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RESEARCH ARTICLE

Growth of Transparent Conductive Oxide SnO_2 Thin Film as H_2 Sensor

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HIGHLIGHTS

> The morphological structure has improved with annealing and the film quality and properties were shown to be highly dependent on temperature.
> The increased annealing temperature was shown to have homogenized the crystallinity of the films.
> It was observed that the sensor response increased after annealing. The increase in sensor response is due to the effect of additional heat treatment.

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ABSTRACT

Tin dioxide (SnO_2) thin films are an advantageous group of metal oxides due to their high electrical conductivity. This transparent conductive oxide has an important place for electronic applications. The USP method, which is one of the thin film preparation techniques, is preferred in gas sensor systems due to its simple use and cheapness. The aim of this study is to examine the morphological and structural properties of tin oxide thin films using ultrasonic spray pyrolysis (USP) technique. The precursor $SnCl_2$ used in the process is 0.1M and 100 mL with deionized water. This solution prepared with deionized water and 0.1M /100mL $SnCl_2$ was sprayed onto the glass substrate for film coating. Significant peaks can be obtained in XRD plots due to evaporation when grown films are annealed at a temperature higher than the process temperature. The bandgap value of the sample before annealing is 2.95 eV, while the bandgap value after annealing is 2.5 eV. The sensor response graph of SnO_2 was obtained for 300°C and 10,000 ppm values. When samples produced at 350 °C were annealed to 450°C, improvement in morphological structure is detected, so the film quality and properties are highly dependent on temperature. The obtained XRD results support that the factor that homogenizes the crystallinity of the films is the increasing annealing temperature. It was observed that the sensor response increased after annealing. The increase in sensor response is due to the effect of additional heat treatment.

Contents

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1. Introduction

The growth of ultrathin SnO_2 layers in semiconductor structures requires a deposition step after Complementary Metal Oxide Semiconductor (CMOS) treatment. It reduces the high power consumption caused by the bulky structure of gas sensor devices and the complexity in production techniques [1]. Gas sensors are bulky devices that have recently been used in industrial applications. They cannot meet consumer requirements because they are difficult to integrate into CMOS technology. A high surface-to-volume ratio is expected for good sensor performance. This ratio is possible with the production of very thin nano-crystalline films. Thus, strong interaction with the surrounding gases occurs [1]. Metal oxide semiconductor-based sensor research has focused on the morphological structure of thin-film structures. The surface area of the metal oxide may vary with the nanostructured model. A more active material area can be created to control the active surface. In order for this area to occur, the contact area between the material and the target gas must be increased. In addition, gas diffusion of target molecules will also become more suitable for gas sensor application, as the large area inside the nanostructure provides a better transport channel [2]. The Ultrasonic Spray Pyrolysis (USP) method, which is preferred for the deposition of metal oxides (SnO_2, ZnO), is a process based on ultrasonic atomization. The generated aerosols are deposited on a heated surface. The advantages of this method over other methods are its low cost, ease of use and quality of the obtained coating. Although the pyrolysis process has similar properties to chemical vapor deposition, the disadvantages of chemical vapor deposition such as high vapor pressure and thermal stability of the precursor are not seen in the pyrolysis process [3].

Metal oxides are the preferred materials for basic research and technological applications due to their diverse electronic and chemical properties. Tin dioxide belongs to the Transparent Conductive Oxides (TCO) material class. TCO has an important place for optoelectronic applications. Tin oxide thin films have some outstanding properties. These are reflectivity for infrared light, transparency for visible light, and low electrical sheet resistance. Therefore, a wide variety of applications such as gas sensors, electrodes in solar cells, infrared reflectors are also preferred [4]. Although tin is used as the main conductive oxide element due to its electrical properties and high availability on earth, the electrical properties alone are not sufficient for the good criteria of TCO as it must have high transparency. Since transparency and conductivity are inversely proportional, the balance between the two properties must be maintained to reach an optimum value. The addition of the doping element helps with this purpose [5]. Tin oxide is widely used in LEDs, thin-film photovoltaics, touch screens [6]. Due to its wide bandgap, SnO_2 is an insulator in its stoichiometric form. In addition, it has high intrinsic defects due to oxygen deficiencies and very low formation energy of tin interstitials. Therefore, these defects occur easily, which explains the high conductivity of pure but non-stoichiometric tin oxide. In addition, the spray parameters can be easily changed. A wide range of control can be achieved by varying the speed and the thickness of the films.

