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A study of morphological, optical and gas sensing properties for pure and Ag doped SnO$_2$ prepared by pulsed laser deposition (PLD)

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Abstract

The pulsed laser deposition method, PLD, has been used in this project to deposit the pure SnO$_2$ and the doped one with Ag at different concentrations (as a thin film) on Si (111) and glass. The aim was to study the influence of doping on surface morphology of the deposits materials using scanning electron microscope (SEM) and atomic force microscope (AFM). The resultant showed that there is a direct relationship between the grain sizes of the nanoparticles observed at the surface and doping concentration which means as the doping concentration increases there will be a similar enhancement in the grain size as well. Additionally, we were able to find that the best concentration of doping at ratio of 3%Ag: SnO$_2$ Similarly, the RMS roughness showed a direct proportion with the doping concentration .It was equal to (11nm) for 3%Ag: SnO$_2$ thin films. Furthermore, we have also investigated the Optical Transmission Spectra of the samples. The characterisations of the gas sensing of these thin films were strongly influenced by the surface morphology. It has been also found that Ag doped nanocrystalline SnO$_2$ gas sensing material was presented a better sensitivity compared to the pure SnO$_2$ and this can be due to the distribution of Ag$_2$O particles in the grain boundaries of nanocrystalline SnO$_2$ and the formation of p–n heterojunction.

Keywords: Pulsed Laser Deposition (PLD), SnO$_2$ thin films and nonstructural.

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1-Introduction

Tin dioxide semiconductor possesses a wide band gap with high chemical stability and excellent optical and electrical properties. It has been widely used for various catalytic applications such as: gas sensing, transparent conducting electrodes and liquid crystal display photocells, detectors, sensors, antireflection coatings...etc. Their properties depend on their microstructure, the quantity of doped impurities and the size effects of their particles. Nanostructure SnO2 particles have been prepared using different chemical methods such as precipitation, hydrothermal, sol-gel, gel-combustion and spray paralysis [1]. Pulsed Laser Deposition (PLD) technique was successfully applied for growing qualified SnO2 thin films. PLD plays a great roll in reducing the chemical contamination due to: the use of laser light, controlling of the composition of deposited structure, and in situ doping. Moreover, it is a versatile and powerful tool for production of nanoparticles with desired size and composition by only manipulating the deposition conditions. [2] It has been always applied as a gas sensing material to detect combustible, toxic and pollutant gases due to its high sensitivity, simple design and its low cost.

Recently, researches have been focused on improving gas sensitivity in addition to reducing the operating temperature by introducing dopants. [4] Reports showed that Ag deposition on the SnO2 surface can promote the increasing of sensor response in correlation with reducing gases by more than 5-12 times. [5]

We report here the deposition of tin oxide pure and doped by Ag thin film on Si (111) substrate at 400°c with oxygen pressure of (5 ×10⁻¹ mbar) and 1.2 J/cm² laser fluence. We also investigated the influence of the Ag- concentrations on the optical, structural sensing and morphological properties of the films.

2. Experimental details

The deposition was carried out using a Q switched Nd:YAG laser at 532 nm (pulse width 7 nsec and laser fluency 1.2 J/cm²). The studied films were prepared by from pure SnO2 and doped by Ag targets films were grown by pulsed laser deposition on glass substrates kept distance of 4 cm from the SnO2 target. During the deposition process, the oxygen pressure was kept at 5×.10⁻¹ mbar at 400°C temperature. The chamber shown in Fig. (1) The SnO2 disc was ablated from 10-100 pulses (10-20 min) to get single layered thin films.

![Fig. (1): System of Pulsed laser deposition (PLD)](image)
2.1 Film characterization

2.1.1 Target preparation
By using a sensitive balance to weigh a fixed percentage of 0.01 gm (1%) of silver (Ag) and 2.99 gm SnO₂ to get the ratio of 3 gm for the mixture followed by mixing by stirrer device, same instructions are followed for the other ratios (2% and 3%), then compress the mixture under 10 Ton (homemade compressor) to get the final pellet of Tin Oxide powder and tin doped Ag of 2.5 cm diameter and 0.4 cm thickness.

