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Ordered Titanium Dioxide Nanotubes for Lossy-mode Resonance-based Humidity Sensing

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Abstract: Ordered titanium dioxide nanotubes on indium tin oxide as a structure supporting lossy-mode resonance is reported. Capability for application of the structure for optical humidity sensing is shown as an application example. © 2022 The Author(s)

1. Introduction

A consecutive growth of interest in optical sensor applications in different industrial and scientific areas has been recently observed. Many novel, high accurate optical sensing platforms are based on recent achievements in nanotechnology, where thin coatings are widely studied [1]. A lossy-mode resonance (LMR) is a phenomenon possible to be obtained thanks to highly controlled nanotechnological procedures, i.e., it can be obtained when certain conditions concerning optical properties of thin film, substrate and external medium, as well as thickness of the film are reached [2]. The LMR sensors, including those based on optical fibers, have been explored for application in chemical or biomedical sensing, in particular label-free biosensing, due to sensitivity to changes in optical properties of the external medium [3]. As this medium in case of label-free biosensing is mainly considered a selectively formed biological layer on the sensor surface coming from water-based solutions [4]. A trend towards miniaturizing sensing devices induces limitation in sensor surface area available for interactions with a biological matter. Thus, technologies offering enlarged sensor surface area, but maintaining small sensor size, are highly expected for high performance sensors [5]. A number of materials offering complex morphology at a nanoscale such as nanowires, nanorods or nanoholes have been reported [6,7]. The nanomaterials are often explored with sensors based on surface plasmon resonance (SPR) effects, where the plasmons are often localized (LSPR) [7]. Unlikely the SPR, LMR can be excited for a wide gamut of materials and exhibits only small mode polarization dependence on observed spectra [8].

In this work we propose a new material solution with enlarged surface area for the LMR sensing applications. The material has been achieved by well-controlled anodization of titanium (Ti) thin film deposited on indium tin oxide (ITO). Anodization technique enables repeatable formation of ordered structure that is crucial for application of proposed strategy at a large technological scale. The process, together with post-processing, results in a development of an advanced geometry of a porous titanium dioxide (titania, TiO_2) ordered at nanoscale. Among different morphology forms of such thin layers or nanoparticles, titania nanotubes attract lot of attention due to large area-to-volume-ratio as well as capability for providing optimal pathways for electron percolation [9]. In other work nanorods on the fiber core have been obtained to increase sensitivity, but at the same time can affect sensor rigidness and thus limit applicability of the device or choice of the platform to be coated [10,11]. We have found that for the nanostructured TiO_2/ITO deposited on silica glass it was possible to observe LMR. Due to enlarged surface area the possibilities of LMR-based sensors can be greatly enhanced [12]. To verify performance of the TiO_2/ITO-based sensor its response to changes in humidity has been studied and compared to results obtained in the same sensing configuration, but using non-nanostructured materials [13].

2. Methodology

2.1. Thin film structure fabrication

To obtain the LMR effect, microscopic slides were first coated with 100 nm of ITO. Magnetron sputtering in a high vacuum chamber with a base pressure of 10^{-5} Pa was used. The process parameters have been like those reported in [4] - optimized to obtain both high electrical conductivity and optical transparency of the material. The plasma discharge during the process was sustained by an RF generator with a frequency of 13.56 MHz and forward power of 150 W. Magnetron operated in Ar atmosphere with a pressure of 0.1 Pa. After the deposition processes, the substrates were annealed at 500 °C for 60 min. Next, on the ITO-coated substrates was deposited thin TiO_2 and thicker Ti suitable for the anodization process. First, with DC magnetron sputtering of Ti in Ar and O_2 atmosphere with a pressure of 0.5 Pa and power of 250 W, a thin, 5 nm of TiO_2 interlayer was deposited on the ITO for enhanced adhesion of Ti. Afterwards, O_2 delivery was stopped and with the same process parameters the deposition continued to obtain Ti thickness of around 1000 nm.

2.2. Ti anodization towards TiO_2 nanotubes

Substrates coated with ITO, TiO_2 and Ti were installed in a thermostatic reactor for anodization. Substrates were connected to power supply as an anode and a platinum mesh served as a cathode (Fig. 1). The reactor was filled with electrolyte containing fluorine ions (F^-) based on solution of 0.27 M NH_4F and 1 M H_3PO_4 in volume of 5% H_2O and 95% of ethylene glycol. Anodization process was held at 23°C with 60 V potential applied for 180 min.

