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# SNO₂ THIN FILMS GAS SENSING PROPERTIES ON VARIOUS ANNEALING TEMPERATURE USING SPRAY PYROLYSIS METHOD.

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**Abstract:** Spray pyrolysis method was used to construct tin oxide thin films onto glass substrates at 250°C in this interpretation. After 120 minutes of annealing in air at different temperatures like 300°C, 400°C, and 500°C the films were examined. Gas sensing properties of prepared films are evaluated at different annealing temperature at various gas concentrations. Some analytic techniques like X-ray diffraction technique (XRD) and scanning electron microscopy (SEM) has been used to classify the prepared films. The crystallinity increased as the annealing temperature was raised, according to the X-ray diffraction results. The crystalline size and grain size calculated from XRD patterns and FESEM images were found to increase as the annealing temperature was increased.

**Keywords:** Thin film, Spray Pyrolysis, Ammonia gas sensor, Annealing Temperature.

Article History

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## INTRODUCTION:

Since the last few decades, there has been a growing interest in producing low-cost SnO2 thin films. Tin oxide is now the most widely used metal oxide semiconductor in sensing devices for its ability to identify highly flammable and toxic gases such as methane, LPG, CNG, CO, CO2, Cl2, H2S, and others [1-4]. At room temperature, it is a tetragonal n-type semiconductor with an energy band gap of about 3.6 eV. It's inexpensive, nontoxic, and has a high oxidizing strength, high photochemical corrosive resistance, and excellent electrical, optical, and piezoelectric properties. In recent years, semiconductor metal oxide films have gotten a lot of attention because of their possible applications [5] LCDs, lithium-ion batteries, and photocatalytic and photoconductive applications,[6-8] solar cells with a transport conductive device [9,10], gas sensor instruments with a gas sensing element [11], transport conducting devices with a gas sensing element [12], and so on. Despite its poor selectivity, SnO2 has been used as a sensing element in the majority of applications due to its high sensing activity and performance at low operating temperatures [13-14].

Thin film-based nerve fibres can be generated using a variety of packaging technologies, including PVD, CVD, sol-gel, spray pyrolysis, and others [15, 16]. There is a versatile process for obtaining pure SnO2 films within these spray pyrolysis methods [17]. Because of its flexibility, low cost, and low solid waste, it is especially appealing. A thin film can be made by spraying, heating, and decomposing a solution of previously salted ion salt onto a flammable substrate [18].

The current study shows the preparation of tin oxide thin films using a spray pyrolysis technique, as well as the effects of additional heat on the structure, sub-structure, and material, as well as the effects of applying thin film SnO2 sensors to the sensors.

## EXPERIMENTAL:

### 2.1 Preparation of solution

Analytical grade chemicals were used in the project. The dihydrate of tin (II) dichloride (SnCl.2H2O) (99.8%, Aldrich) was liquify in a various of solvents. Water and alcohols appeared to be the most popular solvents. Alcoholic solvents were chosen because they have lower surface tension and viscosity, leading to the formation of thin spray droplets as well as successful removal from the deposition chamber during the vapour phase [19].

SnCl2.H2O (0.1 M) was liquify in distilled water to the necessary concentration in this study. To make the solution clearer, a few drops of HCl were applied.

### 2.2 Substrate Cleaning:

In the creation of thin films, clean substrates are crucial. Corning glass substrates of dimensions about 25mm×20mm×2mm were cleaned with detergent solution and then immersed in acidic solution for 24 hours before being cleaned with distilled water and having to wash in acetone. The washed samples were then dried under an infrared light.

### 2.3 Deposition of thin film:

Using air as a gas flow and a glass nozzle with a 0.1 mm bore diameter, a SnCl2.H2O (0.1 M) starting material was dispersed over a heated glass substrate, resulting in very fine droplets touching the substrate. The glass substrate was held at a constant temperature of 250°C. The spray rate was held at 5 mL/min using the air compressor regulator. Spray nozzle and substrate distance kept at 20 cm apart. The films were placed onto heater for 30 minutes at the temperature used to construct the films after the deposition reaction was done to allow enough time and temperature for recrystallization. As a result, well-adherent, whitish-colored, and uniform SnO2 thin films were developed. The following is a representation of the SnO2 formula:

$$SnCl_2 + 2H_2O \rightarrow SnO_2 + 2H_2\uparrow + Cl_2\uparrow$$

### 2.4 Characterization

The electrical and structural properties of the materials have all been investigated. Utilizing CuKα rays with a wavelength of = 1.5418 A, the crystalline structure of the films obtained at various annealing temperatures was investigated using an X-ray diffraction unit. The Scherrer equation [23] was used to measure the average size of grains for tin oxide thin film samples:

$$D = \frac{0.9\,\lambda}{\beta\ \mathrm{Cos}\theta} \quad ......(1)$$

## RUSULT AND DISCUSSION

### 3.1 Structural Characteristics

The impact of firing temperature on film properties has been studied extensively [24]. As the annealing temperature rises, the film's structure transforms from powder solution to crystal, and formation occurs. With regard to the temperature Figure 1 shows the XRD spectra of constructive films on glass substrate and fire in furnace at various temperatures. The all peaks are quite similar to the standard results (ICDT card 880287). The tetragonal phase is represented by all of the peaks. Films on glass substrate have a preference for orientation in the (110) and (101) planes. Table no. 1 shows structural parameters such as dislocation density and crystalline size that are being calculated.

$$d = \frac{\lambda}{2\sin\theta} \quad \ldots\ldots(2)$$

$$Dislocation\ Density = \frac{1}{D^2} \ldots\ldots(3)$$

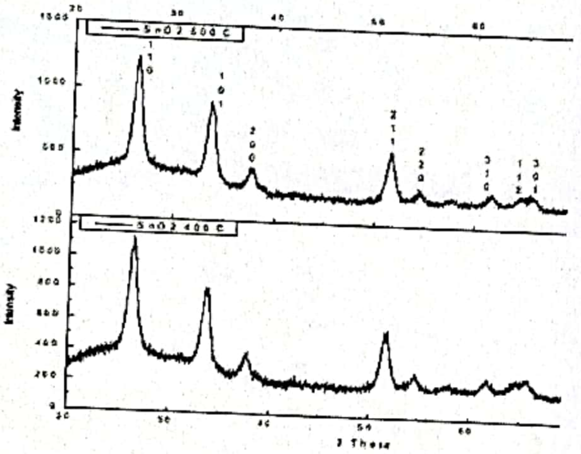

Fig 1. XRD spectra of film annealed at 400 0C and 500 0C

| Annealing Temp (0C) | 2θ | h k l | Standard Intensity | Observed Intensity | Dislocation Density | Crystalline Size |
|---|---|---|---|---|---|---|
| 300 | 26.25 | 110 | 999 | 1123 | 0.0087 | 10.66 |
| 400 | 26.25 | 110 | 999 | 1242 | 0.0074 | 11.55 |

### 3.2 Surface Morphology of films

SEM representations of the surface morphology of tin dioxide thin films with various firing temperatures shows tetragonal structure. With the exception of a slight increase in particle size, the microstructure of these films is very similar. The average particle size determined by SEM images ranges from 115.3 to 140.5 nm. The SEM images show that particle size increases as the annealing temperature rises, reaching an average particle size of 140.5 nm at 500 °C. The average grain size, as calculated by XRD data, was 10.66–11.55 nm, The grain size in SEM was 115.3–140.5 nm, which was slightly smaller.