2.1.2 Specimen cleaning
Two different types of substrates, glass and silicon, were used for depositing thin films by laser ablation:

A- Glass substrate
Glass slides each of 3 x 2 cm² area were used as substrates. They were cleaned by alcohol with ultrasonic waves device (produced by Cerry PUL 125) for 15 minutes in order to remove the impurities and residuals from their surfaces.

B- Silicon substrate
Square-shaped silicon samples each of 1 cm² area, p-type conductivity, resistivity of 1.5-4 Ωcm with (111) orientation, were prepared by using a wire-cut machine. The samples were etched with CP4A solution which consists of HNO₃, CH₃COOH, HF of ratios 3:3:5 to remove oxides. They have been cleaned first by alcohol followed by ultrasonic waves (produced by Cerry PUL 125 device) for 15 minutes and finally cleaned by water and then another time for ultrasonic waves for 15 minutes.

2.1.3 Thickness measurements
Film thickness measurements were performed by optical interferometer. This method based on the principle of interference of light beam which has been reflected from thin film surface and substrate bottom. He-Ne laser of wavelength (632.8nm) was employed; thickness was determined by using the formula:

\[ t = \frac{\Delta x}{x} \times \frac{\lambda}{2} \]  \hspace{1cm} (1)

Where \( x \) is fringe width, \( \Delta x \) is the difference in the distance between two fringes and \( \lambda \) is the wavelength of laser light. Film thickness measurements have also been confirmed by using thickness measuring device (TF companion thin-film measurement & analysis C)2001-2009).

2.1.4 Gas sensor properties
A- Electrode Deposition
In order to measure the electrical properties, ohmic contacts are needed. Electrode deposition process was obtained by the deposition of indium wire of high purity (5 nines) under vacuum. The evaporation process was started at pressure of 10⁻³ mbar. The best condition for good ohmic contact was satisfied by a layer sputtering of 250 nm electrode thicknesses which were deposited on one side of two regions of the sensor. Ohmic contact has been achieved by using Al foil on the Si which was employed as a metal mask as shown in fig (2).
B-Gas sensor measurements

The system shown in Fig (3) is used to check the sensitivity of the film for H$_2$S gas. The system (modified) consists of the following parts:

1- A pump (vacuum pump) of type (rotary) manufactured by a company (Edwards) of type (EDM 12), English-made for pressure of $(10^{-2}$ mbar).
2- Connection pipes.
3- Sensors to measure the vacuum (negative pressure) also manufactured by Edwards.
4- A pressure gauge (Edwards, English origin)
5- A chamber manufactured locally with dimensions $(20 \times 20)$ cm, the chamber contains several holes each of which has been for specific purpose as follow: hole (A) is for pump gas discharge, B hole is a glass window and C hole for the power supply.
6- DC Power supply (Dazheng type)
7- Iron holder for gas composition container.
8- Digital multi meter (resistance gauge).

Figure (3) H$_2$S gas sensor set up.
After connecting the electrodes with Ohmic contact, the sample is mounted on the base inside the chamber. Air resistance was measured (without gas), then gas was pumped, at the same time, the resistance change was measured (every 5 seconds). The current versus voltage in both, presence and absence, of gas were recorded in order to determine the impact of gas on film connectivity. The magnitude of sensitivity can be defined as a change in the resistance of the sample during exposure it to the gas. This was expressed by the relation

$$ S = \left| \frac{R_g - R_a}{N R_a} \right| \times 100 \quad \ldots \ldots \ldots \ldots (2) $$

Where $R_g$ and $R_a$ are the resistances of the sample in the presence and in the absence of the gas respectively. Hydrogen sulfide gas of concentration $(6 \pm 3)$ part per million (ppm) was prepared in the laboratory.

