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Thin films of metal oxides for preparing of a position sensitive photodetector

V. Jelev*, P. Petkov, Iv. Markova, T. Petrov

University of Chemical Technology and Metallurgy, Sofia, Bulgaria

Highly transparent and conductive thin films of F-doped SnO_2 (FTO), and Sn-doped In_2O_3 (ITO) have been deposited on glass and silicon substrates, by spray pyrolysis technique. The deposition temperature 450°C and concentration of $InCl_3$ and $SnCl_4$ in the solutions 0.2 M/l. were used. The effects of the thickness on the film resistivity have been investigated. The physical characterization of the films was carried out by UV-VIS spectroscopy, scanning electron microscopy and AFM. The films are polycrystalline, present an optical transmission higher than 95% in the visible light, and resistivity in the range of $10^{-3} \div 10^{-4}\Omega$.cm. The optical and electrical properties of the films make them suitable for applying in a position sensitive structure "Si-SiO_2-metal oxide". Transient lateral photo effects (LPE) in the films deposited on n-type silicon substrate with native SiO_2 have been investigated. Under the nonuniform irradiation of a light beam a lateral photo voltage (LPV) shows high sensitivity to the light spot position in the oxide films plane. LPV as a function of the position of the light spot have been measured. The position characteristic of the structure is symmetric to the zero and linear in a large active area. The structure can be used to detect very small displacements due to its out put of lateral photo voltage changing linearly with light spot position.

Key words: transparent and conductive metal oxide films, SnO_2 and In_2O_3 thin films, spray pyrolysis method, large area position sensitive photodetectors

INTRODUCTION

Thin films of SnO_2 doped with F (FTO) an In_2O_3 doped with Sn (ITO) are being widely studied during recent years, due to their unique optical, electrical and mechanical properties [1–3]. Because of their high optical transparency in visible region low electrical resistivity and high reflectivity in infrared region of the spectrum [4,5] these films are suitable for various applications: as transparent electrodes in various display devices [6], antireflection coatings for solar cells and heat mirrors [7], hetero-junction solar cells [8], photodiodes [9] and so on.

In the recent times various techniques have been developed for preparation of ITO and FTO thin films with high transmittance and high conductivity such as flash evaporation [10], electron beam evaporation [11], magnetron sputtering [12], chemical vapour deposition [13], sol-gel process [14], spray-pyrolysis [15, 16]. Chemical spray-pyrolysis has advantages among these methods because of the possibilities to obtain large area uniform coatings without high vacuum ambience [17].

The aim of this study was to obtain uniform large area thin FTO and ITO films on a mono-crystal silicon substrate by the method of spray-pyrolysis and to investigate the possibility to prepare of a two dimensional position sensitive photodetector with a Si-SiOx-ITO (FTO) structure.

* To whom all correspondence should be sent:
kazeus@abv.bg

EXPERIMENTAL DETAILS

The chemical reactions that provide thin film formation are:

$$2InCl_3 + 3H_2O \leftrightarrow In_2O_3 + 6HCl \quad (1)$$

$$SnCl_4 + 2H_2O \leftrightarrow SnO_2 + 4HCl \quad (2)$$

The doped In_2O_3 films were deposited by spraying an alcoholic O.25M solution of $InCl_3$ and $SnCl_4$ (as a source of tin dopant) onto the substrates heated at 420-480°C. The films of SnO_2 were obtained from alcoholic O.25M solution of $SnCl_4$ consisting HF as a F dopant at 380–460°C. Monocrystal n-Si (111) plates with resistivity 6–9 Ω.cm and Corning glass were used as substrates. The atomization of the solution was carried out with a sprayer using as Carrier gas argon. The film thickness was measured by the weight method and estimated by a color scale during the process. The measurements of the electrical resistivity were carried out at room temperature using the standard four-probe method. Silver pasted leads were used as a contact to the films. The morphology and microstructure of the films were examined with Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). A spectrophotometer SIMADZU-UV 3600 (300-1800nm) was used to study the transmission spectra of the films deposited onto the glass substrates.