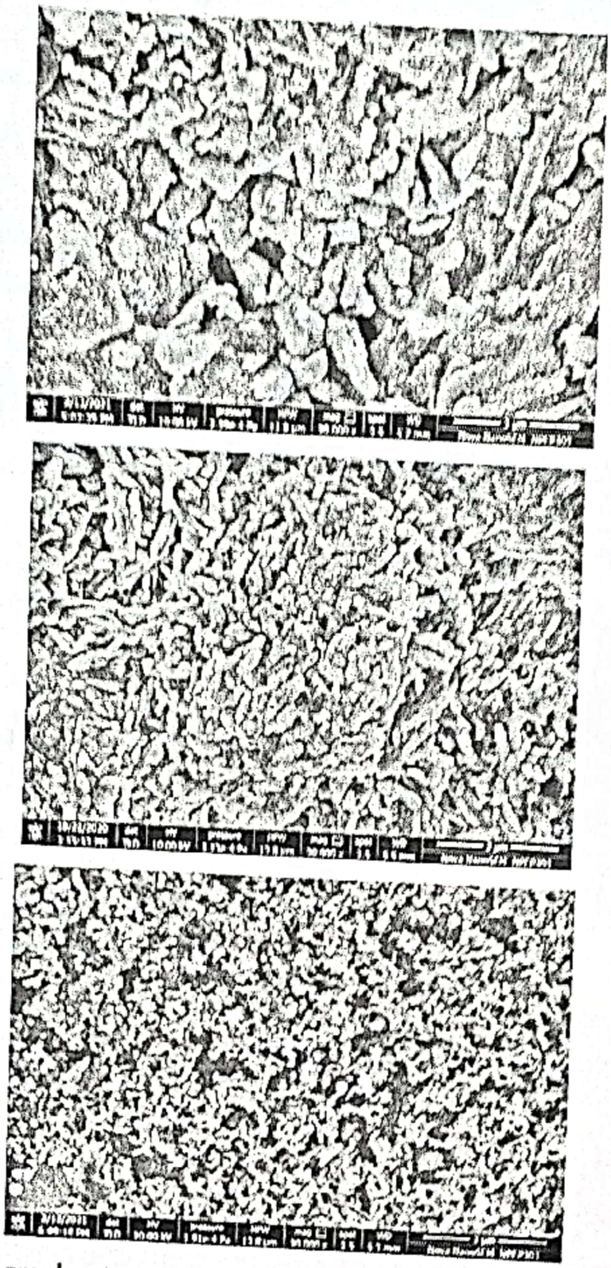

Figure 2. SEM photographs at annealing temperature a) 300 0C b) 400 0C and C) 500 0C

## GAS SENSING PROPERTIES

### 4.1 Static gas sensing properties:

As a function of operating temperature and concentration of target gas, the basic gas sensing properties of tin dioxide thin films were calculated. Various parameters such as sensitivity, selectivity, reaction, and recovery time were used to classify the films in the current research.

Sensitivity is described as S = Ra/Rg, where Ra is the sample's resistance in air and Rg is the sample's resistance in the presence of a target gas measured at different temperatures. The graphs show that the gas response rises with working temperature, peaks at a certain temperature (operating temperature), and then declines. It has been observed that gas responses differ for different gases and often vary with gas concentrations within the same gas. It shows that operating temperatures differ depending on the gas.

Selectivity: The selectivity or specificity of a sensor with respect to a simplifying gas is calculated in terms of size, which contrasts the amount of the interfering gas that produces the same sensor signal. The selectivity profile of various gases for various gas concentrations is shown in figure 5. Among the tested test gases, ammonia showed the best response at a concentration of 3 cc at a temperature of 290oC.

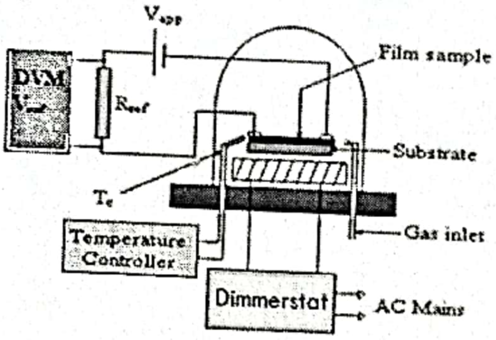

Figure 3. Block diagram of static gas sensing system.

### 4.2 Sensitivity of SnO2 films to Ammonia with Operating Temperature

Experiments were carried out at different operating temperatures to see how the SnO2 films sensing behavior works with different annealing temperatures. For comparison, the ammonia sensing properties of SnO2 samples were obtained at different annealing temperatures throughout similar laboratory conditions. In the construction of gas sensing devices and sensors, the annealing temperature is a critical variable. [25-26]. The sensing materials must be annealed at various temperatures to achieve crystallisation and structural development. A appropriate crystallite size is expected to produce the required electronic properties required for gas sensing applications. Figure 4 shows the relationship between the sensitivity of prepared SnO2 to 3cc ammonia at various annealing temperatures like 300°C, 400°C, and 500°C and the operating temperature. When the annealing temperature was 500 oC, the sensitivity was at its peak. More oxygen vacancy generation occurs during annealing in air, which

improves gas sensitivity. In addition, the increase in sensing characteristics of such ampless as compared to films annealed at 300oC and 400oC is possibly due to the high proportion of crystallisation caused mostly by influence of the annealing temperature. The sensitivity increases from 1500C to 3000C, then decreases as the operating temperature rises. At annealing temperatures of 300oC, 400oC, and 500oC, it showed maximum sensitivity of 5.02, 32.27, and 63.35 to 3 cc of ammonia, respectively.