The USP Method involves a simple technology in which an ionic solution is sprayed onto heated substrates. The bandgap of SnO_2 can be adjusted for use in optoelectronics [7]. A model presented to explain the variation of conductivity, in this case, is based on its induction by adsorption and desorption of gas molecules at the oxide surface and modification of band bending at the near-surface. In this application, tin oxide is an alternative to Sn-doped In_2O_3 (ITO) and Al-doped ZnO oxides. Higher conductivity may have been achieved with the last two types of oxides, but oxides based on SnO_2 allow for improved chemical, mechanical and thermal stability. It is also abundant on earth [8]. Tin oxide is a wide bandgap n-type semiconductor in which natural oxygen vacancies act as an n-type dopant [3]. SnO_2 has been reported by many authors to have a bandgap of 3.6 eV [2]. Tin oxide has a tetragonal rutile structure [4].

The interest in the research of thin films is increasing day by day. Because it responds to demands in both microelectronic technology and energy fields. SnO_2 is promising because it is a commercially used material in gas sensors and an anode material in lithium-ion batteries [6]. It has been revealed that the conductivity of tin oxide thin films depends on the structure of the films and the substrate temperature. While growing the tin oxide nanomaterial, optimum growth parameters can be obtained by changing the growth temperature and growth time [9]. SnO_2 films are particularly stable at high temperatures. Accordingly, it has excellent resistance to strong acids and bases at room temperature. It is also resistant to mechanical wear and adheres easily to many substrates. Many non-doped and doped SnO_2 thin films have been studied for the detection of toxic polluting gases, combustible gases and organic vapors [10]. SnO_2 is an insulator in bulk, exhibits a semiconducting behavior when prepared as a thin film due to deflection. It is abundant in nature, although it is non-toxic [11].

To prepare SnO_2 thin films for TCO applications, ethanol is a better choice due to its higher carrier concentration and lower resistivity values, as well as its good mobility and merit values [6]. Spray pyrolysis does not require high-quality substrates or chemicals. This technique has been used for the deposition of dense films, porous films and powder production. In addition, even multi-layer films can be easily prepared with this technique. It is particularly well suited for high-speed automated mass production. In the spray pyrolysis technique, an ionic solution is prepared with starting materials containing elements with suitable stoichiometric ratios. It is then sprayed onto a heated substrate (about 300°C to 500°C). In this ionic solution, metals, chlorides, nitrates, or acetates are used. In the spraying process, the droplets hit the surface to be coated and spread in a disc-shaped structure.

As a result of these processes, the droplets undergo thermal decomposition. The shape and size of the disc used are directly related to the substrate temperature, the momentum and the volume of the droplet. As a result, metal salts formed from overlapping discs are converted to oxides on the heated surface. The thin film deposition process can be explained by the three main steps of the USP method. These steps are respectively as follows: Atomization of the precursor solution, transport of the obtained aerosol and decomposition of the precursor on the substrate [4]. Some parameters in the

spray pyrolysis technique, such as spray speed, spray duration, precursor concentration and substrate surface temperature, affect the structure and properties of the film. The substrate temperature is a critical parameter because if this parameter is not set correctly, roughness, cracks and distorted crystalline properties will occur in the film. The structure of the films prepared by changing the concentration of the precursor solution varies depending on the molarity [4]. Many thin film deposition techniques such as chemical spray pyrolysis, chemical bath deposition, chemical vapor deposition, thermal evaporation, electron beam evaporation are used for the deposition of films such as SnO_2.

