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Influence of Band Gap Energy and Substrate Temperature on Gas Sensing Properties of Cu-doped $SrTiO_3$ Thin Films

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Abstract: *Metal oxide composite $SrTiO_3$ (STO) thin films have been prepared to analyze on Structural, electrical, optical and gas sensing properties. STO thin films were synthesized by varying substrate temperature using spray pyrolysis technique. The films were deposited at four different temperatures ranging 300^0C to 400^0C. The precursor solution was prepared by dissolving Strontium Chloride ($SrCl_4.5H_2O$) and (TiO_2Cl_2) adding equally 4% of Copper Chloride ($CuCl_2$) in Precursor solution. The deposited films were characterized by using XRD, FE-SEM; UV-Vis-Spectrometry.H_2S gas was used to study the gas sensing behavior.*

Keywords: *Spray pyrolysis, XRD, FE-SEM, Band Gap, H_2S sensor*

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I. Introduction

In the recent year, semiconducting metal oxide thin films have received intensive attention due to their very important role in optoelectronics devices such solar cells, heat reflectors and sensors, Gas sensors. STO is a semiconductor which has been used in making heterojunction thin films, it is preferred because it is a wide band gap semiconductor having good thermal stability & can be used as light dependent resistors sensitive to visible & near infrared light. It is found that substrate temperature influences the structural, optical, electrical properties of thin film [1- 4]. Sensitivity has been attracting more attention and many efforts have been made to enhance the sensitivity and selectivity of gas sensors.

Metal-oxide gas sensors are commonly used in the monitoring of toxic pollutants and can provide the necessary sensitivity, selectivity and stability required [6]. Such sensors find a range of application including the monitoring of traffic pollutants or food quality in specially designed electronic noses [7-8]. Commonly used oxides are tin oxide, zinc oxide, titanium dioxide, iron oxide, tungsten oxide. These materials have successfully been employed to detect a range of gas vapours, particularly ethanol, methanol, ammonia, hydrogen sulphide [9–14]. Thick film technology is often used to fabricate sensors and possesses many advantages, such as low cost, simple construction, small size and good sensing properties [15-16]. In addition, this approach provides reproducible films consisting of a well-defined microstructure with grains and grain boundaries that can be studied easily [17].

Hydrogen sulfide (H_2S) is most famous toxic gas because of bad smell can be perceived at a concentration lower than 0.1 ppm. H_2S gas often produced in coal, coal oil or natural gas manufacturing. The maximum limit of safety exposure is 10 ppm, but high concentrations cannot perceive and they may cause instant paralysis. H_2S has a density similar to air [18]. Therefore, reliable sensors with low cost, low energy consumption having high sensitivity, selectivity and operable in sub ppm (ppb) range of H_2S sensors are in high demand for environmental safety and industrial control purpose.

Research for new good gas sensing materials and the new properties of conventional materials has become an active research field. Concerning the detection of dilute H2S less than 1ppm, thick film sensors using CuO-SnO_2 [19-20] is possible. The known H_2S gas sensors $BaTiO_3$ [21], (Ba0.87 Sr 0.13) TiO_3-BST [22], Cu-BST and Cr-BST [23], CuO-$SnTiO_3$ [24], CuO-ZnO-SnO_2 [25], WO_3 [26-28], and CuO-doped SnO_2-ZnO [29] have been reported to excellent performance. Heterocontact CuO modified SnO_2 [30] and CuO-BSST based H2S gas sensors have been reported for the detection of ppb level of H2S gas at room temperature.

We prepared thin films by spray pyrolysis technique (SP), because of its simplicity and inexpensiveness has found to be better chemical method for the preparation of thin films with larger area. In the chemical spray pyrolysis technique; various parameters like air pressure, rate of deposition, substrate temperature, distance between nozzle to substrate, cooling rate after deposition affect the physical, electrical and optical properties of the thin films [31-32].

The semiconducting metal oxide gas sensors constitute one of the most investigated groups of gas sensors. These sensors have attracted much attention in the field of gas sensing due to their low cost and flexibility in production and simplicity in their use. Numerous researchers have shown that the reversible interaction of the gas with the surface of the material is a characteristic of conductometric semiconducting metal oxide gas sensors. The interaction can be influenced by the natural properties of base material, surface area and micro structure of sensing layers, surface additives, and temperature. Although a good amount of work is done on metal oxide gas sensors [33-35], sensitivity has been attracting more attention and many efforts have been made to enhance the sensitivity and selectivity of gas sensors.

