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An indium oxide electrode with discontinuous Au layers for plasmonic devices

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ABSTRACT

In this contribution we report on a low cost plasmonic electrode for light-sensing applications. The electrode combines a conducting nonstoichiometric indium oxide (InO_x) layer with an ultrathin (~5 nm) discontinuous Au layer. The InO_x and Au layers were deposited on glass substrates by plasma enhanced reactive thermal evaporation and thermal evaporation, respectively. Several device configurations with one or two Au layer(s) sandwiched between InO_x layers were fabricated and characterized. The morphological and structural properties of both Au and InO_x layers were analyzed using AFM and XRD techniques. In particular, the effect of thermal annealing (673 K, 15 min) on the surface morphology of Au layers grown on bare glass and InO_x-coated substrate was investigated. It has been also found that the oxide film grown above an underlying nanostructured Au layer is amorphous, while a reference InO_x film on glass is nanocrystalline with a smooth surface. The electrical properties of InO_x grown on the Au surface are worsened due to Au-induced structural disorder. The observed difference in transmission spectra of the glass/InO_x/Au and glass/Au/InO_x structures indicates the difference in the morphology of the metal layer. Thus, the optical and morphological properties of the InO_x electrode can be varied in a wide range by incorporating several Au layers.

Keywords: plasmonics, localized surface plasmons, nanostructured gold film, indium oxide, reactive thermal evaporation

1. INTRODUCTION

Sensors based on local surface plasmon resonance (LSPR) phenomenon are highly sensitive to variations of the surrounding environment refractive index and have been thoroughly investigated by the research community, targeting biological/chemical sensing applications[1-4]. Nevertheless, there is still a trending demand for cost effective plasmonic nanostructures which can be easily integrated with other optical or/and electronic components to fulfill the lab-on-chip concept[5]. Remarkably, a discontinuous gold film deposited without masking by evaporation or other vacuum techniques may exhibit plasmonic properties[6-8]. These nanostructured films consist of metallic islands separated from each other by inter-island channels. The morphology of this irregular nanostructured surface can be modified by adjusting the deposition conditions or/and by thermal annealing thus controlling the optical properties of the films such as the position and amplitude of the localized surface plasmon resonance absorption peak[9]. However, the poor stability of gold nanoisland films on glass substrate in various solvents, including water, is a major issue[10]. Mechanically, chemically and optically stable gold island films can be formed on indium tin oxide (ITO) surface due to excellent adhesion properties of this material[11, 12].

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In this paper, we report on hybrid indium oxide electrodes with discontinuous Au layers exhibiting plasmonic properties. The thermal evaporation and plasma enhanced reactive thermal evaporation[13] (PERTE) techniques were used to deposit Au and InO_x layers, respectively. A detailed description of the thin-film deposition and characterization methods is the starting point of this work. This follows with an analysis of the surface morphology of gold films directly evaporated on glass and InO_x-coated substrates and subjected to thermal annealing. The optical properties of these films are also presented and discussed. Then, we demonstrate and discuss the effect of the underlying Au layer on the structural and electrical properties of the top InO_x layer. After that, the study is focused on the multilayered structures, where one- or two nanostructured Au layers are sandwiched between InO_x layers. Results have been summarized in the conclusions section.

2. EXPERIMENTAL DETAILS

Ultrathin gold films for this study were prepared by resistive evaporation at a base pressure of about 4×10^{-6} mbar, and a deposition rate of 0.3 Å /s. The deposition rate and thickness were controlled using a STM-100/MF thickness/rate monitor. InO_x films were prepared using an automated rf-PERTE system[14]. The deposition was performed evaporating pure indium in oxygen plasma at 4×10^{-4} mbar pressure, 13 sccm gas flow, 40 W rf-power, 423 K substrate temperature, and about 1.3 Å /s deposition rate.

A Dektak 3 profilometer was used to measure the thickness of InO_x films. A Dimension 3100 SPM with a Nanoscope IIIa controller from Digital Instruments (DI) was used for the AFM measurements. The measurements were performed in tapping mode (TM) under ambient conditions. A commercial tapping mode etched silicon probe from Bruker and a 90×90 μm^2 scanner were used. Grazing-incidence X-ray diffraction (XRD) measurements were performed using a D8 ADVANCE diffractometer with DAVINCI.DESIGN and a LINXEYE-XE detector (Cu Kα^o λ=1.54Å) in the grazing incidence geometry, with an incident beam angle of 1.5°. The sheet resistance of InO_x films was measured using a Veeco FPP-5000 four point probe. The Hall effect and resistivity measurements were performed using 4-terminal van der Pauw geometry. The magnetic field strength was ± 1.1 T. The transmittance of films in the UV/visible/IR region was measured using a Shimadzu UV-3100 spectrophotometer.

