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Plasmonic TiO_2:Au composite layers deposited in situ by chemical spray pyrolysis

I. Oja Acik [a,*], N.G. Oyekoya [a], A. Mere [a], A. Loot [b], L. Dolgov [b], V. Mikli [c], M. Krunks [a], I. Sildos [b]

[a] Laboratory of Thin Film Chemical Technologies, Department of Material Science, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia
[b] Institute of Physics, University of Tartu, Ravila 14c, Tartu 50411, Estonia
[c] Chair of Semiconductor Materials Technology, Department of Material Science, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia

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ABSTRACT

Composite TiO_2 layers with embedded Au-nanoparticles with a size of 8–20 nm were deposited in situ by chemical spray pyrolysis. EDS studies show that increase in the deposition temperature from 260 to 300 °C decreases the [Au]/[Ti] ratio down to the vanishing of Au at in 400 °C. The mean crystallite size of the Au-nanoparticles is slightly decreasing from 17–21 nm to 10–13 nm with increasing deposition temperature from 260 to 300 °C. However, the annealing at 400 °C has minor affect on the size of the Au-nanoparticles. Annealing at 400 °C results in crystalline anatase TiO_2 matrix with its mean crystallite size decreasing with increasing the [Au]/[Ti] ratio in the composite layers. The total transmittance and reflectance spectra of the TiO_2 and TiO_2:Au composite layers are complemented by the Mie calculations, showing that the red shift of the surface plasmon resonance band from 570 to 620 nm is associated with the increase in the refractive index of the TiO_2 matrix.

1. Introduction

Metal oxide layers with noble metal nanoparticles have drawn great interest, particularly by their wide range of applications in optics, nanoelectronics, biomedicine, catalysis and photovoltaics. Metal nanoparticles such as gold, silver and copper are the most common ones used to obtain the surface plasmon resonance effect. Adjustment of spectral position for surface plasmon resonance allows additional artificial control of light absorption and scattering in optical plasmonic materials [1–3]. Spectral position of plasmon resonance depends on the size and shape of nanoparticles, distance between them and permittivity of environment and metal [4]. The metal oxide layers with metal nanoparticles have been deposited by several methods, such as spin-coating [5,6], magnetron sputtering [7] and spray pyrolysis [8–12]. Also, a combination of two wet-chemical [13] or chemical and vacuum-based methods [14] have been used to obtain a metal oxide layer with metal nanoparticles.

Chemical spray pyrolysis (CSP) is a low-cost material deposition technology; here the solution of appropriate precursor materials is deposited in the form of fine droplets onto the preheated substrate where the growth of thin film takes place. To obtain Au-NPs by spray pyrolysis, either preformed nanoparticles are added into the spray solution [12,15] or NPs are generated during the spray pyrolysis deposition process via thermal decomposition of Au-precursor salts such as $HAuCl_4 \cdot nH_2O$, $HAuCl_4$ and $HAuCl_4 \cdot 3H_2O$ [8–11]. Thermoanalytical studies have shown that the decomposition of $HAuCl_4 \cdot 3H_2O$ into pure gold and gaseous products takes place in the temperature range of 75–320 °C in air [16]. Recently, it has been shown that SnO_2 [9], ZnO [8,10] and ZrO_2 [11] thin films with Au-nanoparticles could be deposited in situ by chemical spray pyrolysis method at temperatures of 400 °C or above. However, TiO_2 layers with preformed Au-nanoparticles have been deposited at significantly lower temperature of 200 °C by spray [12,15]. Moreover, it has been shown lately that Au-NPs deposited by spray method have enhanced the out-put characteristics of the dye-sensitized [12] and sprayed inorganic thin film [17] solar cells.

In this study, we report on the TiO_2:Au composite layers deposited in situ by single-step chemical spray pyrolysis method. The effect of the Au concentration in the spray solution as well as the deposition and annealing temperatures on the TiO_2:Au composite layers will be discussed.