In this paper Spray Pyrolysis method was used for fabricating Cu-STO thin films, the purpose of this work was to investigate the effect of energy band gap of and substrate temperature ranging from 300^0C to 400^0C on sensing properties of Cu-STO thin film.

II. Materials and Method

2.1. Fabrication of Cu-STO thin film

All the chemicals used for the synthesis of Cu-STO thin films were of analytical grade and were used without further purification. Stannous chloride ($SrCl_4.5H_2O$) used as the precursor that was obtained from Thomas Beker, India. $TiO2Cl_2$ is obtained from sd-fine chemicals, India. Copper Chloride ($CuCl_2$) was used as dopant; it is purchased from Thomas Baker, India. Commercially available laboratory glass slides of dimensions 25 mm x 75 mm and thickness 1mm were used as substrate our home made chemical spray pyrolysis setup is adopted for the synthesis of Cu-STO films.

The precursor's solution was prepared by the dissolving in d-ionized water with 0.1M concentration. The nozzle was kept at a distance of 27cm from the substrate during deposition and the solution flow rate was held constant at 5 LPM. When aerosol droplets came close to the substrates, a pyrolysis process occurred and highly adherent Cu-STO films were produced for different substrate temperatures ranges 300^0C to 400^0C. Once the spray is completed the heater was turned off and the films were allowed to attain the room temperature [36-38].

2.2. Characterization of Cu-STO thin films

The so prepared Cu-STO films were used for further characterization. X-ray diffractometer (Ultima IV Japan) with CuKα radiation (λ=1.5405 Å) at 40 mA and 40 kV at a scanning rate of 0.02^0C per second was used to study the crystalline state of these films. Morphological properties of the films were studied using Filed Emission Scanning Electron Microscopic (FE-SEM) [39]. Optical properties of the films were studied using UV-VIS spectrometer in the wavelength region 300 – 800 nm.

2.3. Gas Sensing Measurements

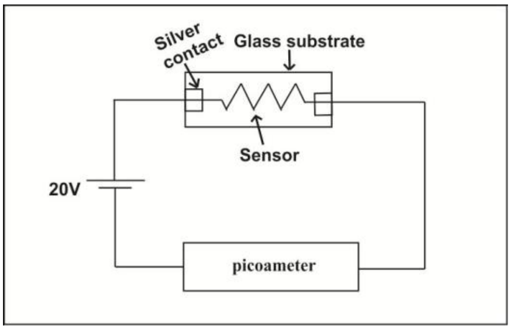

Fig.1. Circuit used for the gas sensing mechanism

The fig.3 shows the circuit used for the gas sensing mechanism. The circuit consists of the thick-film on glass substrate interdigitated with silver contact provides better ohmic contacts, sensor serves as resistance in the circuit. A 20 Volt dc power supply was used to apply a voltage across the circuit. The arrangement was used to detect the various oxidizing and reducing gases within a concentration range of 30-3300 ppm. For each concentration, readings were taken in picoameter (PA) after equilibrium conditions were reached within the gas chamber. The theoretically predicted increase/decrease in resistance of the oxide layer upon expose to gases has been experimentally observed. The fundamental sensing mechanism of metal oxide based gas sensors relies on a change in electrical conductivity due to the interaction process between the surface complexes such as O-, O_2^- , H+, and OH- reactive chemical species and the gas molecules to be detected. Many different oxides have been investigated for their gas sensing properties.

III. Results and Discussion

Cu-STO thin films were deposited by the Spray Pyrolysis technique. Deposited films were transparent.

3.1. Structure Analysis

3.1.1. XRD analysis

The structure of Cu-STO thin films at different substrate temperatures was investigated from XRD Pattern and is presented in Figure (1). From the XRD pattern, the average crystallite size is estimated using Debye Scherer formula. The XRD pattern for the temperature 400°C having major peak more intense than those obtained at lower temperatures. This confirms the improvement of crystalline nature at higher temperatures. As temperature of the substrate is increased the crystallite density increases and also the peaks become thinner and refined as confirmed by the reduction in Crystallite size which will reduce grain boundary scattering of charge carriers.