RESULTS AND DISCUSSION

The electrical and optical properties of the films depend on the technological parameters: the substrate temperature, the spraying rate, the angle of spraying, the distance between the nozzle and the substrates, and the quantity of impurity in the spraying solution, which in turn influence on the microstructure, stoichiometry and physical parameters of the layers. The best results (lowest resistivity and highest transparency in the visible spectrum) were obtained at Ts = 450°C (for In_2O_3 films) and 430°C for SnO_2 films, the spraying angle 45°, spraying rate 0,08 $cm^3.s^{-1}$. Under this technological conditions the influence of film thickness on the electrical resistivity was examined. The sheet resistance (Rs) of the films decreases with increase in thickness/deposition time (Fig. 1).

The lowest Rs were reached in the range of the thickness 150–300 nm. As the thickness of the films was uniform, the resistivity ρ of the films can be calculated from the equation $\rho = Rs.d$, where d is the film's thickness. A low resistivity was measured for the 200-250 nm thick ITO films in the range of $3.10^{-4} - 7.10^{-4}$ Ω.cm and for 250–300 nm thick FTO films – $2.5.10^{-4} - 5.10^{-4}$ Ω.cm respectively.

The In_2O_3: Sn and SnO_2: F films deposited on a glass substrate were investigated concerning the optical transmission by spectro-photometrical method in UV, VIS spectral ranges (300–1800 nm). The transmission characteristics are presented in Fig. 2.

A high transparency (over 95%) can be seen in the VIS spectral ranges for the two kinds of the films.

The SEM and AFM were used to characterize the surface morphology. The SEM and AFM images of all samples displayed a homogeneous surface with small crystallite size (granular structure) (Fig. 3).

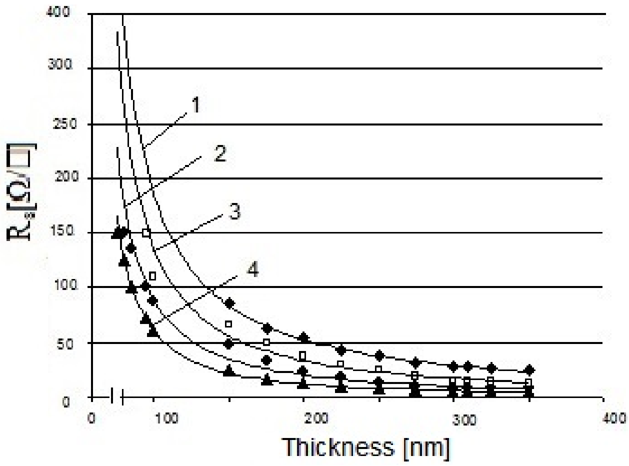

Fig. 1. The sheet electrical resistance (Rs) of the films as a function of the film's thickness: (1) pure In_2O_3 film; (2) doped In_2O_3; (3) pure SnO_2; (4) doped SnO_2.

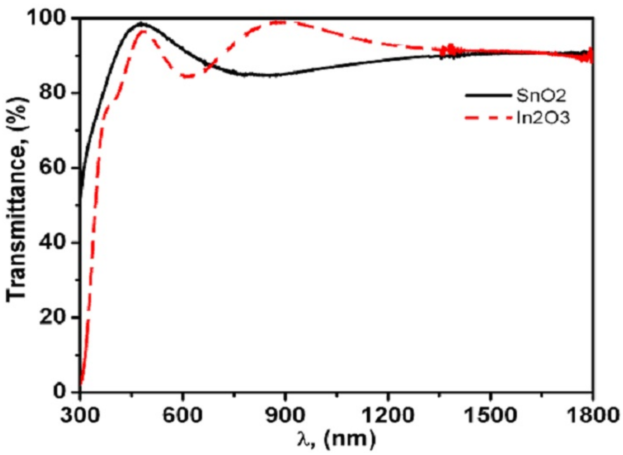

Fig. 2. Optical transmittance of doped SnO_2 and In_2O_3 films on a glass substrate with thickness 200 nm at 450°C.

