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Indium Tin Oxide Synthesized by a Low Cost Route as SEGFET pH Sensor

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Polycrystalline ITO films with good optoelectronics characteristics and homogeneous surface has been obtained upon annealing at 550 °C in N^2 atmosphere using a low-cost chemical vapor deposition (CVD) system. The films were evaluated as pH sensors in separative extended gate field-effect transistor (SEGFET) apparatus, exhibiting a sensitivity of 53 mV/pH, close to the expected Nernstian theoretical value for ion sensitive materials. The use of CVD process to synthesize ITO, as described here, may represent an alternative for fabrication of SEGFET pH sensors at low cost to be used in disposable biosensors since H^+ ions are the product of several oxireductase enzymes.

Keywords: *ITO, CVD, pH sensor, field-effect transistor*

1. Introduction

Indium tin oxide (ITO) has emerged as important engineering materials, since their versatile optical and electronic properties have found application in many fields including optoelectronics and photonics[1]. ITO semiconductors show high transmission in the visible region, high reflectance in the infrared and high electrical conductivity. Due to the latter properties, ITO has been used as optically transparent conducting electrode in a range of applications[2-4]. Recently, ITO films have been used as work electrode in the development of bioengineering devices such as ion sensors and biosensors[5-7]. The emerging sensor and biosensor technology based on ITO films has emerged as an advantageous alternative for applications in medicine[8,9].

ITO can also be applied to detect H^+ ions. In this case, two types of electronic devices can be used to pH sensing: a conventional ion sensitive field-effect transistor (ISFET)[10] and a separative extended gate FET[11,12]. ISFET comprises a metal oxide semiconductor field-effect transistor (MOSFET) without gate metallization, being its insulator gate in direct contact with the solution[10], whereas a SEGFET comprises a chemically sensitive membrane as separative extended gate (SEG) connecting to the gate of a commercial MOSFET[11,12]. The latter configuration is advantageous for sensing, since the sensor is isolated from the chemical environment and can be reused.

Synthesis of ITO has been carried out by several methods, including RF magnetron sputtering[13], electron[14] or ion beam evaporation[15], pulsed laser ablation[16], sol-gel process[17] and chemical vapor deposition (CVD)[18,19]. The relative simplicity and low-cost of ITO films synthesized by CVD have made this technique technologically advantageous.

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This paper reports on the synthesis and characterization of ITO films to be applied as pH sensor in a SEGFET configuration using the inexpensive CVD technique at very low-cost effective procedure. Measurements of the drain current (I_D) as function of the drain to source voltage (V_{DS}) or as function of the gate to source voltage (V_{GS}) were used to characterize the ITO films as SEGFET pH sensor.

2. Experimental

2.1. *ITO synthesis and characterization*

ITO films were deposited on glass substrates (Corning 7059) using a commercial atomizer (HuaYi Sprayer) according to the literature[18]. A methanol solution (0.1 M) of indium chloride ($InCl_3$. 3.5 H_2O, 99.99%, Merck) and tin chloride ($SnCl_4$. 2 H_2O, 99.99%, Merck) was prepared with 5 wt% of Sn concentration. Substrate temperature was fixed in 300 C and the solution was sprayed manually on glass substrates. After deposition, ITO films were thermally treated at 550 C in N_2 atmosphere for 1 hour. Film thickness can be controlled by the amount of sprayed solution.

Surface morphology and thickness of ITO films were examined using a scanning electron microscope (SEM, model: Phillips XL 30) set at an operating voltage of 20.0 kV. The optical transmission of the ITO films on the glass substrates were measured using a spectrophotometer (UV-Vis, Varian 634) in the wavelength range of 300 to 800 nm. The study of crystalline ITO films phases were investigated by the X-ray diffraction technique (XRD) (D/MAX-200). The X-ray patterns were taken from monochromatic CuK radiation source (λ = 1.5418 Å). Film resistivity was measured using the van der Pauw method[20].

2.2. *ITO as pH sensor: measurement system*

SEGFET configuration comprises two parts[11,12]: the chemically sensitive membrane, formed by the ITO film (contact area of 35 mm^2) connected to the gate terminal of a commercial MOSFET (CD4007UB) with its gate replaced by a reference electrode of silver/silver chloride (Ag/AgCl/ Sat. KCl). A programmable curve tracer (Tektronix-370A) was used to record the data. Measurements of the drain current (I_D) as function of the variable voltages (V_{DS} or V_{GS}) in different pH buffer solutions (5 min after immersion) were carried out to determine the pH sensitivity of the ITO films. Figure 1 shows the scheme of the SEGFET measurement system.