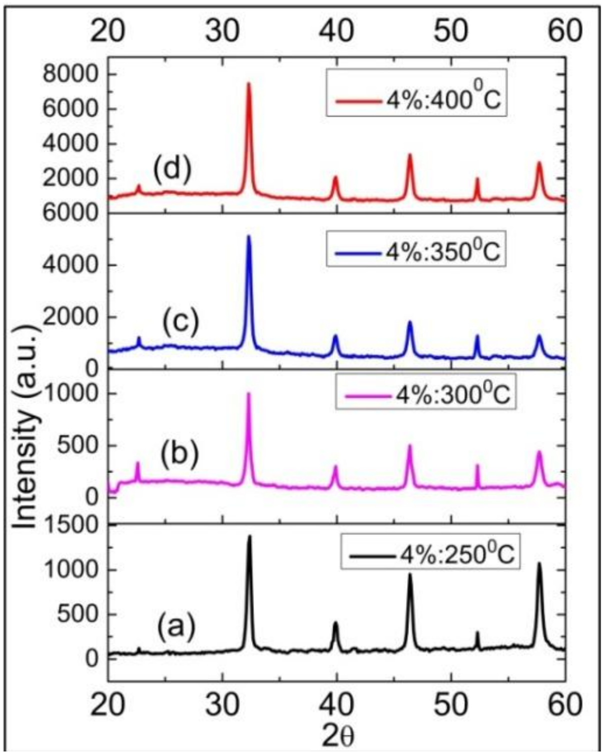

Fig.2.X-ray diffraction pattern of spray deposited Cu-STO thin films with variation of substrate temperature.

The increase in dislocation density with increase in substrate temperature is due to the rise in vacancy concentration which promotes electron transfer. The lattice constants show a decrease in dimension as temperature increases which agrees with the reduction in crystal size [40-41]. The practical size for Cu-STO thin film with different temperature is estimated and is given in table -1.

Table: 1.Estimation of particle size of Cu-STO films for different substrate temperatures.

Sample	**Particle Size (nm)**
Cu-STO;4%:250^{0}C	8.77
Cu-STO;4%:300^{0}C	9.23
Cu-STO;4%:350^{0}C	7.21
Cu-STO;4%:400^{0}C	6.57

3.1.2. Morphological Analysis

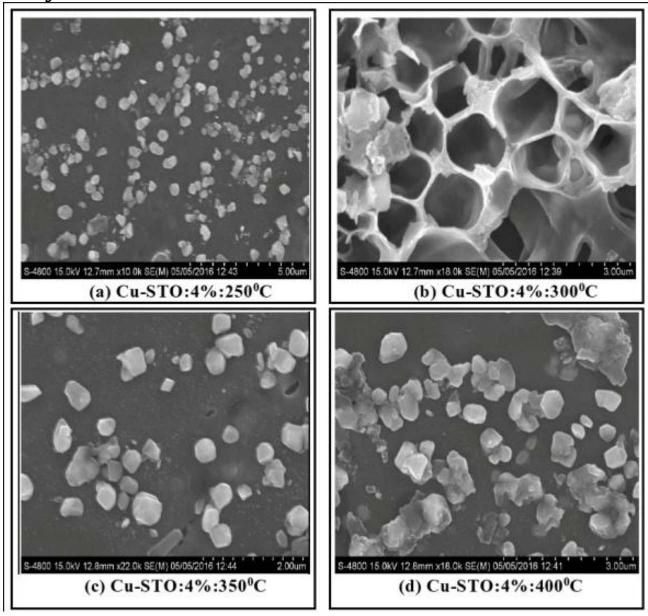

Fig.3. FE-SEM Image of Cu-STO with Different Substrate Temperature.

The surface morphology of Cu-STO thin films at different substrate temperatures was investigated from field emission scanning electron microscopic (FE-SEM) images and is presented in Fig.(2). Grain shaped small grains with smooth surface and dense packing are seen at 350^0C. No distinct shape is apparent at other temperatures though the film is densely packed with grains. At 300^0C substrate temperature thin film grain boundaries are prominent and porosity has exhibited maximum sensitivity to H2S. The sensitivity decreases for higher substrate temperature.