With the USP technique, useful for the industrial production of tin oxide-based oxides, thin films can be deposited more quickly on a large platform. Optimum pyrolytic degradation is possible with the right precursor selection. In this process, droplet size and distribution are important. In addition, the choice of precursor affects the morphological properties of thin films [6]. The gas detection sensitivity of the SnO_2 thin film is important depending on the crystallite size, the crystallite orientation at various film thicknesses of the deposited sample, the deposition technique and temperature. It revealed control of the application-dependent roughness of the sample by changing the molarity of the precursor solution. Also, the film spreads uniformly across the substrate [12].

To analyze films with different additive concentrations, some parameters need to be known. These parameters are dielectric constant, refractive index, extinction coefficient, dispersion factor, volume energy loss function, surface energy loss function, optical conductivity and optical density [13]. The tin atom is located in the center of the six oxygen atoms placed at the corners of a regular octahedron. For tin oxide to be an insulator it would have to be completely stoichiometric. It is possible to analyze from XRD data. This analysis is supported by the transmission electron microscope outputs and the corresponding field electron diffraction model. The morphology of thin films can also be studied using atomic force microscopy.

Examination of optical properties is possible with UV-Visible spectroscopy. Because it reveals the formation of nanostructures more accurately. Preliminary electrical analysis of these films is performed using a two-probe semiconductor characterization system, this analysis is linked to the result of UV spectroscopy. Considering the impedance analysis, it was observed that the impedance remained constant at high molarity and the barrier height remained constant at high frequency [12].

In conclusion, semiconductor oxide thin films are materials with numerous applications in electronic devices. It is especially promising in energy conversion studies. In addition, post-annealing processes are also of interest. Because there are studies on the effect of substrate temperature, texture, microstructure and doping [14].

In this paper, it is aimed to examine whether the annealing process contributes to improving the structural and sensing properties of tin oxide thin films after the process is completed.

2. Material and Method

USP technique is more economical than other techniques and is suitable for thin film production since it can be easily intervened in the production process. It is also preferred because it does not require a vacuum environment for its production. In the production process, which is followed step by step, large surfaces can be coated.

Four steps were followed in the study. The first three of these are thin film production techniques. The fourth step is the annealing process of the sample whose coating is completed.

2.1. Cleaning

The glasses were cleaned with soapy water, ethanol and propyl alcohol, respectively, and left to dry in a clean environment without touching any surface.

2.2. Solution Preparation

In order to produce thin film, 0.1 Molar and 100 mL precursors was prepared by using 2.2563 g of tin chloride with a molecular weight of 225.63 g and deionized water. (0.1M x 0.1L = 0.01 mol, 0.01 mol SnCl2:2.2563 g) This solution was coated on the cleaned glass surfaces with a thin layer of SnO2 using deposition times of about 1 hour

2.3. Thin Film Production with USP Method

The following steps were followed in thin film production with the USP method:

- SnCl2 (Tin Chloride) was chosen as the source chemical.
- Pure water was chosen as the solvent.
- Attention was paid to the cleanliness of all materials used.
- The USP system was turned on and the substrate temperature was adjusted to 350 °C.
- The cleaned glasses were placed in the chamber.
- The solution was connected to the system with the help of a syringe.
- The temperature was started to be applied.
- When 350 °C is reached, the spray apparatus (Nozzle) is activated.
- The air pump was turned on and set.

2.4. Annealing Process

Samples grown at 350 °C were annealed at 450 °C. Then, the XRD and absorption results of these samples prepared at different temperatures were compared.

3. Results and Discussion

3.1. Crystal Structure

It was observed that the XRD peaks were more pronounced when the tin oxide film-coated at 350 °C was annealed at 450°C (Figure 1). The XRD (A, B, C, D) peaks of the sample

grown at 350 °C and then annealed at 450 °C have (110), (101), (200) and (211) orientations, respectively. SnO annealed at 450 °C have (110), (101), (200) and (211) orientations [15, 16].

