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PROCESSING AND CHARACTERIZATION OF SN O_2 THIN FILM FABRICATED MECHANISM FOR SUITABILITY OF SENSOR APPLICATIONS

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Abstract - *In the last few decades Tin Oxide (SnO_2) based gas sensors have gained eminence. Oxide sensors are usually screen printed on bulk heater substrates. Less power consumed thin film sensors are basically suited for battery operated systems and are agreeable and can be incorporated with the standard silicon based electronic processing. During electronic processing, the spin coating is also an accepted thin film fabricated mechanism. Processing of SnO_2 thin films are intended for suitability of sensor applications. Techniques such as dip coating, low rpm films using a conventional metallographic polishing system and a specially fabricated spin coater are adapted during experimental investigation. Assorted difficulties observed during processing of thin films and consequent thermal behavior using tin based sols. The experimental investigation analyses and employs corrective measures at every stage of dispensation. A spin coater was developed and employed for processing the thin films. It is modified by employing the confinement ring for uniformity and repeatability. Thin films were coated using the sol prepared from $SnCl_4$ and isopropyl alcohol and were heat treated at different temperatures. The validation of the work is presented by demonstrating a method of processing crack free, uniform SnO_2 thin films using a laboratory designed, fabricated and suitably modified spin coater that runs at 4000 rpm and their thermal treatment at 500^oC in a single step.*

Keywords *- Processing of SnO_2 Thin Films suitable for sensor application, Tin Oxide (SnO_2) based gas sensors, spin coating.*

I. INTRODUCTION

State of the art commercial metal oxide gas sensors rely on thick film materials mainly screen printed onto bulk ceramic heater substrates [1]. In the last few years, there was an increasing interest in the field of gas sensors based on semi conducting materials. These thick film metal oxide gas sensors found wide applications in a variety of gas monitoring and alarm applications [2]. Thick film deposition of metal oxide materials is a mature technology that offers low cost and considerable versatility towards different application needs. Disadvantages of this technology are poor selectivity, baseline drift and an appreciable consumption of electrical energy for heating thick film sensors into their normal range of operation temperatures [3].

Such gas sensing elements, due to their bulky nature, exhibit heating power consumptions of the order of several hundred mW per sensor element and thus render such sensors unattractive for battery operated or bus-interconnected systems. Moreover, the high power consumption of commercial metal oxide gas sensors is also a serious obstacle in the achievement of gas sensor arrays consisting of gas sensing elements with systematically varying cross sensitivity profiles. In order to enable solutions ranging from simple low power consumption gas sensing elements to complete sensor arrays, future metal oxide sensors need to be miniaturized in size while the sensor processing needs to be compatible with standard silicon foundry processing routines.

From this point of view, the preparation of thin films based devices is a powerful approach in the resolution of the just mentioned problems. Tin oxide thin films are technologically important and find applications in areas such as electroluminescent displays, heat reflectors, mechanical surface coatings, sensor devices, spectrally selective reflectors and solar cells. Physical methods for thin films deposition such as evaporation, sputtering, and laser ablation are highly developed. Much fewer studies, however, have so far been devoted to chemical deposition routes. These latter techniques offer several potential advantages such as simple and low cost deposition equipment, easy modification of the starting chemistry and hence efficient control over the morphology and composition of the final materials. Finally chemical processing routes can also provide specific surface chemistry peculiarities that may result in outstanding sensor performance [4]. On the other hand, chemical deposition techniques may be affected by uniformity and substrate adhesion problems, which result from the lyophobic nature of the substrate surfaces. These problems can be solved by improving the viscosity and the surface tension of the solutions by adding polymers or surfactants, but in some important cases, like the deposition of SnO2 thin films from $SnCl_4$ based solutions [5], even such an approach may result ineffective. For this reason, we tried to develop an alternative deposition process by modifying the method of placing the substrate over the equipment. This procedure is very effective and could give uniform thin films with good sensitivity. Since for technological applications cheaper materials can play an important role, it is the aim to obtain SnO_2 thin films

using the glass as substrate.
A number of processes, though existing in the preparation of thin films, a more promising alternative technique has evolved that can prepare SnO_2 in the form of thin films with great ease by spin coating and dip coating.

Spin coating is the technique used now- a- days to prepare thin films and powders. Unlike other methods, it represents a simple and cost effective processing method. Even multi layered films can be easily prepared by this method.

SnO_2 is used as initial material for coatings due to its uniform surface properties and special properties like high light transmittance, low emissivity, low sheet resistance and high infrared reflectivity and its high sensitivity in the presence of very small amounts of gases [6] like carbon monoxide, methane, ethanol etc.