3. RESULTS AND DISCUSSION

During the deposition process of Au layers, nanometer-sized metal clusters are created through nucleation and growth. Above a critical thickness, these islands coalesce to form a conducting network. In this experiment, Au layers have been evaporated on soda-lime glass, and also on glass substrates with a 60-nm-thick InO_x coating. The substrate temperature was as high as 453 K in order to minimize undesired coalescence phenomena. The targeted Au layer thickness of 5 nm is approximately equal to half the percolation threshold thickness for the used deposition conditions. Nanostructuring of Au was done by 15 min annealing in nitrogen atmosphere at 673 K. The postdeposition annealing turns the color of the Au film on glass from blue to light pink. Fig. 1 shows AFM images of the Au layers on glass and glass/InO_x substrates before and after annealing. Here, all surface topology data are plotted on the same scale for easy comparison. Evaporation of Au on bare glass results in a quasi-continuous film with 2.4 nm root mean square (RMS) roughness (Fig. 1a). Annealing leads to the formation of nanoislands with a mean diameter of 34 nm and an average height of 16.8 nm (Fig. 1b). A fine grained structure is observed in the Au layer grown on InO_x surface (Fig. 1c). Here, the RMS roughness is 1.83 nm, the mean diameter of grains is 28 nm, and the average grain height is 10.8 nm. The annealed sample shows nanoislands with a mean diameter of 39 nm and an average height of 19 nm (Fig. 1d).

Transmission spectra of unannealed and annealed glass/Au and glass/InO_x/Au structures are shown in Fig.2. A single minimum in the spectra is associated with intense localized surface plasmon absorption. The curve shape, absorption intensity and position (λ_{min}) of the LSPR band are strongly influenced by the thickness of the nanostructured gold layer, the interface material as well as by the post-treatment. Annealing of the glass/Au sample leads to a blue-shift of the long-wavelength band edge due to the formation of gold nanoislands (Fig. 2a). The as-deposited glass/InO_x/Au sample exhibits much stronger absorption spreading to the near-infrared region (Fig. 2b). Indeed, the Au layer grown on the InO_x surface is smoother than the layer on the bare glass as that reported above. Therefore, its optical properties are similar to that for quasi-continuous metal films. The transmission curve of the annealed glass/InO_x/Au sample indicates the successful formation of gold nanoislands.