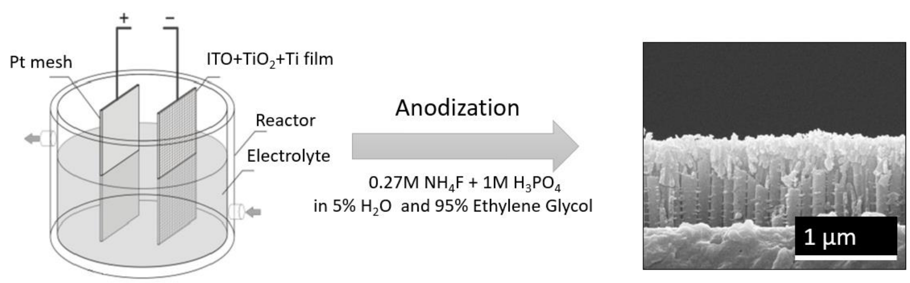

Fig 1. Schematic representation of the anodization process and SEM image (sied view) of the obtained TiO_2 nanotubes.

Through the anodization process the TiO_2 structures grow out of the Ti layer. During this process three reactions occur in electric field, i.e., oxidation of Ti layer to TiO_2, etching of the oxide layer and dissolution of TiO_2 by fluorine ions producing TiF_6^{2-} complexes. Those reactions compete, however in optimal conditions tubular nanostructures are formed. The geometry during anodization can be controlled by process parameters such as type of electrolyte, voltage, time, stirring speed, as well as temperature. In this work parameters were optimized to receive a thin-walled nanotubes array.

2.3. Optical measurements

The LMR effect occurs in a certain wavelength range where coupling occurs between lossy-modes guided in a thin film and modes in a waveguide. Optical measurement of the sensor, as a transmission spectrum, was monitored in the wavelength range of 400-1700 nm using a broadband light source and a spectrometer (Fig. 2). In the setup the coated glass slide was put between two multimode fibers and coupled with them via free-space coupling as described in [13].

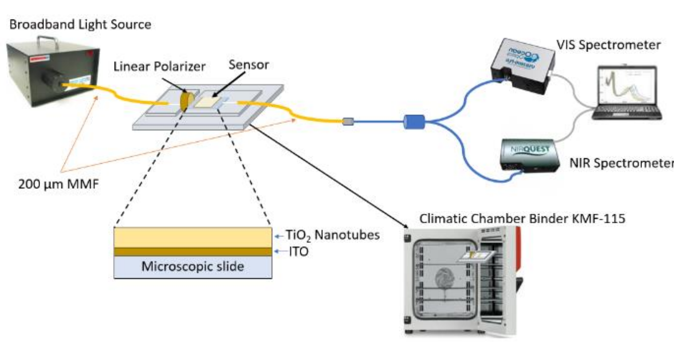

Fig. 2. Schematic representation of an optical setup used in this experiment.

3. Results and discussion

Before the anodization, prepared titanium films on ITO covered glass were inspected using SEM to verify if the materials are suitable to successfully performing of the process. Satisfactory quality of the thin film samples is shown in Fig. 3(A). Next, morphology of anodized substrates was inspected too and an example of the obtained images is shown in Fig. 3(B). Uniform formation of titania nanotubes on the whole processed area is observed. Additionally, no cracks or large debris are visible which is crucial for further optical measurements. The performed studies have proven that the density of the nanotubes can be controlled with the electrolyte type, as well as applied voltage and the temperature.

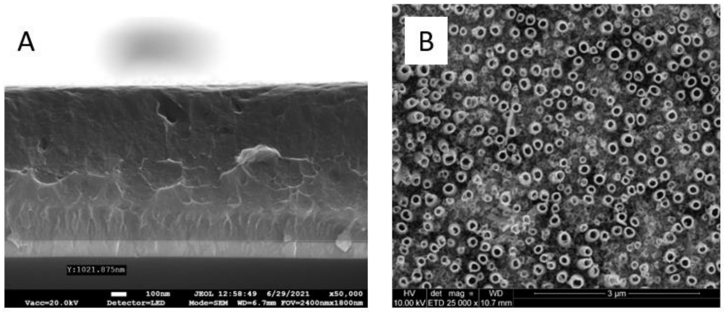

Fig 3. (A) SEM image (side view) of the Ti/ITO thin-film-structure before the anodization and (B) top view of the nanostructure obtained after the anodization. In (B) the tubular morphology after anodization is clearly observed.

