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Synthesis of In_2O_3 Nano Powder by Aloe Barbadensis Miller Extract And Its Application As H_2S Gas Sensor

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Abstract. In this work In_2O_3 nanocrystalline powder has been synthesized with cubic structure by simple, cost effective and eco friendly route using Aloe Vera barbadensis Miller species available in our region having orange colour flowers. X-ray diffraction (XRD) and EDAX confirmed that synthesis is viable and complete. The synthesized nano powder was used as functional materials for fabrication of thick films on alumina substrate using standard screen printing technique. The fabricated thick films were fired at temperatures 600,700 and 800°C respectively. The film fired at 700°C shows low resistivity and high response to H_2S gas.XRD of powder and films confirmed base centered cubic phase with (222) plane orientation.SEM of powder shows cauliflower like structure. Electrical measurement of film showed n-type semiconductor. Thick films fired at 700°C showed highest sensitivity towards 100 ppm concentration of hydrogen sulphide gas at low temperature 150^0C.The sensor exhibits quick response in ~ 6 second.

I INTRODUCTION

Hydrogen Sulphide gas (H_2S), which is usually produced in coal mines, oil and natural gas industries, and sewage Plants is malodorous and toxic [1,2]. The high concentration of hydrogen sulphide exposure can cause deep health effect on human respiratory system and could induce neurological sequelae [3]. Therefore for protection of human health and environment, detection and monitoring of H_2S is necessary

Semiconductor metal oxides-based gas sensors have been vastly studied and researched because of their low-cost synthesis, simplicity in operation, great stability and it also offers multi properties which can be useful in the development of new technology. The various metal oxides such as ZnO, SnO_2, TiO_2, WO_3, Fe_2O_3, Cr_2O_3,Mn_2O_3, CO_3O_4, In_2O_3, WO_3, TiO_2, V_2O_3, GeO_2, Nb_2O_5, MoO_3, Ta_2O_5, La_2O_3, CeO_2, Nd_2O_3 and their multi oxides such as in bulk as well as nano forms have been extensively utilized for different gas sensing applications [4-11].

Amongst all these oxides, In_2O_3 has gathered distinctive attention because of its remarkable properties and various applications. The major setback in the utilization of this material is its high cost. Numerous methods have been reported for the development of such oxides [12,13]. The methods that researchers have focused on development of such oxides have been economic and environmental friendly for synthesis of nanoparticles (NPs). Methods such as Green method incorporates the effect of cost-effective solution for the synthesis of nanoparticles by the usage of plant extract [14].

Despite of the numerous methods reported for preparation of In_2O_3, utilization of plant in synthesis of nanoparticles is one of its kind, leading to truly green chemistry that technologists and researchers are looking out for. Aloe Vera plant is incorporated in the synthesis of oxide nanoparticles, which demonstrates a super magnetic, antibacterial, anti-inflammatory, UV protective, immunomodulatory and burn healing promoting properties. Aloe Vera is highly utilized in cosmetics, drinks, detergents, as well as in stockings, diet foods, toothpaste and clothing. It has established itself as a remarkable ingredient in the healing for atherosclerosis, allergies, AIDS, prevention of radiation-induced dermatitis, wound healing, psoriasis, insomnia, cancer, and several other diseases [15]. Amongst the 400 different species of Aloe Vera, barbadensis Miller is the most popular and is biologically active.

Kumar et al [16] reported development of CuO nanoparticles in monoclinic phase with average particle size of

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20 nm using Aloe Vera plant extract which demonstrates enhanced anti-bacterial activity when used against fish pathogens. Varghese et al [17] also reported photo degradation and antibacterial activity of ZnO nanoparticles synthesized using Aloe Vera plant extract. Renugadevi et al [18] reported the synthesis of silver NPs using Azadirachta indica leaf extract incorporating microwave irradiation method. Ayeshamariam et al. [19] reported the one of its kind syntheses of In_2O_3 and ZnO NPs with particle size that ranges from 10 nm to 30 nm using Aloe Vera extract solution with Indium nitrate and Zinc nitrate respectively. Maensiri et al. [20] synthesized In_2O_3 NPs of particle size 5 to 50 nm by simple method using Aloe Vera extract solution and Indium acetyl acetonate.