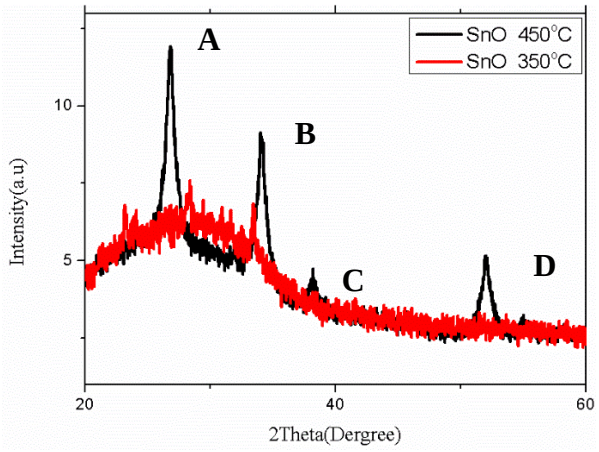

Figure 1 XRD SnO coated at 350 °C and annealed at 450 °C

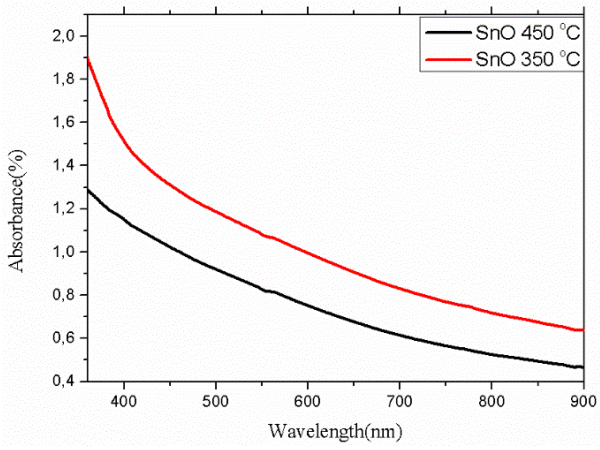

Figure 2 Absorption graphs of SnO-coated sample at 350 °C and annealed at 450 °C after coated at 350 °C

At the substrate temperature above 400°C, most of chemicals in precursors evaporate and SnO_2 film forms. Therefore, low intensity peaks are disappeared and the strongest peak is obtained. On the other hand, it is clear that the absorption percentage has decreased (Figure 2) by increasing annealing temperature 350 °C to 450 °C. The absorption spectra of samples were obtained in the visible spectral region 300-900 nm. Figure 3 shows the band gap value of the film with a substrate temperature of coated at 350 °C and annealed at 450 °C. It has been reported that some thin film exhibit a direct bandgap of 2.7 eV [17]. Respectively the band gap values of SnO are 2.95 eV (Figure 3) and 2.5 eV (**Error! Reference source not found.**).