2. Experimental

TiO_2 films and TiO_2 films with Au-nanoparticles were deposited in situ by sol-gel chemical spray pyrolysis method. The spray solution (sol) was composed of titanium (IV) isopropoxide (0.2 mol L^{-1}) and acetylacetone in a molar ratio of 1:2 in ethanol [18,19]. Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) was used as precursor for the synthesis of gold nanoparticles (Au-NPs). The $HAuCl_4 \cdot 3H_2O$ salt was dissolved in ethanol with the solution concentration of 0.10 mol/L. A proper amount of $HAuCl_4 \cdot 3H_2O$ solution was added to the TiO_2 spray solution. The Au concentration in TiO_2 spray solution ([Au]/[Ti]) was 0, 2.7 or 5.4 at%.

* Corresponding author. Tel.: +372 620 3369; fax: +372 620 3367.
E-mail address: ilona.oja@ttu.ee (I. Oja Acik).

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TiO_2 films were deposited for reference. The spray solution was applied to the preheated glass and indium tin oxide covered glass (glass/ITO) substrates at tin bath temperatures of 260, 300 or 400 °C in air, employing pulsed sprays, where each cycle consisted of 1 min of spraying followed by 1 min of pause. Two spray cycles were deposited with a spray rate of 3.0 mL min^{-1}. As-deposited films were subjected to annealing at 400 °C for 1 h in air. Hereinafter, the as-deposited and annealed films will be referred to as TiO_2, TiO_2:Au(2.7), TiO_2:Au(5.4) according to the concentration of the Au in the spray solution. For example, TiO_2:Au(2.7) refers to the film with an Au concentration of 2.7 at% in the spray solution.

The obtained TiO_2 films and TiO_2 films with Au-nanoparticles (TiO_2:Au) were characterised by optical transmittance spectra, scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods. The total transmittance spectra of the films were measured in the wavelength range of 300–800 nm on a Jasco V-670 UV–VIS–NIR spectrophotometer equipped with an integrating sphere. The surface morphology, cross section and elemental composition of the layers was studied with the help of a scanning electron microscopy and energy-dispersive X-ray analysis (EDS) using a Zeiss HR FESEM Ultra 55 with Bruker EDS system ESPRIT 1.8 or EVO MA 15 Zeiss using the Oxford Instruments INCA Energy system. An acceleration voltage for SEM measurements was 4.0 kV and for EDS analysis 7.0 kV. The crystal structure of the samples was characterised by XRD and Raman methods. XRD patterns were recorded by a Rigaku Ultima IV diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV at 40 mA) and using the silicon strip detector D/teX Ultra. The mean crystallite size was calculated using the Scherrer formula. Raman spectra were acquired on a micro-Raman spectrometer HORIBA Jobin Yvon Model HR800 using 532 nm laserline for excitation. The Raman peak analysis is based on Lorenzian-fitting performed in the range of 100–200 cm^{-1}. Mathematical modelling of light extinction was realized by Mie calculations.

3. Results and discussion

3.1. Morphology of the layers

The SEM cross-sectional images of as-deposited TiO_2, TiO_2:Au(2.7) and TiO_2:Au(5.4) layers grown at 300 °C are compared in Fig. 1. As seen, the TiO_2 film (Fig. 1a) possesses a dense morphology with the thickness of ca 150 nm. The addition of 2.7 at% of Au in the TiO_2 spray solution results in compact TiO_2:Au(2.7) layer (Fig. 1b). Increasing the [Au] in spray solution up to 5.4 at% results in cracked TiO_2:Au(5.4) layer. The thickness of the TiO_2:Au films increases from 270 nm to ca 900 nm with increasing the [Au] concentration in the spray solution from 2.7 to 5.4 at% (Fig. 1, Table 1). The TiO_2:Au(2.7) and TiO_2:Au(5.4) layers deposited at 260 °C were cracked; however, a dense TiO_2 layer can be deposited at this temperature (Fig. not shown). Increasing the deposition temperature to 400 °C resulted in TiO_2 films and TiO_2:Au layers with similar compact morphology and thickness (Table 1) independent of the Au concentration in the spray solution.

The cracking of the TiO_2:Au layers deposited at lower temperatures and/or high [Au] concentrations in the spray solution is related to higher amount of organic residues in these samples [16,20].

As a result of annealing, the grain-like structure characteristic for the TiO_2 films becomes visible, irrespective of the [Au] concentration in the spray solution and the deposition temperature (an example on Fig. 2a).