The contemporary work explores electrical and gas sensing facets of nanocrystalline In_2O_3 based thick film resistor synthesized using Aloe Vera plant extract. In_2O_3 nanocrystalline powder has been synthesized by simple, inexpensive and eco-friendly method, by incorporating Aloe Vera barbadensis Miller, a species available in abundance in our geographical location. Thick films were fabricated on alumina substrate using screen printing techniques and their gas sensing properties towards 100ppm hydrogen sulphide (H_2S) was investigated.

II EXPERIMENTAL

In a typical method of synthesis, Indium (III) acetyl acetonate (Alfa Aesar, 98%) was utilized as an initial chemical material for In_2O_3. The leaves of Aloe barbadensis Miller species were collected and thoroughly cleaned using tap water. The 35-gm pulp of leaves was extracted and boiled in 100 ml of de-ionized water; thus, Aloe Vera extract solution was formed. 3 gm of Indium (III) acetyl acetonate was firstly dissolved in 30 ml Aloe Vera extract solution with incessant stirring at 60°C for a few hours and then dried at constant temperature using, magnetic stirrer cum heater. The dried precursor (brownish colored) was churned using mortar and pestle and then calcined in a muffle furnace at 450°C for 2 hours. The dried precursor then turned into a yellowish coloured In_2O_3 nanocrystalline powder.

The laboratory developed yellowish In_2O_3 nanocrystalline powder was used as fundamental material and was incorporated for the development of thick films. The dimensions of samples were 20mm X 10 mm. The detailed process of fabrication of thick films has been explained elsewhere [21].

Fig.1 shows XRD pattern of In_2O_3 calcined powder at 450°C. The XRD reflection can be indexed to cubic In_2O_3 (JCPDS card number 06-0416), no other peaks can be found, unveiling their phase-pure cubic structures. In_2O_3 is grown in body centered cubic (BCC) phase with (222) plane orientation. Scherrer formula was used in the calculation of average crystallite size which was 10 nm. Fig 2 explicates SEM images of In_2O_3 sample calcined at 450°C revealing a cauliflower like structure. The SEM observation demonstrates no definite shape of particles. The particles are remarked by agglomeration. The XRD pattern of In_2O_3 thick film resistor (TFR) samples at various firing temperatures from 600 to 800°C are demonstrated in Fig. 3.