3.2. Optical properties

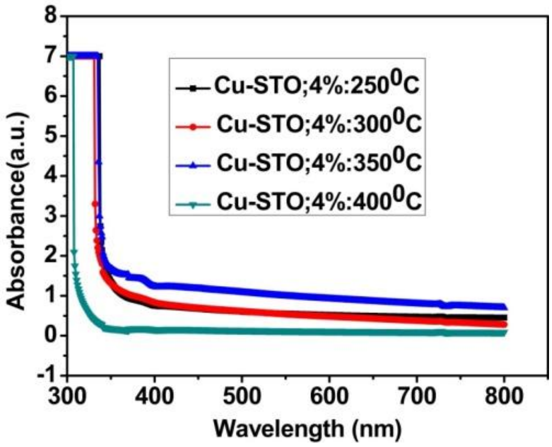

Fig.4. Absorbance spectra of samples

Absorption curves of Cu-STO film with different Substrate temperature, observed that as substrate temperature increases the absorbance peak shift towards the higher wavelength region indicating the decrease in optical band gap [42]. The band gap of these films estimated to be in the range of 2.8-3.5 eV. The absorbance curve of the Cu-STO thin films with different substrate temperature Show in Fig. (3). At 300^0C substrate temperature thin film energy gap is 3.5 eV has exhibited maximum response to H_2S. The sensitivity decreases for higher substrate temperature. The energy gap for Cu-STO thin film with different temperature is estimated and is given in Table -2.

3.2.1. Band Gap energy

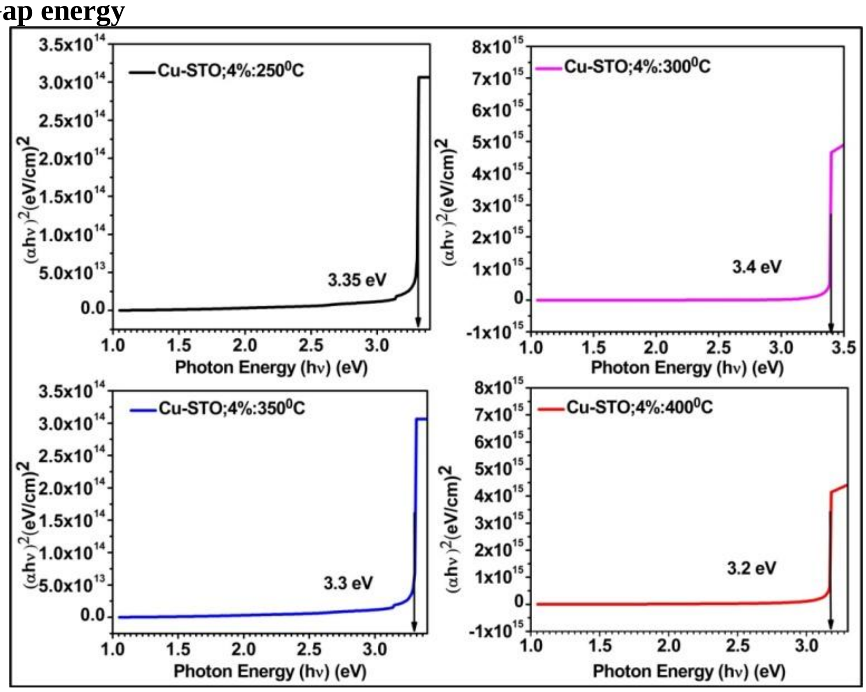

Fig.5. Tauc plot according to the absorption coefficient to estimate the band gap of the Cu-STO films at different substrate temperatures.

The term "band gap" refers to the energy difference between the top of the valence band to the bottom of the conduction band. Electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the band gap energy. The band gap energy of insulators is high (> 4eV), but lower for semiconductors (< 3eV). The energy band gap in some semiconductors tends to decrease as the volume ratios are changing. The energy gap for allowed direct transition materials can be estimated by plotting a graph between $(\alpha\ h\nu)^2$ and ($h\nu$) in eV, a straight line is obtained and the extrapolation of this line to $(\alpha h\nu)^2 = 0$ gives the value of the direct band gap of the materials presented in Table-2. The thickness of the thin films is measured using micro gravimetric method.

Table: 2. Estimation of band gap energy of Cu-STO films for different substrate temperatures.