3. Results and Discussion

ITO films with thickness about 200 nm (estimated by profilometry) and resistivity in the order of 10^{-4} W.cm (measured using the van der Pauw method)[20] was deposited on glass substrate by CVD. In the case of ITO conducting thin film, indium oxide (In_2O_3) based material have been doped with Sn to improve the electrical conductivity. Sn acts as an n-dopant material in the In_2O_3 lattice, in substitution to indium atoms, since In has valence 3^+ and Sn has valence 4^+, thus adding electrons in the conduction band. Furthermore, oxygen vacancies can donor two electrons, *i.e.*, both oxygen vacancies and the donor atoms (Sn) contribute to improve ITO conductivity[1,21].

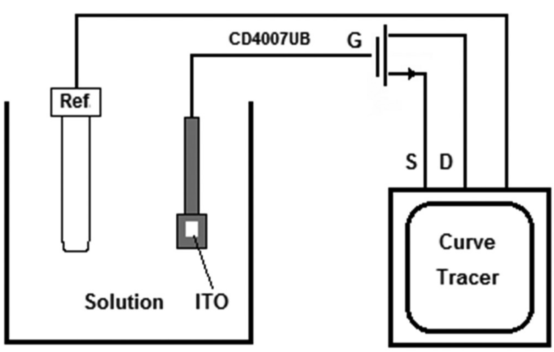

Figure 1. Scheme of the SEGFET architecture and the measurement system.

Figure 2 shows the optical transmission spectrum of the synthesized ITO film. Optical transmittance changes significantly by increasing annealing temperature and reaches a maximum transmission for ITO films thermally treated at 550 °C, in agreement to what has been reported.[22] The optical absorption spectrum (Figure 2, inset) gives an estimated value for the ITO film band gap when an abrupt change in the slope of the absorbance curve is observed[23]. The associated band gap energy of 3.9 eV characterizes the semiconductor properties of the material.

Figure 3 shows the XRD spectrum of the ITO film deposited onto glass substrate (for comparison, the results of In_2O_3 powders are also shown). XRD diffractograms revealed that ITO films become polycrystalline when deposited at higher substrate temperature and crystallize in a cubic bixbyite structure (In_2O_3)[24,25]. The peaks observed for 2θ angle associated to the planes (222) and (400) may be observed. The preferential growth of the ITO films is the (222) plane and this orientation should be dependent on the deposition conditions[25].

Surface morphology of the ITO films deposited onto glass substrates was examined by SEM as shown in Figure 4. After annealing at 550 °C, films with a rough polycrystalline formation with grains and any voids of about 1 μm in diameter were obtained. This represents a large grain misalignment, which is a very crucial requirement in thin film for electronic devices involving oxide materials.

The I_D-V_{DS} characteristics curves of the ITO film as SEGFET pH sensor are shown in Figure 5a. A SEGFET operates similarly to MOSFET except that, for the former, a voltage in the reference electrode (V_{Ref}) replaces the gate-source voltage (V_{GS})[11,12]. The drain current is now a function of pH value, since the potential on ITO surface changes due to concentration of H^+ in the solution. Based on MOSFET equations, in the non-linear region I_D is expressed as:

$$I_D = \frac{1}{2}\beta(V_{GS} - V_T)^2 \quad (1)$$

and in the linear region:

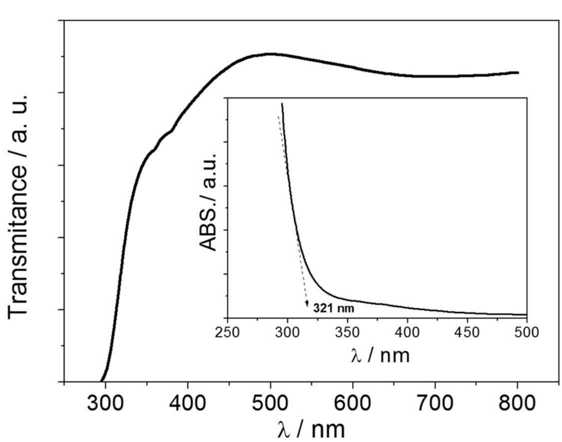

Figure 2. Transmission spectrum of the synthesized ITO film. Inset: Absorption spectrum of the same film.