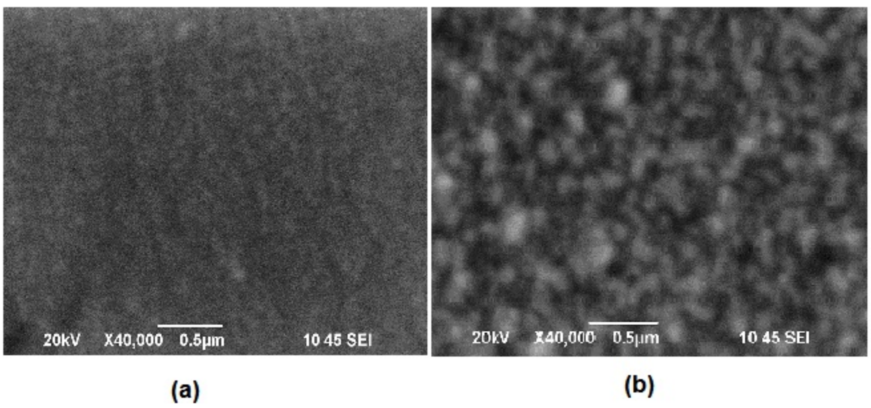

Fig. 3. SEM image of the surface of In_2O_3 (a) and SnO_2 (b) obtained at a magnification 40000.

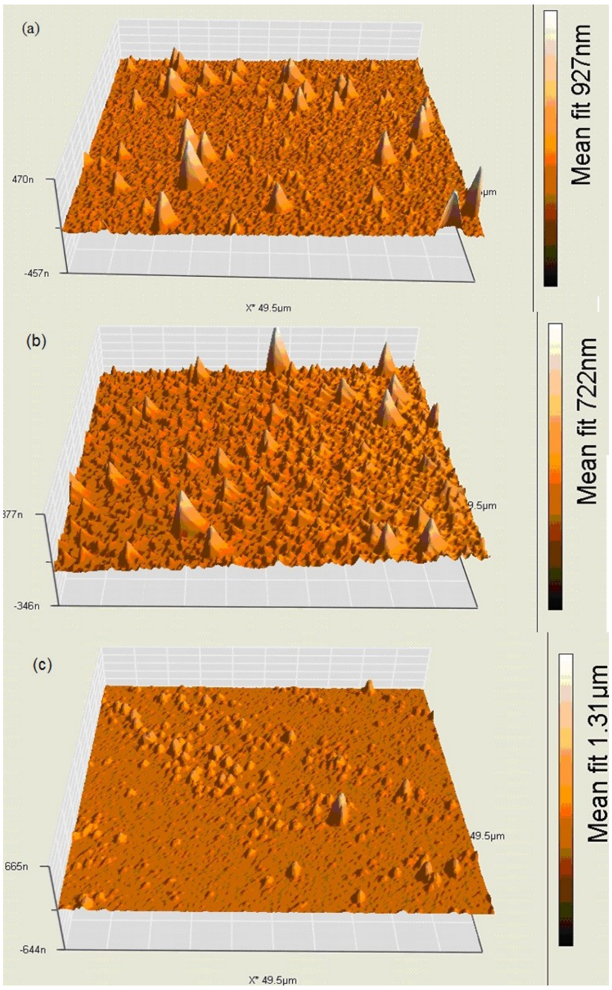

Fig. 4. 3D image of the topography of the layers of In_2O_3 with a thickness: 163 nm (a), 210nm (b) and 300nm (c).

The particles are close together without any pores separating them. The grain size and the roughness of the SnO_2 films are bigger than that of In_2O_3.

The AFM surface morphology of ITO films with different thickness is shown in Fig. 4 (a–c).

Whit increasing the thickness of the layers the grain size increase and the surface became more uniformity.

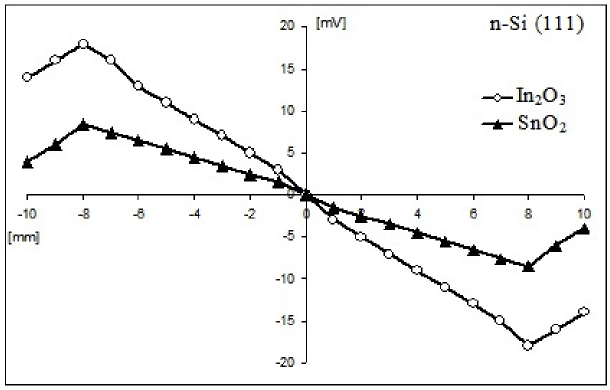

Fig. 6. Position characteristics of the two types of structures.

