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Thin films composed of Ag nanoclusters dispersed in TiO_2: Influence of composition and thermal annealing on the microstructure and physical responses

J. Borges[a,*], M.S. Rodrigues[b,c], C. Lopes[b], D. Costa[b], F.M. Couto[d], T. Kubart[e], B. Martins[c], N. Duarte[c], J.P. Dias[c], A. Cavaleiro[f], T. Polcar[a,g], F. Macedo[b], F. Vaz[b]

[a] Department of Control Engineering, Faculty of Electrical Engineering, Czech Technical University in Prague, Technická 2, Prague 6, Czech Republic
[b] Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[c] Instituto Pedro Nunes, Laboratório de Ensaios, Desgaste e Materiais, Rua Pedro Nunes, 3030-199 Coimbra, Portugal
[d] Physics Sciences Laboratory, Norte Fluminense State University, Campos, 28013-602 RJ, Brazil
[e] Solid-State Electronics, Department of Engineering Sciences, Uppsala University, P.O. Box 534, Uppsala SE-751 21, Sweden
[f] SEG-CEMUC, Mechanical Engineering Department, University of Coimbra, 3030-788 Coimbra, Portugal
[g] National Centre for Advanced Tribology at Southampton (nCATS), University of Southampton, Highfield, SO17 1BJ Southampton, UK

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ABSTRACT

Noble metal powders containing gold and silver have been used for many centuries, providing different colours in the windows of the medieval cathedrals and in ancient Roman glasses. Nowadays, the interest in nanocomposite materials containing noble nanoparticles embedded in dielectric matrices is related with their potential use for a wide range of advanced technological applications. They have been proposed for environmental and biological sensing, tailoring colour of functional coatings, or for surface enhanced Raman spectroscopy. Most of these applications rely on the so-called localised surface plasmon resonance absorption, which is governed by the type of the noble metal nanoparticles, their distribution, size and shape and as well as of the dielectric characteristics of the host matrix. The aim of this work is to study the influence of the composition and thermal annealing on the morphological and structural changes of thin films composed of Ag metal clusters embedded in a dielectric TiO_2 matrix. Since changes in size, shape and distribution of the clusters are fundamental parameters for tailoring the properties of plasmonic materials, a set of films with different Ag concentrations was prepared. The optical properties and the thermal behaviour of the films were correlated with the structural and morphological changes promoted by annealing. The films were deposited by DC magnetron sputtering and in order to promote the clustering of the Ag nanoparticles the as-deposited samples were subjected to an in-air annealing protocol. It was demonstrated that the clustering of metallic Ag affects the optical response spectrum and the thermal behaviour of the films.

1. Introduction

Materials tailored at the nanoscale, e.g. in the form of nanoparticles, have unique physical and chemical properties compared to their bulk form [1]. Among them, silver (Ag) and gold (Au) are the two most studied plasmonic materials since when they are embedded in a dielectric matrix they manifest localised surface plasmon resonances (LSPR) in the visible range [2–4]. The LSPR effect occurs when the metallic nanoparticles are well-separated and have dimensions significantly smaller than the wavelength of the incident electromagnetic field [3]. It is responsible for a broad and intense absorption of light in the vicinity of the resonance frequency and the enhancement of the local electromagnetic field [1]. The LSP resonance frequency, bandwidth and peak height depend markedly on the nanoparticles composition, their shape, size and size distribution and also on the host dielectric matrix [5]. The well-known dependence of LSPR on the refractive index of the surrounding medium is also particularly important for the detection of chemical and biological species [6,7]. In this particular point, the use of high sensitive and low cost plasmon-based optical sensing platforms can be useful in a wide range of fields such as food quality and safety, medical diagnostics and environment monitoring [7] and in Surface-Enhanced Raman Scattering (SERS) [8,9]. The

* Corresponding author. Tel.: +351 253510471.
E-mail addresses: joelborges@fisica.uminho.pt, jborges@ipn.pt, joelborges22@gmail.com (J. Borges).

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latter example is a well-established analytical technique used for the detection and recognition of molecular species even if they are in very low concentration; however it depends on the development of high-quality SERS active substrates being an area of great interest for the scientific community [8–11].

Due to its chemical inertness and biocompatibility, Au is the preferred noble metal for biological applications [2]. However, Ag is preferable in some cases for example in SERS since it can produce higher enhancement factors [8,9].

In recent works it was studied the influence of gold concentration, dispersed in a TiO_2 matrix, and annealing temperature on the microstructural features and optical response of Au:TiO_2 thin films [12–15]. The overall set of results showed that the growth of Au nanoparticles/clusters with different sizes and size distributions is highly dependent of the annealing temperature [14] and, on the other hand, the intermediate Au contents, i.e. between 5 and 15 at.%, can produce a spectrally broad LSPR bands [16,17]. At the same time, it was also observed the crystallisation of the TiO_2 host matrix in anatase (from 400 °C) and rutile (from 700 °C).

In this work, several thin films with a wide variation of silver noble metal (Ag) concentrations were prepared by magnetron sputtering deposition using a Ti target with small pellets of Ag placed on the preferred erosion zone. In order to study the influence of Ag concentration and annealing temperature on the microstructure of the films and how those features are correlated with the optical and thermal properties of Ag:TiO_2 films, the samples were subjected to a thermal treatment in air atmosphere.