SEM images show that separately placed Au-NPs cover the surface of the TiO_2:Au(2.7) and TiO_2:Au(2.7) layers when deposited at 300 °C and annealed at 400 °C for 1 h in air (Fig. 2a,b). The size of the Au-NPs on the surface of the TiO_2:Au(2.7) and TiO_2:Au(5.4) layers remain in the range of 15–25 nm and 5–10 nm, respectively. Moreover, SEM cross-sectional ASB (angle selective back scattering) image (Fig. 2c) shows that the Au-NPs are embedded in the TiO_2:Au composite layer with a particle size distribution ranging from 8 to 20 nm. A significant decrease in

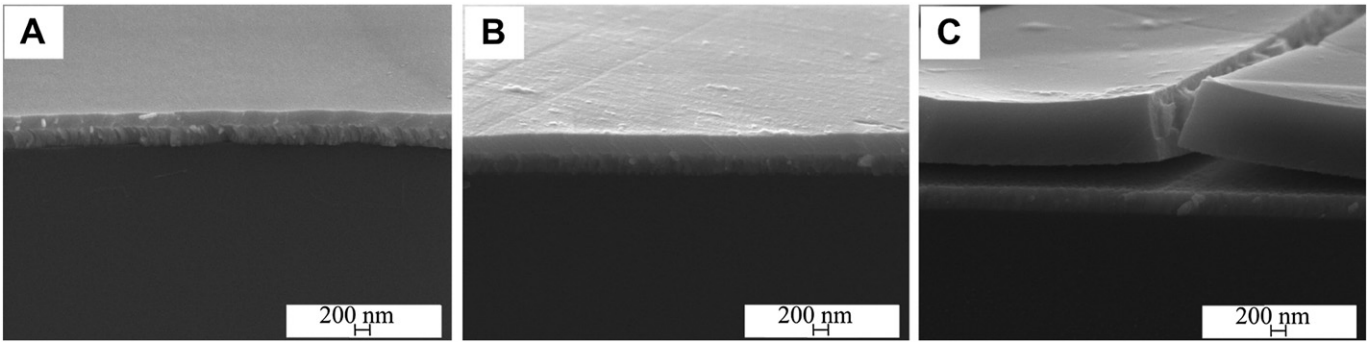

Fig. 1. Cross-sectional images by SEM of the as-deposited (A) TiO_2, (B) TiO_2:Au(2.7) and (C) TiO_2:Au(5.4) layers grown onto glass/ITO substrate at 300 °C.

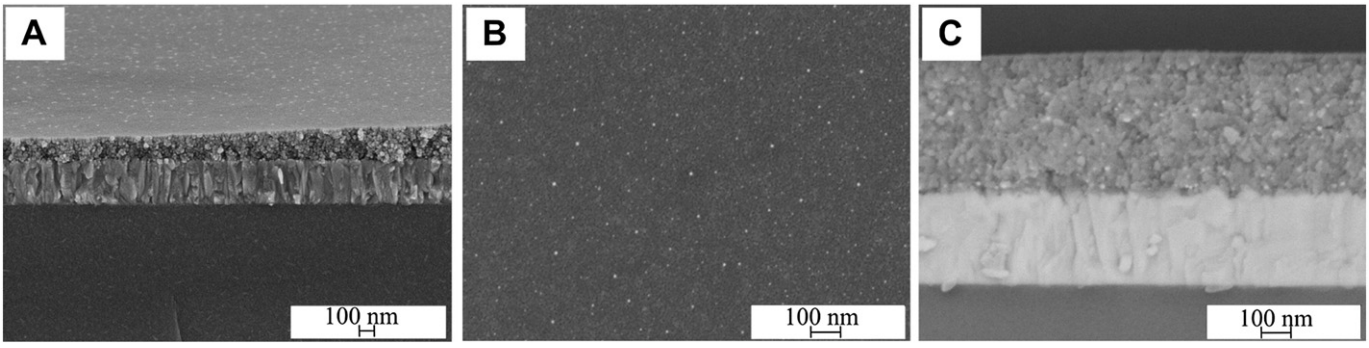

Fig. 2. SEM images (A) cross section of the TiO_2:Au(2.7) layer, (B) top view of the TiO_2:Au(5.4) layer and (C) cross-sectional ASB image of TiO_2:Au(5.4) layer deposited onto glass/ITO substrate at 300 °C and annealed at 400 °C.