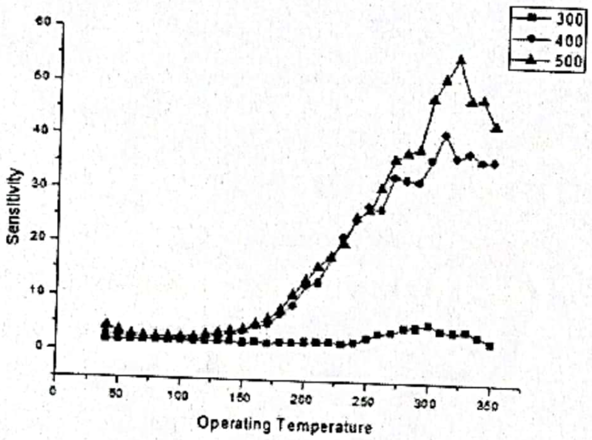

Figure 4. Sensitivity vs Operating Temperature

### 4.3 Difference in sensitivity with Ammonia gas concentration

Figure 5 depicts the relationship amongst SnO2 sensing behavior and ammonia gas concentration at a temperature of 290 0C. The sensitivity goes high at 3 cc ammonia concentration and then decreases linearly. The linear relation in sensitivity and ammonia concentration at low concentrations may be present in the form of enough sensing areas on a film to function on ammonia. Low gas concentrations result with less gas molecule surface coverage, resulting in less surface reactions with surface adsorbed reactive species and gas molecules. Because of the broad surface coverage, an increase in gas concentration increases the surface reaction. As the surface coverage of gas molecules reaches saturation, further increases in the surface reaction would be incremental.

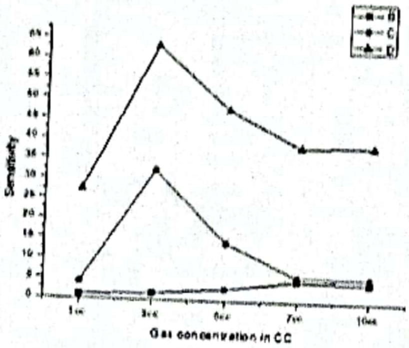

Figure 5. Sensitivity vs Gas concentration in CC

### 4.4 Selectivity of SnO2 samples for Various Gases

The sensor's sensing capabilities for a number of all other gases have been investigated in addition to ammonia to determine its selection. The ability of a sensor to respond to a particular gas with the presence of all other gases is known as selectivity. The histogram of the selectivity of SnO2 film samples to various gases is shown in Figure 5. The susceptibility values to various gases at various annealing temperatures are shown in the table 2. Ammonia (3cc at 290°C) had the highest selectivity of all the gases measured, including NH3, CO2, Acetone and ethanol. The selectivity improves as the annealing temperature rises.

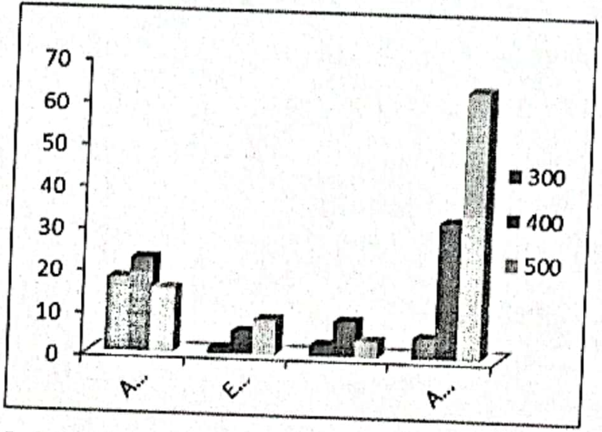

Figure 5. Selectivity graph of SnO2 thin films at different gases

| Annealing Temperature | Acetone | Ethenol | CO2 | Ammonia |
|---|---|---|---|---|
| 300 $^{0}$C | 17.50 | 1.42 | 2.82 | 5.02 |
| 400 $^{0}$C | 22.20 | 5.47 | 8.41 | 32.27 |
| 500 $^{0}$C | 15.14 | 8.32 | 3.96 | 63.35 |

Table 2. Selectivity of SnO2 thin films at various gases

## CONCLUSION:

Spray pyrolysis was used to develop SnO2 thin films on glass substrates using SnCl2.2H2O as a precursor. The impact of annealing temperature on the surface morphology, crystalline status, and gas sensing properties of the films has been studied. Crystalline size and average grain size increases with increasing annealing temperature. Surface morphology has a major impact on the gas sensing properties of these films. For an exposure of 3 cc ammonia, the optimum sensitivity was obtained at a temperature of 100oC. The results of the ammonia sensing studies show that SnO2 films prepared by spray pyrolysis are a suitable material for ammonia sensor fabrication.

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