The crystalline structure of the films has been determined by using x-ray diffraction (Philips PW 1050 X-ray diffract meter of 1.5°A from Cu-Kα. Additionally, the surface morphology was examined using: Scanning Electron Microscopy (SEM–JEOL 7000), also by Atomic Force Microscopy (AFM) (Digital Instruments Nanoscope II) and Scanning Probe Microscope (AA3000). Optical Transmission spectra of all the films were recorded using a UV-VIS spectrophotometer (Perkin Elemer Company). The gas sensing measurement was achieved. Thin reported films were exposed to 3 ppm H$_2$S gas concentration.

3- Result and discussion

SnO$_2$ films doped with noble metal (Ag) with (1, 2 and 3 wt %) under $5 \times 10^{-4}$ mbar Oxygen pressure, 400 °C substrate temperature and 1.2 J/cm$^2$ laser fluence on Si (111) wafer diffraction peaks located at $2\theta=28^\circ$ corresponding to Silicon substrates were shown in fig (4), no diffraction peaks of Ag or other impurity phases were found in these samples: at 1wt% concentration of the film showed diffraction peaks located at $2\theta=26.8^\circ, 2\theta=34.09^\circ, 2\theta=38.16^\circ, 2\theta=39.16^\circ$, and $2\theta=42.4^\circ$ which correspond to the (110), (101), (200), (111) and (210) peaks respectively. By increasing the doping to 2wt%, film showed diffraction peaks located at $2\theta=26.6^\circ, 2\theta=33.95^\circ, 2\theta=38.02^\circ$, and $2\theta=38.21^\circ$ that correspond to (110), (101), (200) and (111) peaks respectively. Films doped with 3 wt%, diffraction peaks were located at $2\theta=26^\circ, 2\theta=34.1^\circ$ and $2\theta=38^\circ$ that corresponding to the (110), (101) and (200). The peak positions of the plane were shifted to lower $2\theta$ values with increasing the amounts of Ag content. It has been reported that the c-axis bond of Ag doped with SnO$_2$ lattice was as the doping increased. According to that increase in peak intensities were seen which is basically due to the replacement of the Ag ions (122 pm diameter) were substituted into the Sn+ (71 pm) in the lattice of SnO$_2$ film. All XRD patterns of films reflect that the crystal lattice of doped SnO$_2$ did not undergo significant changes. XRD analysis also did not detect the dopant phase, these due to the low concentration of dopants. This result agrees with S. H. Jeong. The XRD analysis showed that the FWHM of SnO$_2$ doping with Ag decreases with increasing the concentration of doping, while the mean grain size were increased as shown in fig (4).
SEM images of the SnO₂ pure and dopant with noble metal for film deposited at fixed substrate temperature of 400 °C, at oxygen pressure of (5 × 10⁻¹ mbar) and 1.2 J/cm² laser fluence as shown in Fig. 5. The SnO₂ pure thin film possesses morphology of homogeneous surface, with a wide size distribution. It has been found that the samples of dopant SnO₂ with noble metal were homogeneously distributed, fine pores in all the coatings. However, the results showed a correlation between grain size and doping concentration. The dispersions of silver clusters on the SnO₂ films were observed by SEM analysis. The images showed white areas in this micrograph (Fig. 5) which refer to the existence of silver while the black area refers to SnO₂. The clusters were well distributed on the SnO₂ surface and quite uniform. 

Fig(4) XRD patterns of SnO₂ films grown on Si Doping with noble metal of Ag a) 1% Ag:SnO₂ b) 2% Ag:SnO₂ c) 3% Ag:SnO₂
Fig. (5): mage of the SnO₂/Si thin films pure and doping (1, 2, 3)% noble metal Ag with substrate temperature 400 °C and laser fluence 1.2 J/cm² with O₂ pressure 5×10⁻¹ mbar where a) SnO₂ pure b) SnO₂:1%Ag c) SnO₂:2%Ag d) SnO₂:3%Ag.

The calculated grain sizes by SEM micrograph are illustrated in table (1).