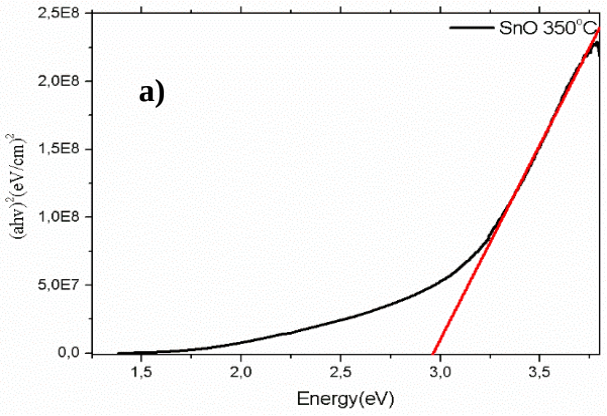

Figure 3 Bandgap size of SnO coated at 350 °C

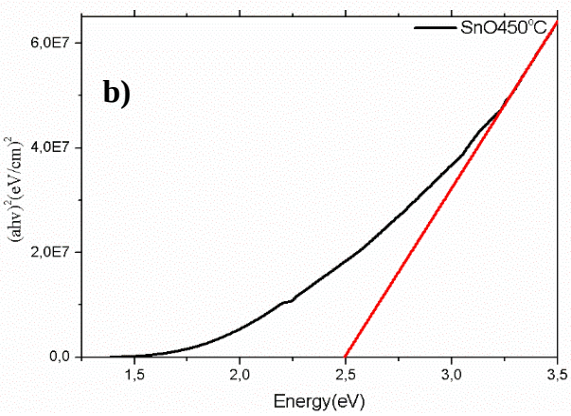

Figure 4 Bandgap size of SnO annealed at 450 °C after coated at 350 °C

3.2. Sensor Testing

The sensor response of the SnO_2 thin film prepared by the USP technique to the hydrogen gas is presented in Figure 5 and Figure 6. When the sample growth at 350 °C was subjected to the sensor test, it was observed that there was no response (Figure 5). Therefore, it was subjected to the sensor test again after annealing at 450 °C. This process was carried out at 10,000 ppm and 300 °C. Dry air was applied for 1200 seconds in the beginning and H_2 gas was applied for 1200 seconds in the second round. Then, in the 3rd round, 1200 seconds of dry air was applied, followed by 1200 seconds of H_2 gas application in the 4th round. At the end of 7 consecutive rounds, it was determined that the reflex of the sensor response of the sample annealed at 450 °C was effective (Figure 6).

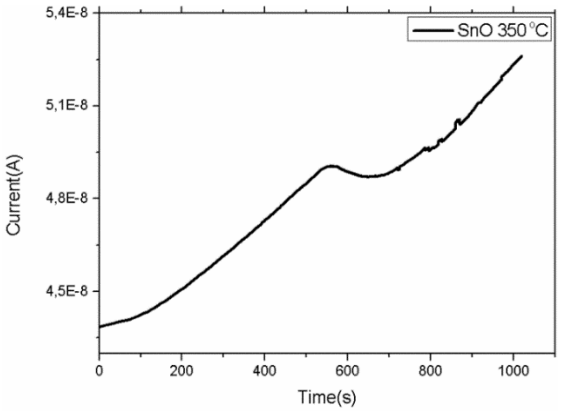

Figure 5 Dynamic Response coated at 350°C SnO_2 thin film prepared with USP

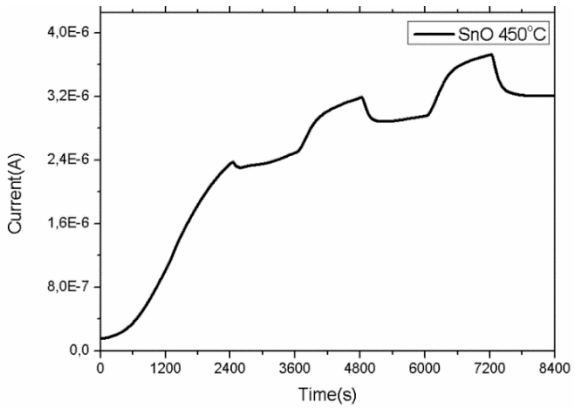

Figure 6 Dynamic Response graph of the sample coated at 350 °C SnO_2 thin-film prepared USP annealed at 450 °C after

4. Conclusion

Thin SnO_2 films can be produced by ultrasonic spray coating. It is possible to produce gas sensors on transparent surfaces without losing their transparency. However, transparency-performance optimization should be made between sensor performance and film thickness. SnO_2 thin-films were deposited on glass substrates for one hour by spray pyrolysis technique.

The precursor $SnCl_2$ used in the process is 0.1M and 100 mL with deionized water. Morphology was observed for the prepared films. Quality and film properties are highly dependent on temperature. Because when the samples produced in 350 °C were exposed to 450 °C, an improvement in the morphological structure was detected. XRD results also support the improvement of crystallinity of the films with increasing annealing temperature. Morphological modification of the SnO_2 nanostructure was successfully done by ultrasonic spray pyrolysis. The sensor test of the optimum sample was performed at 10,000 ppm. It was observed that the sensor response increased after annealing. The absorption spectra of samples were obtained in the visible spectral region 300-900 nm. The band gap values of SnO are 2.95 eV and 2.5 eV for 350 °C and 450 °C respectively. For Figure 6, all three measurements were made at 10,000 ppm. It is seen that the sensor response curves get better as time progresses. It is thought that this is due to the effect of additional heat treatment at this temperature. However, further studies are planned to clarify this situation.

The results obtained with USP are promising for the preparation of a sensitive and cost-effective gas sensor active metal-oxide thin-films.

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