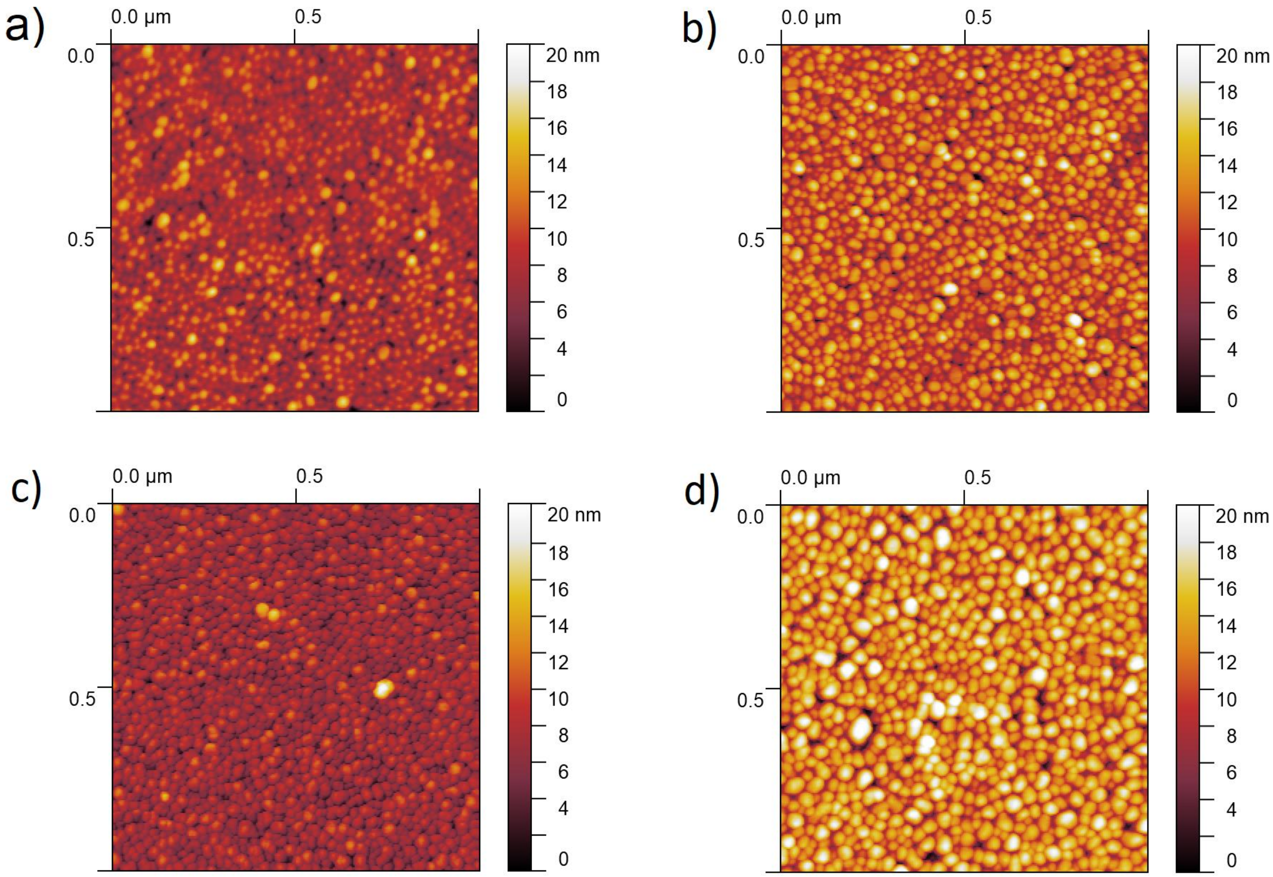

Fig. 1. AFM images: the glass/Au sample before (a) and after (b) annealing; the glass/InO_x/Au sample before (c) and after (d) annealing.

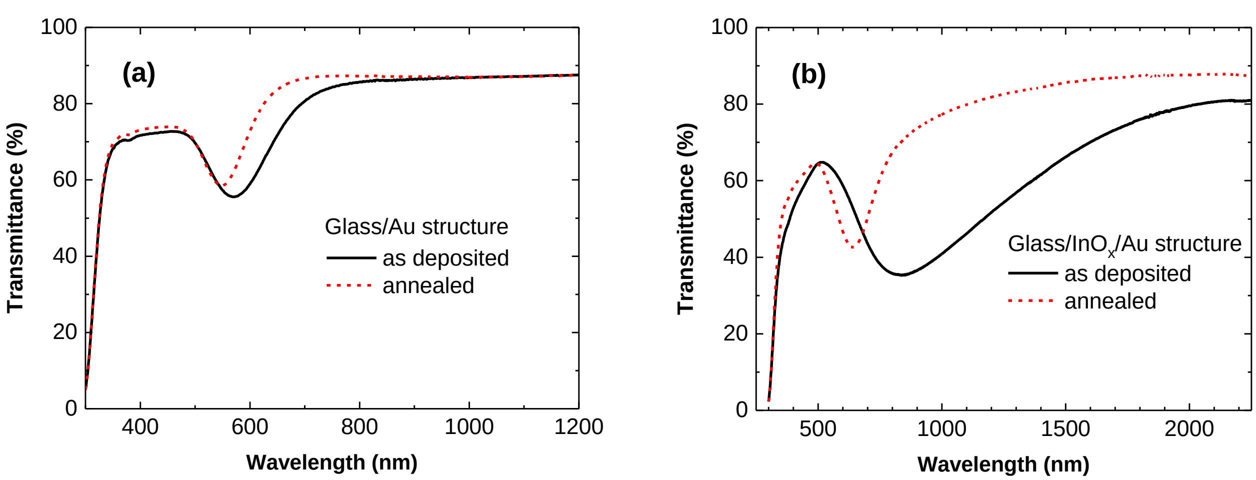

Fig. 2. Transmission spectra of (a) glass/Au and (b) glass/InO_x/Au structures before and after annealing.

In order to evaluate the influence of the underlying discontinuous Au layer on the upper InO_x layer, its structural and electrical properties were studied. Fig. 3 shows grazing-incidence X-ray diffraction patterns of the glass/InO_x and glass/Au/InO_x structures. For these structures, the 100-nm-thick InO_x layer was deposited in the same run at a substrate temperature of 423 K. The data comparison shows that the InO_x layer deposited on bare glass is nanocrystalline with a predominant orientation of (222) crystal plane (curve 1), while InO_x deposited on the glass/Au substrate is amorphous (curve 2). For nanocrystalline InO_x, the average crystallite size is 229 Å by Scherrer's formula. The high-intensity diffraction peak at 38.2° is related to Au crystallization and can be associated to standard Bragg diffraction (111) of face-centered cubic lattice. The suppression of crystalline growth by the discontinuous Au layer is a surprising result. The Au-stimulated crystalline growth of ITO films by sputtering and pulsed laser deposition techniques has been reported in several works[15, 16]. Note that the growth mechanism of plasma-enhanced reactive thermal evaporation is basically different in comparison to the mentioned above techniques. The main difference is that oxidation of In occurs on the film surface and the mobility of indium atoms is crucially dependent on the surface roughness.