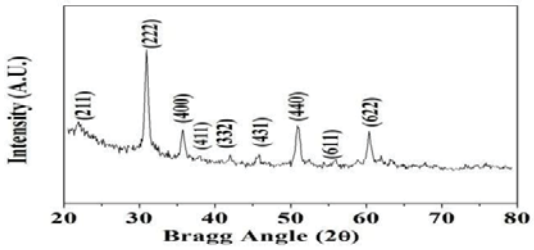

FIGURE 1. XRD of In_2O_3 powder calcined at 450°C

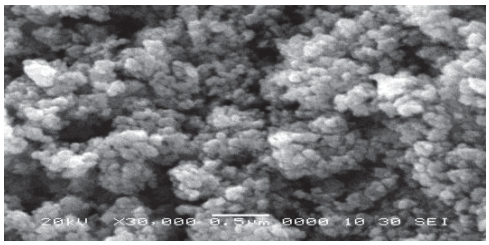

FIGURE 2. SEM Image of In_2O_3 powder calcined at 450°C

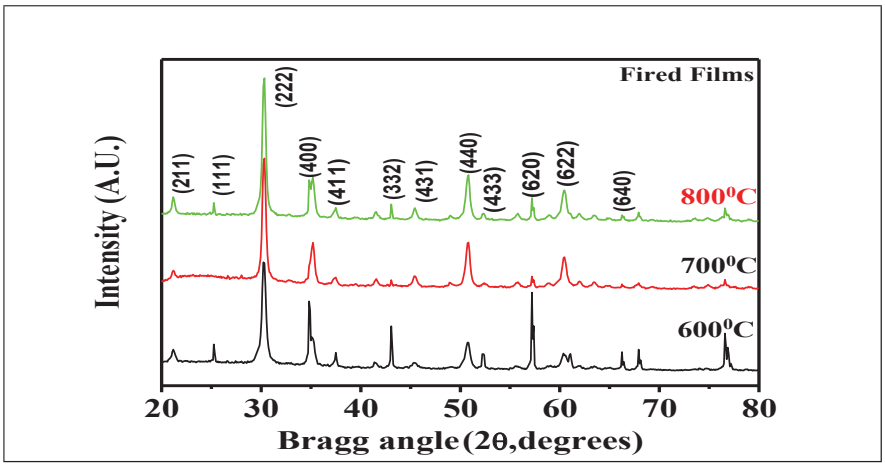

FIGURE 3. XRD of In_2O_3 Thick Films fired at 600 to 800⁰C

Scanning electron microscopy is a convenient method to study the microstructure of In_2O_3 thick film samples Fig..4 (a) ,(b) and (c) demonstrates SEM images of In_2O_3 thick films fired at 600⁰C, 700⁰C and 800⁰C. From SEM images it is observed that the grain size and crystalline quality increased with increase in firing temperature. The voids that are seen between the particles in the micrographs arise because of the evaporation of the organic solvent which gets instilled at the time of the firing of the films. An increment in the grain size and decrement in porosity along with increased firing temperature is observed in the In_2O_3 films.

Thickness Measurement

Thickness of the fired films was measured by incorporating a Profilometer (Dektek-150) and a force of 5 mg was applied. Thickness of samples were observed ranging from 16 µm to 18 µm (±2 µm) .

Electrical Characterization of In_2O_3 TFRs

Figure 5 shows variation of resistance with temperature for In_2O_3 thick films fired at temperature 600⁰C, 700⁰C, 800⁰C respectively in air. At higher temperature oxygen adsorbates are desorbed from surface of film and carrier concentration increases due to intrinsic thermal excitation. The decrease in resistance with increase in temperature is due to lattice vibrations or due to increasing drift mobility of charge carriers, which shows behavior of n type semiconductor

Gas Sensitivity with Operating Temperature

The measurement of ppm level gas sensing characteristics was conducted using simple home-built static measuring system which is discussed elsewhere [22]. The samples were characterized for 100 ppm gas concentrations under normal laboratory conditions (40% relative humidity) of hydrogen sulphide (H_2S). Gas sensing properties were studied as a function of operating temperature of the sensors. Estimation of sensitivity required sensor temperature increment from room temperature to 300⁰C in an air ambient and in test gas ambient (air and test gas mixture) by measuring resistance as a function of temperature, simultaneously. A change in resistance was measured as a function of temperature in both the ambient and the relative difference in the resistance was taken as a measure of the gas sensing properties.

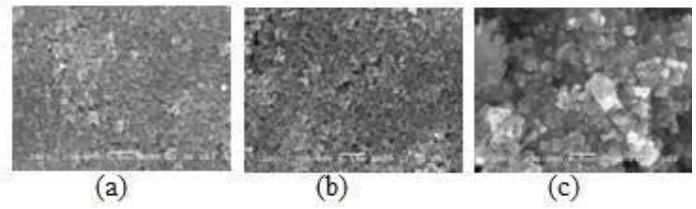

FIGURE 4. SEM Images of In_2O_3 thick films fired at (a) 600˚C (b) 700˚C (c) 800˚C

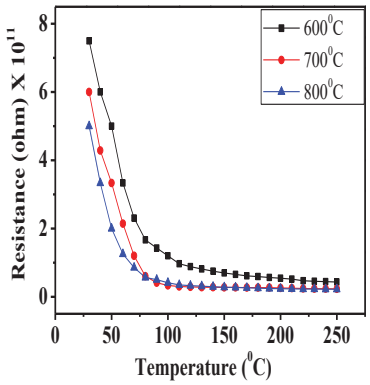

FIGURE 5. Variation of Resistance with Temperature of In_2O_3 thick films fired at 600˚C, 700˚C and 800˚C

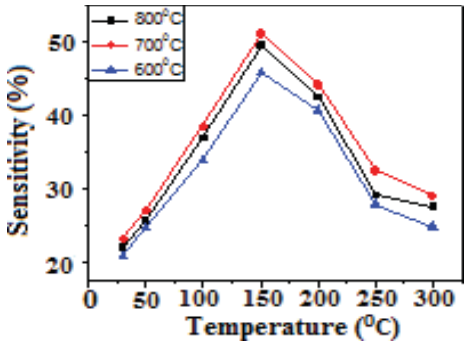

FIGURE 6. Sensitivity as a function of operating temperature for 100 ppm H_2S for thick films fired at 600˚C, 700˚C and 800˚C

Figure 6 shows response of 100 ppm concentration of hydrogen sulphide as function of operating temperature for thick films fired at temperature 600^0C, 700^0C, 800^0C respectively. The sensor show maximum response towards H_2S gas at operating temperature 150^0C for film fired at 700^0C.The film fired at 700^0C shows small particle size, better adhesion to substrate and small resistivity .The magnitude of sensitivity value for H_2S gas is 53% which is more than earlier reported work [23].