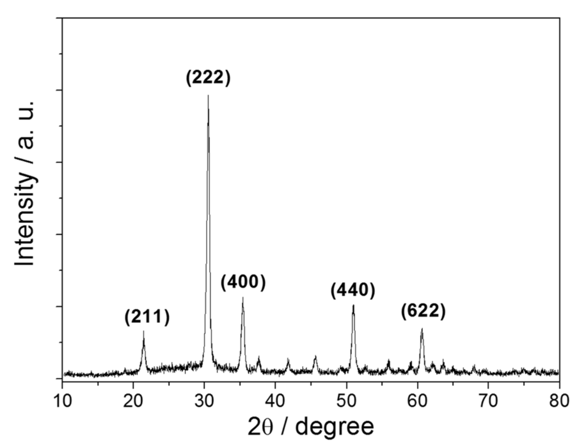

Figure 3. X-ray diffraction of ITO film deposited onto glass substrate. The peaks of the In_2O_3 powders are shown for reference.

$$I_D = \beta\left[(V_{GS} - V_T)V_{DS} - \frac{1}{2}V_{DS}^2\right] \quad (2)$$

where β is a conduction parameter, V_{DS} is the drain - source voltage, and V_T the threshold voltage, *i.e.* is defined as the minimum voltage required to make the transistor ON, which is dependent on the pH value[11,12]. Based on equation 1, $I_D^{1/2}$ presents a linear pH response and can be expressed as a function of pH value, as seen in Figure 5b.

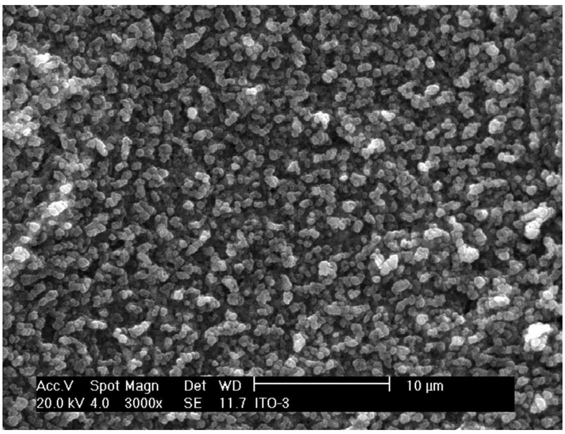

Figure 4. SEM image of the synthesized ITO film.

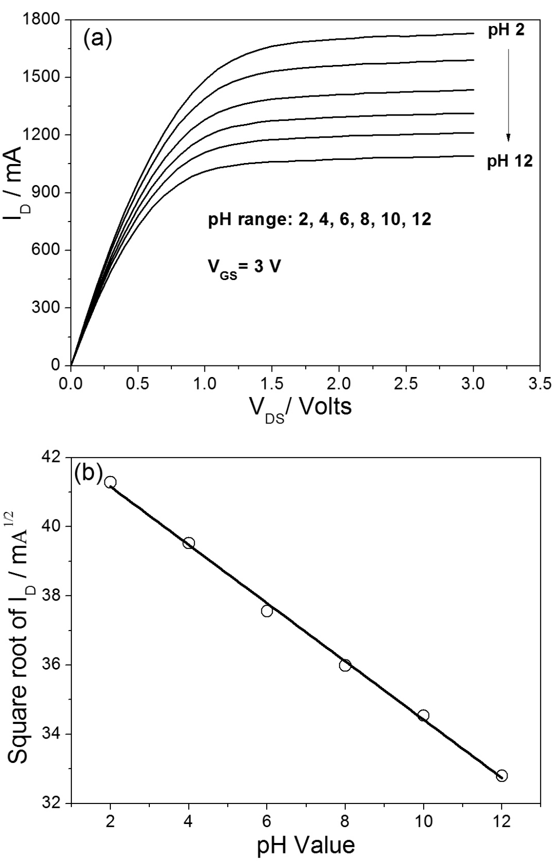

Figure 5. I_D-V_{DS} characteristics for constant V_{GS} of the ITO film as separative extend gate-FET in the pH range from 2 to 12: (a) I_D-V_{DS} characteristics, and (b) square root of I_D.