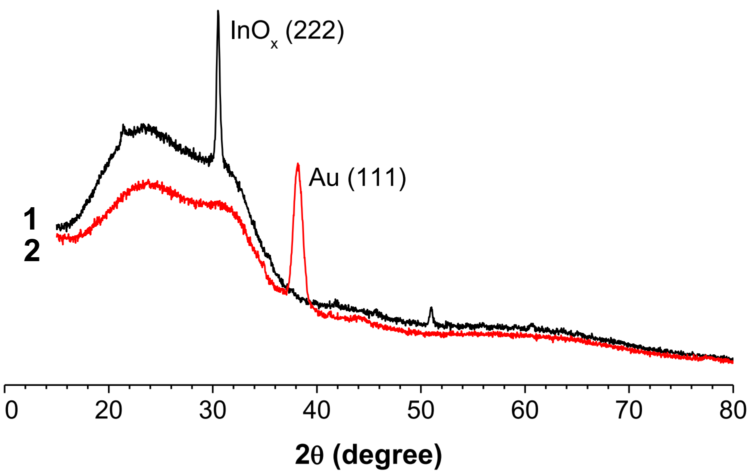

Fig. 3. Grazing-incidence X-ray diffraction measurements for the glass/InO_x (curve 1) and glass/Au/InO_x (curve 2) structures.

The electrical properties of InO_x grown above the Au layer are also distinct from that for a reference glass/InO_x sample. Table 1 summarizes the Hall data for two pairs of samples with different thicknesses of the InO_x layers. The layers were deposited at 423 K. For 53-nm-thick InO_x layers (samples #1 and #2), the resistivity increases by a factor of 5 due to the Au buffer. The related decrease in both the electron mobility and electron density is caused by the Au-induced structural disorder as that reported above. For about twice thicker layers (samples #3 and #4), the resistivity increases by a factor of 4. The difference in the Hall mobility values becomes smaller because the average crystallinity depends on the film thickness.

Table 1. Hall data for InO_x layers deposited on the glass substrates with and without a discontinuous Au layer.

N°	Structure	Thickness, nm	R, Ω/sq	ρ, Ω·cm	n, cm^{-3}	μ, $cm^2V^{-1}s^{-1}$
1	Glass/Au/InO_x	53	348	1.84E-3	2.33E20	14.5
2	Glass/InO_x	53	67	3.54E-4	3.69E20	47.8
3	Glass/Au/InO_x	94	160	1.50E-3	1.89E20	22
4	Glass/InO_x	107	35	3.74E-4	3.68E20	45.4

We have also performed an annealing experiment with a glass/Au/InO_x structure to predict the effect of annealing on multilayered structures. Fig. 4 shows the transmission spectra of the glass/Au/InO_x structure before and after 1-hour annealing at 673 K. It results in the minor changes in the spectrum: (i) λ_{min} shifts from 677 to 668 nm; (ii) the transmittance decreases by about 2% at $\lambda > 1$ μm. It can be concluded that the top InO_x layer prevents structural modifications of the underlying Au layer. Note that the plasmon resonance wavelength of the hybrid structure is red-shifted in comparison to λ_{min} = 585 nm for the reference glass/Au sample due to the increase in the refractive index of the medium[17].

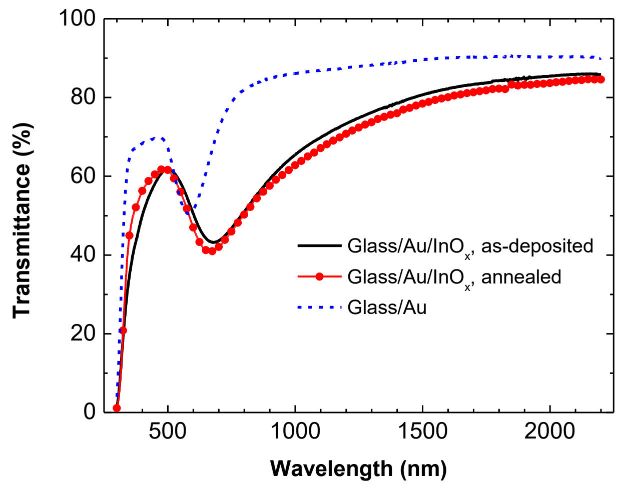

Fig. 4. Transmission spectra of the glass/Au/InO_x structure before and after annealing. The spectrum of the glass/Au substrate is also shown.