The films have a very smooth surface, which is beneficial for their application in optoelectronic devices with transparent conducting layers.

In this work we used the films deposited onto silicon substrate with a thin 2 nm native SiO_2, to prepare a structure Si-SiO_2-ITO or FTO, which works on the base of the lateral photovoltaic effect (LPE) (Fig. 5 a, b).

This structure detects very small displacements due to its output of lateral photovoltage changing linearly with light spot position, over the metal oxide plane, between two Ag contacts.

The contacts distance was 40 mm.

All samples were scanned with a light spot with diameter 0.5mm and the resulting photovoltage was measured using standard lock-in techniques.

The LPV measurements of the structure show good linear characteristics with LPV sensitivities (Fig. 6)

LPV is the largest when the incident radiation spot is closest to the electrodes and shows linear decrease as the spot is scanned away from the contacts, becoming zero at the midpoint of these two contacts.

LPV sensitivities are about 20 mV/mm for the structure with In_2O_3 film and 8 mV/mm with SnO_2 film. The results show that Si/ITO structures have bet-

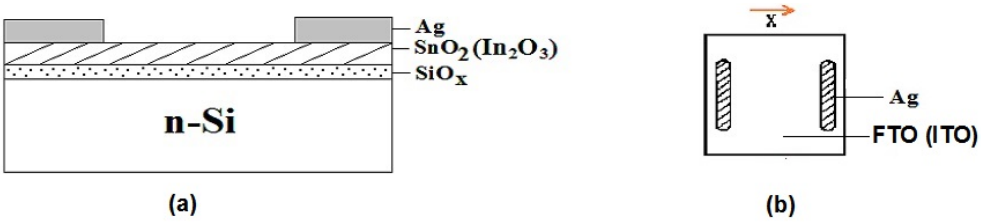

Fig. 5. Schematic view of a two dimensional position sensitive photodetector: (a) cross section, (b) over view.

ter LPV sensitivities than Si/FTO, which relates with the properties of the oxide materials.

CONCLUSION

The results demonstrate the availability of the as examined metal oxide thin films for optoelectronic device applications and especially for preparing position sensitive sensors.

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ТЪНКИ СЛОЕВЕ ОТ МЕТАЛНИ ОКСИДИ ЗА ПОЛУЧАВАНЕ НА ПОЗИЦИОННО ЧУВСТВИТЕЛЕН ФОТОДЕТЕКТОР

В. Желев, Пл. Петков, Ив. Маркова, Т. Петров

Химикотехнологичен и металургичен университет, бул. "Св. Кл. Охридски" №8, София, България

(Резюме)

Получени са прозрачни проводящи слоеве легирани с флуор (F) SnO_2 (FTO) и легирани с калай (Sn) In_2O_3 (ITO) чрез пулверизиране на 0.2 M алкохоло-водни разтвори на In_2Cl_3 и $SnCl_4$ върху нагряти при 450°C подложки от стъкло и монокристален силиций. Изследвана е зависимостта на електричното съпротивление на слоевете от дебелината им.

Оптичните свойства са охарактеризирани с UV-VIS, микроструктурата и морфологията на повърхността - със сканираща електронна микроскопия (СЕМ) и AFM. Слоевете са поликристални, с високо оптично пропускане (над 95%) във видимата област и специфично съпротивление в диапазона $10^{-3} \div 10^{-4}$ Ω.cm. Отлагането на слоеве с високи прозрачност и проводимост върху окислени силициеви подложки, дава възможност да бъдат изготвени позиционно чувствителни структури от типа Si-SiO_2 – метален оксид, действащи на основата на латерален фотоефект.

Снети са позиционните характеристики на структурите. Те притежават висока линейност, стръмност и симетричност. Така създадените структури могат да бъдат използвани за прецизно измерване на линейни и ъглови отмествания.