2. Experimental details

The thin films, composed of silver (Ag) dispersed in a TiO_2 matrix, were deposited by reactive DC magnetron sputtering in a home-made deposition system. More details about the system can be found elsewhere [18].

For the deposition of the thin films it was used a titanium target ($200 \times 100 \times 6\,mm^3$, 99.8% purity) containing various amounts of Ag pieces, or "pellets" (thickness: 1 mm, disk area: $16\,mm^2$). The pellets were placed on the preferred erosion zone of the Ti target ("erosion track"). In each deposition, the number of Ag pellets was increased (from 1 to 6) in order to enhance the flux of Ag atoms towards the substrate. The purpose of this methodology was to obtain thin films with different Ag concentrations. The DC power supply was set to operate in the current regulating mode, using a constant current density of $100\,A\,m^{-2}$ on the Ti-Ag target. The films were prepared using a gas atmosphere composed of Ar (partial pressure of 4.0×10^{-1} Pa) and O_2 (partial pressure of 5.6×10^{-2} Pa). The working pressure (about 4.5×10^{-1} Pa) was constant during the deposition of the film. The oxygen partial pressure was chosen according to the hysteresis experiment, which is described in [14]. Moreover, the conditions described above are similar to those used to produce the Au:TiO_2 system [14], where the Au pellets are here "replaced" by Ag.

The films were deposited onto silicon with (1 0 0) orientation, for characterisation purposes (composition, structure and morphology); glass (ISO 8037) and fused silica (SiO_2), for the optical and thermal characterisations. The substrates were placed in a grounded (GND) rotating holder (9 r.p.m.), heated at 100 °C using a resistor. Prior to depositions, the substrates were subjected to an in-situ etching process by applying to them a pulsed DC current of 0.5 A (T_{on} = 1536 ns and f = 200 kHz) during 1200 s, in a pure argon atmosphere (partial pressure of 4.0×10^{-1} Pa).

After the deposition of the films, an in-air annealing process was carried out in order to promote the Ag clustering, as consequence of Ag diffusion throughout the host matrix. In this way it is possible to tailor the structural and morphological features of the plasmonic nanostructures. The annealing temperatures used were between 200 and up to 800 °C, with a heating ramp of 5 °C min^{-1} and an isothermal period of 1 h. The samples were let to cool down freely and then removed from the furnace, after they reached the room temperature.

The chemical composition of the films was analysed by Energy-dispersive X-ray Spectroscopy (EDS), using a JEOL JSM-5310/Oxford X-Max.

The structural analysis of the coatings was carried out using Grazing Incidence X-Ray Diffraction (GIXRD), with a Philips X-Pert diffractometer (Co-Kα radiation), operating at an angle $\theta = 2°$. The scans were done between 15° and 80°, with a scan step of 0.025° and an acquisition time of 1 s. By using the Winfit software, the XRD patterns were deconvoluted, assuming to be Pearson-VII functions in order to estimate the grain size of the clusters from the integral breadth method.

The morphological features in cross section view were probed by scanning electron microscopy (SEM), using a Zeiss Merlin instrument, equipped with a field emission gun and charge compensator. Both in-lens secondary electron and energy selective backscattered electron detectors were employed. The growth rate was calculated by the ratio between the average thickness (estimated by cross-section SEM analysis) and deposition time (90 min.).

The films transmission coefficients (300–900 nm) were measured in glass, for annealing temperatures up to 500 °C, and in fused SiO_2 substrates, for annealing temperatures above 500 °C. The measurements were performed in a Shimadzu UV-3101 PC UV–Vis–NIR.

For thermal properties measurements a non-stationary photothermal technique, namely modulated infrared photothermal radiometry (MIRR) [19] was used. Basically, the sample is heated with an intensity modulated laser beam and the infrared response at the same frequency is recorded. The experimental setup uses a DPSS 532 nm laser for excitation and an acousto–optic modulator to modulate the incident light from nearly DC up to 100 kHz. A set of two BaF_2 lenses are used for collecting and focusing the infrared response from the sample into an IR HgCdTe detector. The resulting electric signal is then pre-amplified and fed into a lock-in SR830. All the data acquisition process is controlled by software. Extensive information and details on the technique can be found elsewhere [20,21]. Since the penetration depth of the generated "thermal waves" depend inversely on the modulation frequency, this technique is particularly useful to study thin films and coatings. From the behaviour of the amplitude and phase lag of recorded signals, the thermal diffusion time and the thermal effusivity ratio can be estimated using the two-layer model proposed by Fotsing et al. [22]. Knowing the thermal diffusion time and the thickness, measured by SEM, the thermal diffusivity can be immediately calculated.

3. Results and discussion

3.1. Deposition characteristics, structure and morphology of the films

3.1.1. Deposition characteristics of the Ag:TiO_2 system

It is well known that the processing conditions (discharge conditions, plasma composition, deposition characteristics, etc.) should be carefully selected since they are of paramount significance for the microstructural (structure, morphology, phase composition) evolution of the films during its growth and hence for the final overall physical responses [23].

In order to study some of those deposition-related features, the evolution of the target (cathode) potential during the growth of the film, as well as the deposition (growth) rate of the films were firstly analysed. The values of those parameters are plotted in Fig. 1

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