Hybrid electrodes were prepared by consecutive deposition of Au and InO_x layers with an oxide layer thickness of 60 nm. Four device configurations were fabricated: (i) glass/InO_x/Au/InO_x/Au; (ii) glass/InO_x/Au/InO_x/Au/InO_x; (iii) glass/Au/InOx/Au; (iv) glass/Au/InO_x/Au/InO_x. Electrodes I and II were fabricated skipping the Au nanostructuring step. The transmission spectra of the electrodes are shown in Fig. 5. The multilayer structures exhibit a transmittance maximum of 50-55% in the green that is about 15% less than that for the structures with a single gold layer (see Fig. 2 and 4). However, the transmittance minimum is much lower, about 20%, resulting in a steeper curve slope between the min and max points. For electrodes I and II, the 25 nm red-shift is observed in this wavelength interval that is a response to the refractive index increase by the top InO_x layer (Fig. 5a). About the same red-shift of λ_{min} is observed for electrodes III and IV (Fig. 5b). The electrodes with demonstrated plasmonic properties are attractive for bio-sensing applications. For instance, a simple biosensor can be realized by integrating the hybrid electrode with a photodiode and using an LED as a quasi-monochromatic light source.

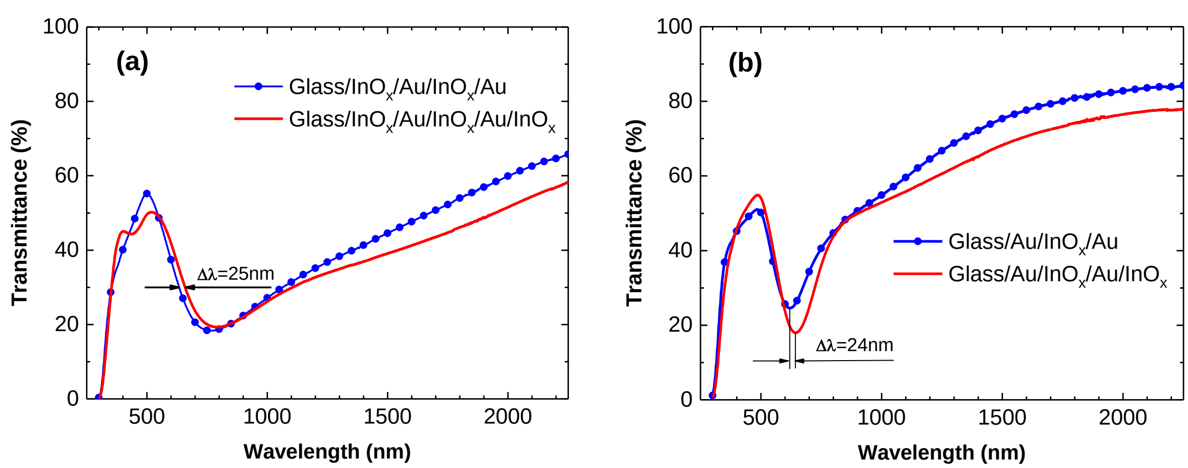

Fig. 5. Transmission spectra of multilayered structures with (a) unannealed and (b) annealed Au layers.

4. CONCLUSIONS

In this work, we have proposed simple and low-cost methodologies to produce the InO_x-based electrodes with nanostructured Au layers. The electrodes of various configurations have been fabricated using the rf-PERTE and thermal evaporation techniques. The morphological and structural properties of Au and InO_x layers were determined using AFM, XRD, and SEM techniques and correlated with deposition conditions and post-treatment. The effect of substrate material on the surface morphology and optical properties of gold films was also studied by comparing the results for bare glass and InO_x-coated glass substrates. Although Au layers grown on bare glass or InO_x surfaces are quasi-continues, their plasmonic properties can be enhanced by 15 min annealing at 573K due to the formation of 30-40 nm particles. We also observed a difference in structural properties of InO_x films deposited on glass and glass/Au substrates. The underlying Au layer effectively suppresses the crystalline growth of InO_x leading to a deterioration in the electrical properties of the oxide layer. The optical characterization of hybrid electrodes with two embedded discontinues Au layers show their suitability for plasmonic sensing devices.

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