Table 1: Shows the grain size of the SnO₂ pure and doping with (Ag) noble metal at different concentration deposited at Oxygen pressure 5×10⁻¹ mbar with 400 °C substrate temperature and 1.2 J/cm² laser fluence

| Sample          | Grain size (nm) |
|-----------------|-----------------|
| SnO₂ pure       | 14              |
| SnO₂ :1% Ag     | 18              |
| SnO₂ :2% Ag     | 22.86           |
| SnO₂ :3% Ag     | 26.89           |

The AFM images of SnO₂ /Si films pure and dopant with noble metal sample were presented in Fig. 6. The RMS roughness and the grain size have got correlation with the percentage of the doping concentrations of noble metal (any increment in the in the percentage of doping there will be a relative increase value of the grain size). This consistent with Adawiya J. Haider et al. [8] These samples are very rough with RMS values (4.7, 6.7, 7.3 and 11) for thin films pure and doping with (1, 2 and 3)% respectively.
Fig. (7) shows the spectral optical transmittance for SnO$_2$ pure and doped by (1, 2, 3) % Ag deposited on glass substrate. The transmission of doped SnO$_2$ is found to be decrease and this possibly due to increase of the Ag content. With Ag content increasing, the absorption edge slightly shifted to a longer wavelength region. The decrease of transmittance at doping concentrations may be due to the enhancement of photon scattering by crystal defects which created by doping. The spectral dependence shown in the Fig. (7) reveals two main regions of interest: the fundamental absorption and the interference oscillation region. If the thickness (t) is not uniform or is slightly tapered, all interference effects will be smoothed out in the transmission curve, and the presence of these oscillations in Fig (7) reflects an indication of good optical quality of the films.
Under the same experimental conditions, Results showed an increase in the Ag content to 3 wt% resulted in a decrease in the band gap to about \((3.92-3.78)\) eV, as shown in the fig (8). The decrease of \(E_g\) value can be related to the crystallinity of the thin film. This decrease in energy gap can be due to the prohibited impurities that led to the formation of donor levels within the energy gap near the conduction band. Thus will absorb photons of low energy, this is an agreement with Adawiya. J.Haider el at. [8]
I/V characteristics for undoped SnO₂ and Ag-doped SnO₂ as shown in Fig. (9) with and without exposure of H₂S gas respectively. Both graphs show rising slopes with exposure to the gas for Ag-doped SnO₂ films deposited on silicon substrate at different concentration at Oxygen pressure 5×10⁻¹ mbar and 1.2 J/cm² laser fluence. At fixed substrate temperature (400°C). The figure shows an increase current with increase doping concentration and decrease resistance according to C.H. Liu, L.Zhang et al. Also, it can observe that the values of the current with the gas are more than the values without gas. However, the electron moves from the gas into a material film, causing a resistance of sensors which can be decreased upon exposure to H₂S, which corresponds with the typical n-type semiconducting behavior. The type of the SnO₂ pure and doped thin film is n-type and this indicated by using (Hall effect).

Fig (10) below utilizes the gas sensitivity of SnO₂ pure and Ag doped SnO₂ on silicon substrate at different concentration for the same experimental conditions and 1.2 J/cm² laser increase with increase doping concentration this is an agreement with Jianping Zhang et al. Ag doped nanocrystalline and SnO₂ gas sensing material presents better sensitivity compared to pure SnO₂, due to the distribution of Ag₂O particles in grain boundaries of nanocrystalline SnO₂ and the formation of p–n heterojunction.
4- Conclusions.

The surface morphology of the deposit materials have been studied by using scanning electron microscope and atomic force microscope. RMS roughness increased with increasing doping concentration, the samples are very rough with RMS value of (11 nm) for SnO₂ thin films doped with 3% (Ag). UV-VIS transmittance measurements have shown that our films are highly transparent in the visible wavelength region, with an average transmittance of ~90% which makes them suitable for sensor applications. Dopants such as Ag shifted the absorption edge of SnO₂ into the visible region. The sensitivity toward H₂S gas has been measured under 3 ppm concentrations. SnO₂ doped with noble metal has sensitivity higher than pure SnO₂.

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