Figure 7 shows variation in sensitivity with increasing H_2S gas concentration at 150^0C (which is optimal temperature) for optimized sensor fired at 700^0C. The film was kept constant at optimal temperature and the different gas concentrations of gases were injected into the test chamber. The sensitivity increases linearly up to 200 ppm and afterwards it attains saturation level.

Figure 8 shows variation in sensitivity (100 ppm concentration of H_2S) with time in seconds. The sensor has excellent response of ~ 6 second and it took longer time of 30 minutes to reach its initial value. The sensor was found very sensitive to H_2S gas below 200 ppm with quick response time and possesses good reproducibility

Sensing Mechanism

In semiconductor metal oxide gas sensors, the sensing mechanism is based on the adsorption and desorption of the gas molecules on the surface of the sensing materials, which can cause the change in resistance [24, 25, 26]

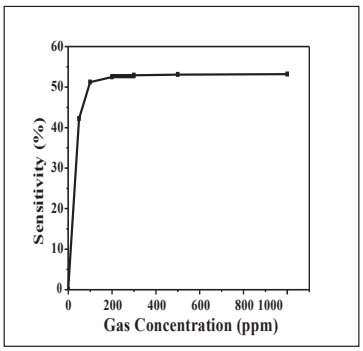

FIGURE 7. Variation in sensitivity with H_2S gas concentration at optimal temperature 150°C

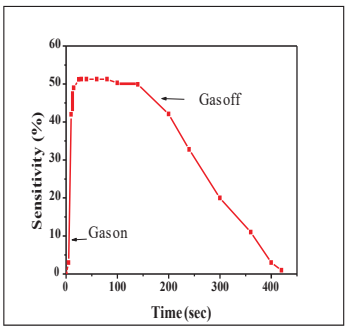

FIGURE 8. Response and recovery time of Sensor (H_2S gas,100 ppm)

The smaller particle size offers larger surface area due to which adsorption –desorption rate increases which enhances sensitivity of sensor [27]. Atmospheric oxygen can get adsorbed on to this surface site. The different oxygen species are formed on surface depending upon operating temperature.

The atmospheric oxygen acquires electron from conduction band of In_2O_3 and form O_2^- species on surface, so resistance of sensor increases. It is described by Eq.1.

$$O_{(gas)} + 2e \longrightarrow O_{2(ads)}^- \qquad [1]$$

The reducing gas reacts with $O_{2(ads)}^-$ species and releases electron back to conduction band and forms RO. It is described by Eq.2

$$R + 2O_{2(ads)}^- \longrightarrow RO + e^- \quad [2]$$

The H_2S gas can react rapidly with adsorbed oxygen, therefore releasing captured electrons back to bulk. Therefore, the surface reactions between the H_2S and the oxygen species can be described as follows in eq.3.

$$H_2S + 3O_{2(ads)}^- \longrightarrow H_2O\,(g) + SO_2\,(g) + 6e^- \quad [3]$$

In presence of H_2S gas it forms H_2O and SO_2 gas and releasing electron back to conduction band thus decreasing resistance of sensor

CONCLUSION

Nanocrystalline powder of pure In_2O_3 was synthesized successfully using simple cost effective and eco-friendly route using Aloe Vera plant extract. XRD and EDAX confirmed that synthesis is viable and complete. In_2O_3 thick films have been deposited on alumina substrate using screen printing technique. It was found that film fired at 700°C offer high response to H_2S gas .XRD study revealed polycrystalline morphology of In_2O_3 thick films and its grain size increases with an increase in firing temperature of the films. The sensor fired at 700°C exhibit highest sensitivity towards H_2S gas at operating temperature 150°C. The sensor exhibits an excellent response of ~6s. It took ~ 30 minutes to recover its initial value; however, by adding suitable dopant one can convert this sensor into a commercially viable device and shorten the recovery time.

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