It is known that the ITO-LMR sensors are capable of quantitative measurements of RI changes in a surrounding medium. With grown of of the TiO_2 nanotubes the RI of the structure is effectively lowered when referring to solid TiO_2, due to air-filled pores in the structure. However, the nanostructure doesn't limit obtaining the LMR effect. First, a sensor was interrogated in a room conditions while exposed to the air (Fig. 4(A) & 4(B)). Measurement was made for a TE light polarization, achieved with linear polarizer placed at the sensor's input. It must be noted that the LMRs are clearly visible despite relative thick layer of nanotubes grew on top of ITO. In visible spectral range a few minima are observed, and some more can be registered in NIR range. One of these well-seen in NIR was further analyzed as a response to humidity variations. A series of measurements in climate chamber was performed in 4 cycles of changing humidity ranging from 30% up to 90%, changed in steps with a difference of 20% each. Simultaneous control measurements with built-in climate chamber humidity sensor were registered and compared to the optical sensor (Fig. 4(C)). For humidity measurements each step is clearly observed while tracing the wavelengths corresponding to the LMR minimum (observed in air at 1115 nm). The sensor has shown an overall 45 nm shift across humidity change from 30 to 90%. Relative humidity (RH) changes for each 20% increment were 5, 10 and 30 nm. Those shifts translate to sensitivity reaching 0.25, 0.5 and 1.5 nm/RH% respectively. Readouts were stable and fully reversible during each cycle of increasing and decreasing humidity. Measured sensitivities are roundly 3 times higher when compared to previously reported similar LMR sensor, but based on a single solid film [13]. Complex morphology surely increases the area available for interactions with an external medium, what results in increased sensitivity.

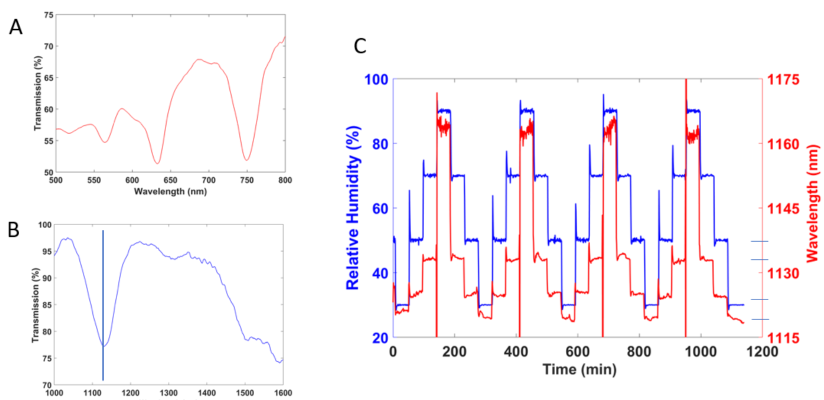

Fig. 4. (A) TE mode transmission spectrum of the sensor in visible range and (B) in NIR range with highlighted LMR minimum considered further for humidity sensing. (C) Sensogram showing shift of the LMR wavelength with humidity change (red) and control readout of built-in chamber sensor (blue).

4. Conclusions

In this work we have introduced a new material, i.e., ordered titanium dioxide nanotubes, to the sensors based on the lossy-mode resonance (LMR) effect. The material was obtained by well-controlled anodization of a relatively thick (1 µm) titanium layer deposited on indium tin oxide. All the materials were deposited using magnetron sputtering. Despite achieved nanoporous structure, the material can be effectively used in LMR devices. The surface area of the material is highly enhanced comparing to application of solid materials. As proven in this work, the LMR effect can be traced for planar waveguides and applied for humidity sensing. Comparing to alternative sensing devices based on solid materials [13], the ordered titanium dioxide nanotubes may offer roundly 3 times higher sensitivity. We perceive the material fabrication technology to be fully transferable to a smaller planar or cylindrical platform, such as e.g., gratings or D-shape fibers, for obtaining other highly sensitive devices. Both the deposition and the anodization processes can be upscaled towards mass production of the material, with a high control over properties of the nanotubes, such as density, wall thickness or size. We believe that the material can find many other s ensing applications, including the biosensing.

5. Acknowledgments

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