II. LITERATURE REVIEW

The application of thin films in modern technology is widespread. Several methods to grow thin films of inorganic compound semiconductors are taking vital role in the advancement of technologies. To obtain precision in the performance of thin film based devices, control over the film properties is necessary. Therefore many sophisticated techniques are employed for thin film deposition that can be broadly divided into two groups based on the nature of deposition process that is physical or chemical. The physical method includes physical vapor deposition, pulsed laser ablation, molecular beam epitaxial and sputtering. Somehow, too much interest is paid only on methods like pulsed laser ablation and sputtering. The other methods are overlooked by most of the scientists. The chemical method comprise of gas phase deposition methods and solution techniques. The gas phase methods are chemical vapor deposition, atomic layer epitaxy, while spray pyrolysis, sol gel, spin coating and dip coating methods employ precursor solutions. SnO_2 is used as the initial material for thin film preparation.

2.1 Introduction to SnO_2

The structure and properties of SnO2 are as follows:
SnO2 is also known as stannic oxide which is found naturally as cassiterite that appears to be a white to off white or sometimes grey crystalline solid. The density of tin oxide is 6.9 to 7 g/cc and its melting point at 1630°C. It has a tetragonal rutile structure. Its unit cell has 2 tin and 4 oxygen atoms as in the figure.

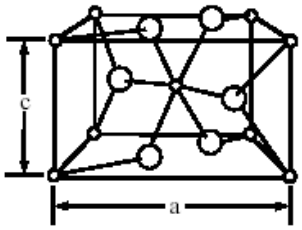

Fig1. Unit cell of the crystal structure of SnO_2.

Large circles are oxygen atoms and the smaller ones are tin atoms (a=b=4.737 A°, c= 3.185 A°)
The tin atom is at the centre of six oxygen atoms placed at the corners of a regular octahedron. Every oxygen atom is surrounded by three tin atoms at the corners of an equilateral triangle. If tin oxide was completely stoichiometric, it would be an insulator. However, in practice, deposited tin oxide layers contain a reasonable number of oxygen vacancies, making electrons available for conduction. In applications such as low-E coatings and solar cells, the tin oxide layers are chemically doped, for example, by fluorine or antimony, to further enhance the conductivity.

The reason why tin oxide is used as initial material is due to its wide applications in various fields. The various applications include: Heating elements in aircraft windows studied by Clough, T.J Grosvcenor, Mukherjee.A et al. As per their studies a thin tin oxide coating is applied on the window. A potential applied over the tin oxide coating heats it up and an ice or fog on the window will evaporate. This is used for anti static coating on instrument panels. Houng K.H, Bull, Gazdag E. Ligeti, Kane J Ling studied the use of tin oxide films as transparent electrodes in electroluminescent lamps and displays [7]. Their application in gas sensors is studied by Berger P., Beche E., Chambandet. A., Kim, K.H. Park, Dimeo, Chaparala P.Brown., J.R. Cheney, D.J. Jones. If a tin oxide surface is exposed to air oxygen absorbs on to it as O2- or O-. When reducing gases such as H2, CH4, Co are introduced the absorbed oxygen species are removed through the oxidation of such reducing gases and the captured electrons are restored to the conduction band. Applications of tin oxide thin films in Solar Cells is elucidated by Gordon, Plattner R.Stetter, Boiko, Kopach, G.S Chernikov, J.Leonard, Saxena, A.K.Singh. Because of its transparent and conductive properties, fluorine doped tin oxide layers are often used as top electrode in e.g. amorphous silicon solar cells [8]. Protective and wear-resistant coatings on glass containers are studied by Nakagawa M., Amanto. T and he claimed that most of the glass bottles produced nowadays is coated with a 10-100 nm thin layer of tin oxide. The bottles have equal or higher strength as non-coated bottles but can weigh till 20% less, and can be recycled more often. Tin oxide thin films are applied as Infrared reflectors for glass windows. Linder G.H, Mc Curdy R.J, Stewart-Davis, Goodman

found a way to improve the insulating properties of glass window by applying fluorine doped tin oxide coating. The coating reflects infrared radiation emitted by objects in a room (around 10 μm), almost doubling the insulating property of the window. With all the alluring applications and advantages of tin oxide scientists showed interest in developing the tin oxide thin films by using various preparation methods.

2.2 Preparation of SnO_2 thin films

The methods employed for the deposition of tin oxide thin films are broadly classified into three categories depending on the process used for coating the films. They are physical methods, chemical methods and solution methods.

