena are revealing to be an important solution for several applications, namely those of optical biosensing. The main reasons are mostly related to their high sensitivity, with label-free detection, and to the simplified optical systems that can be implemented.

For the present work, the optical sensing capabilities were tailored by optimizing LSPR absorption bands of nanocomposite Au/TiO_2 thin films. These were grown by reactive DC magnetron sputtering. The main deposition parameters changed were the number of Au pellets placed in the Ti target, the deposition time, and DC current applied to the Ti-Au target. Furthermore, the Au NPs clustering, a key feature to have biosensing responses, was induced by several post-deposition in-air annealing treatments at different temperatures, and investigated via SEM analysis. Results showed that the Au/TiO2 thin films with a relatively low thickness (~100 nm), revealing concentrations of Au close to 13 at.%, and annealed at temperatures above 600 °C, had the most well-defined LSPR absorption band and thus, the most promising characteristics to be explored as optical sensors. The NPs formation studies revealed an incomplete aggregation at 300 and 500 °C and well-defined spheroidal NPs for higher temperatures. Plasma treatment with Ar led to a gradual blue-shift of the LSPR absorption band, which demonstrates the sensitivity of the films to changes in the dielectric environment surrounding the NPs (essential for optical sensing applications) and the exposure of the Au nanoparticles (crucial for a higher sensitivity).

1. Introduction

Localized Surface Plasmon Resonance (LSPR) has emerged as a capable approach in the field of label-free biosensing, which is dominated by Surface Plasmon Resonance (SPR) sensors [1,2]. Both SPR and LSPR phenomena are based on the resonance of incident electromagnetic (EM) waves with collective oscillations in noble metal/dielectric interfaces [3–5]. These oscillations lead to strong EM fields with absorption bands at a specific wavelength [6], that are sensitive to changes in the refractive index (RI) of the surrounding medium [7–9].

Abbreviations: at.%, atomic percentage; EM, Electromagnetic; LSPR, Localized Surface Plasmon Resonance; NPs, Nanoparticles; RBS, Rutherford Backscattering spectrometry; RD, Reference Deposition; RI, Refractive Index; SEM, Scanning Electron Microscopy; SPR, Surface Plasmon Resonance; TF, Thin Film; XRD, X-Ray Diffraction.

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http://dx.doi.org/10.1016/j.apsusc.2017.09.162
0169-4332/

In the case of SPR biosensing, the evanescent field has a long decay, which translates in a penetration into the dielectric medium higher than 100 nm [10,11]. Thus, this technique is more prone to detect changes in the refractive index in large areas of the dielectric medium [12], but it also makes it more susceptible to interferences from other analytes in the sample, and temperature fluctuations. Furthermore, it requires sophisticated optics [13], such as prisms, waveguides, fiber optics or gratings [14].

On the other hand, in LSPR, the EM field confinement is stronger near the nanoparticles (NPs) [15], and a smaller penetration of the evanescent field into the dielectric is observed [15]. In fact, it can be lower than 10 nm [10,11], translating in an increase of sensitivity for RI changes near the NPs surface [10,12,13,16].

A simpler way to observe the LSPR absorption band is by transmitted EM radiation, described as Transmission LSPR (T-LSPR) [17–19], which can simplify the detection system [20] and conveniently be detected by a standard spectrophotometer [17]. This approach has been demonstrated to be widely suitable for optical sensing and comparable to SPR in terms of sensitivity, outmatching it in terms of fabrication cost and experimental setup, but maintaining the possibility of detection of wavelength shifts (of the transmittance spectra) [12]. However, the development and production of reliable T-LSPR platforms requires thin films (TFs) composed of noble metal NPs supported by a host matrix, and having reproducible and stable optical properties [21]. The main objective of the proposed work is to produce these nanocomposite thin films with optimized LSPR absorption bands for optical sensing.

In terms of materials preparation for optical sensing, magnetron sputtered nanocomposite TFs, with noble metal NPs embedded in a dielectric matrix [22], such as those composed of Au [23–25] or Ag [26] dispersed in TiO_2, have already shown potential as LSPR platforms [23]. The LSPR absorption bands can be tuned by changing the concentration of the noble metal [27] and applying a thermal treatment, which affects the size, distribution and shape of the NPs [28,29]. In addition, other structural and morphological changes can also occur in the surrounding dielectric medium, which affect also this LSPR absorption bands tuning, and thus, the optical sensing responses [25]. Depending on the temperature and time used in the annealing steps, an evolution of the LSPR absorption band is observed [26,30].