Sample	Band gap (eV)
Cu-STO;4%:250^{0}C	**8.77**
Cu-STO;4%:300^{0}C	**9.23**
Cu-STO;4%:3500C	**7.21**
Cu-STO;4%:400^{0}C	**6.57**

3.3. Electrical properties

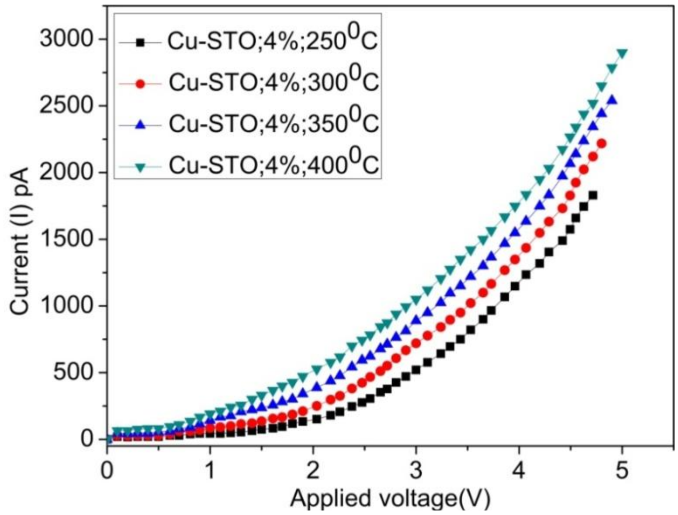

Fig.6.I-V characteristics of Cu-STO thin films.

Table: 3.Estimation of resistance of Cu-STO films for different substrate temperatures.

Sample	Resistance (k Ω)
Cu-STO;4%:250^{0}C	3X10^8
Cu-STO;4%:300^{0}C	4X10^8
Cu-STO;4%:350^{0}C	2X10^8
Cu-STO;4%:400^{0}C	1X10^8

Room temperature electrical resistivity measurements were made by Keithley picoameter. The I-V characteristics curve of the Cu-STO thin films with different substrate temperature shown in Fig.6.The electrical resistivity of the film is found to decrease with increase in substrate temperature. This may be due to the improvement in crystallinity of the film which in turn improves the mobility of the charge carriers. Inter granular effects play a major role in the transport of charge carriers in polycrystalline thin films. With increase in substrate temperature the crystal size is observed to decrease indicating the grain shaped growth of the crystal and the number of crystallites/unit volume is also found to increase which reduces the grain boundary potential. At 300^{0}C substrate temperature thin film resistivity is 4X10^8 KΩ has exhibited maximum sensitivity to H_2S. The sensitivity decreases for higher substrate temperature.

3.4. Gas Sensing Properties

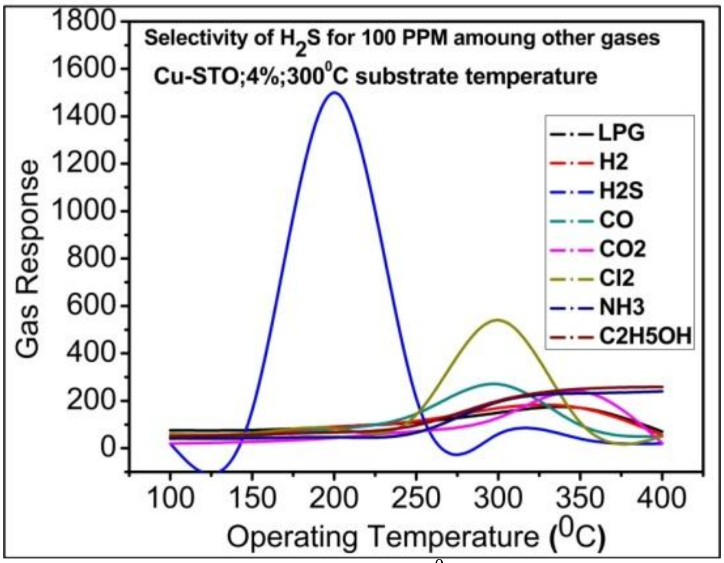

Fig.7. Selectivity of H_2S gas at substrate temperature 300^{0}C and operating temperature 200^{0}C for 100 ppm of H_2S.

In present study we have recorded the gas sensor response using Laboratory gas sensor setup to sense H_2S gas the substrate temperature increases sensitivity thin film decreases [43]. At 300^{0}C substrate temperature thin film shows exhibited maximum response to H_2S.The gas response characteristics are shown in fig.7.

IV. Conclusion

In the Paper as substrate temperature while deposition of Cu-STO thin film the XRD peaks become sharper indicating the decrees in particles size and improved crystalline. In morphological analysis the particle size decrees. In UV-VIS Spectrum analysis the absorption edge shifted towards higher wave length indicting the decrease in energy gap. From I-V characteristics it is found that resistance decreases with substrate temperature and the gas sensitivity decreases with substrate temperature. For substrate temperature 300^{0}C were observed that fine porous, high energy gap, more resistance and thin films are exhibited maximum response to H_2S.

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