Figure 6a shows the corresponding I_D-V_{GS} characteristics curves of the ITO as SEGFET pH sensor. As shown in Figure 6b, a linear response of V_{GS} in the pH range of 2-12 may be observed. The sensitivities of the ITO SEGFET was calculated from the slope in the Figure 6b for fixed I_D = 200 µA. ITO films presented a sensitivity about 53 mV/pH unity, close to the expected Nernstian theoretical value (59,15 mV/pH)[26] to pH sensors and in and in good agreement with commercial ITO films pH sensors[5], which presented 58 mV/pH of sensitivity[5]. Comparing with other synthetized ITO films, a sensitivity of 50 mV/pH was found by Lue et al.[27] using ITO deposited on flexible polyethylene terephthalate (PET) by RF sputtering[27]. ITO films fabricated via anodic oxidation exhibited a sensitivity of ca. 54 mV/pH in a pH range from 2 to 12[28]. Therefore, our results indicate that the CVD technique is an alternative route to construct pH-sensitive materials in a simple and low-cost way. In the other words, the results indicate that active sites in ITO films are involved in the formation of a charged double layer with the distribution of the potential between the film and the glass surface.

The ITO sensitivity may be explained by the well-known site-binding model theory[29]. According to this theory, three sites can be found on ITO surface, *viz.*, negatively charged ITO^- groups, neutral ITOH groups and positively charged

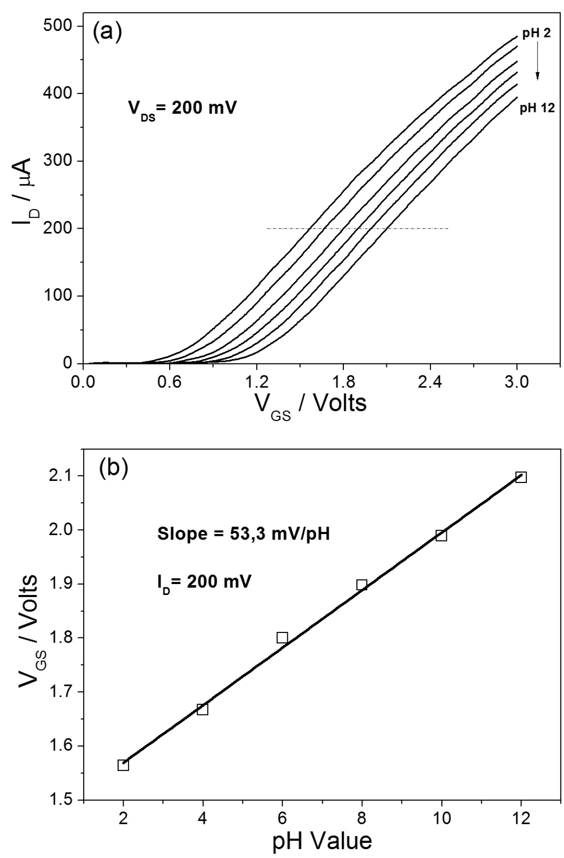

Figure 6. I_D-V_{GS} characteristics for constant V_{DS} of the ITO film as separative extend gate-FET in the pH range from 2 to 12: (a) I_D-V_{GS} characteristics, and (b) sensitivity calculated when I_D was fixed in 200 µA.

ITOH⁺ groups. The total surface charge can be altered by complex formation on ITO surface. Upon changing electrolyte pH, a change in the protons concentration occurs at ITO surface, modulating the drain-source current in the SEGFET device.

4. Conclusions

This study presented the ITO film deposited on glass substrates by low cost CVD spray system. Homogeneous ITO films with low resistivity and high optical transmittance were obtained. The pH sensing characteristics of the films were also analyzed using a SEGFET configuration. ITO films presented a Nerstian pH response sensitivity of ca. 53 mV/pH. The use of CVD process in junction with SEGFET configuration represents a low cost alternative and appears to be beneficial for real applications in the fabrication of membranes for pH sensors and as a sensitive substrate for biosensors since H^+ is the product of several oxireductase enzymes.

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