Nonetheless, in magnetron sputtered nanocomposite TFs, the noble metal NPs stay embedded in the dielectric matrix [22], and due to the low penetration evanescent field characteristic of LSPR [15], the sensing area is completely covered by the TiO_2 matrix. To overcome this hurdle, Pedrueza et al. have studied the possibility of exposing partially the Au NPs to air, by removing layers of TiO_2 matrix with hydrofluridic (HF) acid (a strong acid, used in etching and lithography techniques) [31]. The results showed a blue-shift in the LSPR absorption band, corresponding to a decrease of the RI, due to a partial exposure of the Au NPs [31].

In the present work, several samples were prepared using different deposition conditions, in order to achieve optimal LSPR absorption bands in Au/TiO_2 TFs for application in T-LSPR sensors. Considering as reference the conditions used in recent works [23–27,30], different parameters were varied, namely the deposition time (DT), applied DC current and Au content, maintaining the same thermal treatment protocol. The surface of the films with the most suitable LSPR peak for optical sensors, was also submitted to a post-annealing physical activation/etching using argon plasma to (i) expose the gold nanoparticles and (ii) study the optical sensitivity of the films to surface changes.

2. Experimental details

The Au/TiO_2 TFs were prepared by reactive magnetron sputtering in a custom-made equipment, using a direct current (DC) power supply, operating in the current regulating mode. A pure Ti target ($200 \times 100 \times 6\,mm^3$, 99.99% purity), containing different amounts of Au pellets incrusted on its preferential sputtering zone, was sputtered in an atmosphere composed of Ar (partial pressure of 3.8×10^{-1} Pa) and O_2 (partial pressure of 4×10^{-2} Pa). The base pressure of the system was always below 6×10^{-4} Pa and the working pressure was about 4.2×10^{-1} Pa. The TFs were deposited on glass lamellae, fused silica and Si (p-type, Boron doped) substrates. The sample holder was grounded in all depositions. In order to promote the adhesion of the TFs, the substrates were *ex-situ* cleaned and plasma etched, using a *Zepto* plasma system (*Diener Electronic*). These plasma treatments were performed in an Ar atmosphere (pressure of 70 Pa), using a 40 kHz RF generator, operating at a power of 100 W, for 900 s.

For this study, the main parameters changed were the number of Au pellets placed in the target, the applied DC current and the deposition time (Table 1). The main purpose is the comparison of the characteristics of the TFs (composition, structure and microstructure) and their optical properties, with Reference Deposition (RD) conditions from previous works, and with the pure matrix itself (TiO_2). The TiO_2 and RD films were deposited using a current of 2 A (100 $A.m^{-2}$) during 150 min, and using 2 Au pellets for the latter (Table 1). The number of Au pellets was decreased to 1 and increased to 3, in relation to RD, in order to have different concentrations of noble metal in the TiO2 matrix. The exposed area of each pellet was about 15 mm^2, corresponding to Au fraction areas in the target erosion zone varying from 0.3% to 0.9%. The DC current applied to the Ti-Au target was also changed, varying from 1 to 2.5 A, in order to change the flow rate of atoms towards the substrates, corresponding to current densities between 50 $A.m^{-2}$ and 125 $A.m^{-2}$. Finally, the deposition time was decreased from the RD film for 45 and 90 min in order to lower the thickness of the films.

In a second step of the nanoplasmonic TFs' preparation, several post-deposition thermal treatments were carried out, with heating ramps of 5 °C/min and different isothermal temperatures, from 200 °C to 700 °C. After each annealing treatment, samples remained in the oven to cool down freely until reaching room temperature.

Rutherford Backscattering Spectrometry (RBS) was used to determine the chemical composition of the TFs. Measurements were performed at 1.4 MeV with ^1H and 2 MeV with ^4He (normal incidence). The chamber had three detectors: at a 140° scattering angle; and two pin-diode detectors located symmetrically to each other, both at a 165° scattering angle respective to the beam direction. The data were analysed with the code NDF [32,33].

Structural investigations of the coatings were conducted by *in situ* high temperature X-ray diffraction (HT-XRD), measurements were made in a Bragg–Brentano configuration using the Brucker

Table 1
–Deposition conditions. RD is the reference deposition. Common conditions are Ar flow 25 sccm, O_2 flow 7 sccm and substrate holder grounded.

Deposition	RD	TiO_2	T45	T90	I1	I1.5	I2.5	Au0.3	Au0.9
Deposition time (min)	150	150	45	90	150	150	150	150	150
Current on target (A)	2	2	2	2	1	1.5	2.5	2	2
Au fraction on target (%)	0.6	0	0.6	0.6	0.6	0.6	0.6	0.3	0.9

Please cite this article in press as: M.S. Rodrigues, et al., Optimization of nanocomposite Au/TiO_2 thin films towards LSPR optical-sensing, Appl. Surf. Sci. (2017), http://dx.doi.org/10.1016/j.apsusc.2017.09.162