The physical methods include Physical Vapor Deposition, Laser ablation, pulsed laser deposition, sputtering and many others. Most common methods employed by a number of scientists are pulsed laser deposition and sputtering. Here also these methods are briefly explained. The chemical methods of film coatings are Chemical Vapor Deposition, Spray Pyrolysis. All the chemical methods are widely employed. Solution methods (sol-gel methods) employ dip coating and spin coating to prepare thin films from tin oxide materials.

III. HIGH RPM SPIN COATING EXPERIMENTS

Experiments at higher rpm are in general carried out using commercial spin coaters operating at 3000-5000 rpm. In our investigation, due to the lack of available set up, it was decided to develop a spin coater indigenously and carryout experiments at about 4000 rpm.

3.1 Indigenous development of spin coater

A high speed A/C motor (50W, 230 V, 50 Hz, 19000 rpm,) that is generally used for juice mixers or in coffee shops is used. An aluminum plate is turned into a circular form with dimensions 4 inch diameter. This plate is fixed to the motor using araldite. This set up (fig.10) is securely tightened using plywood planks and fasteners and fixed to a table for sturdiness to eliminate any vibrations that might be possible at high speed operations. Henceforth, this equipment is called SPIN COATER in the investigation. A varying voltage resistor is connected to the motor so that it can run at different rotating speeds by varying the voltage. A minimum of 40 volts is required for the motor to spin. The rpm of the motor can be steadily increased by increasing the voltage applied. At full voltage, the motor attains the full speed of 19000 rpm with no load. A voltage of 60 V is required for the motor to operate at a speed of 4000 rpm. Approximately at 50 V, the aped of the motor is about 3200 rpm and 70 V reaches to about 4800 rpm. In the present investigation, most of the experiments were carried out at a voltage of ~ 60 V with an average speed of 4000 rpm. The advantage of the high speed spinner is that it allows the evaporation of the base alcohol effectively during spinning while the liquid is being spread along the wheel. This will also prevent the liquid from being thrown out of the substrate. Another advantage of the high speed spinner is it can form very thin films according to the equation

$h=h0/ (1+4kh_o2t)$ 0.5 where ho is the film thickness at time t=0 and $K= \rho\omega^2/3\eta$

where ρ is the fluid density ω is the rotation rate measured in rad/sec

Viscosity and density are expected to increase as evaporation progresses, so care is to be taken while applying the equations. Early stages of fluid thinning where evaporation did not become predominant, thinning rate dh/dt= -2kh3

Later when solvent evaporation becomes predominant, at Constant evaporation dh/dt = -2 kh3-e. Where e is the evaporation rate Meyerhofer assumed early stages are as flow dominated while latter stages evaporation dominated. He set transition point at condition where evaporation rate and viscous flow rate become equal.

final thickness (hf) = co[(e/2(1-co)k)]1/3 where co is the concentration of solids in the sol $e=c\omega^{½}$ where c is a constant. Finally $h=A\ \eta 0.45\omega-0.62$

There are spotty patterns (Fig. 2 a) and uneven thickness (Fig. 2 b) of the films.

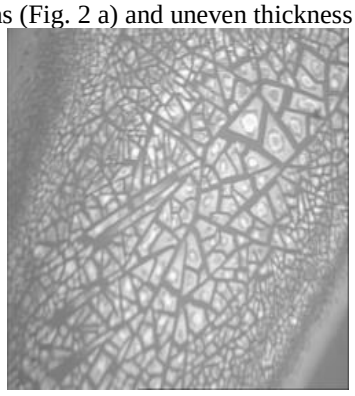

Fig 2 a

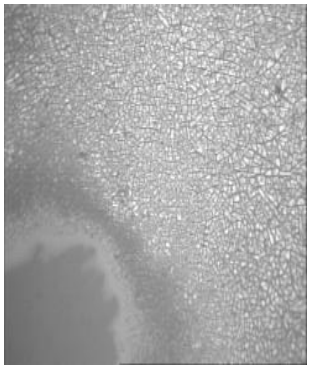

Fig 2 b

Severe cracking in dip coated films after heat treatment at 500°C.

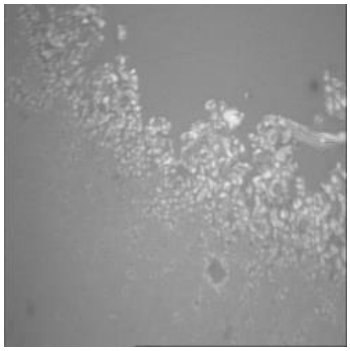

Fig 2 c

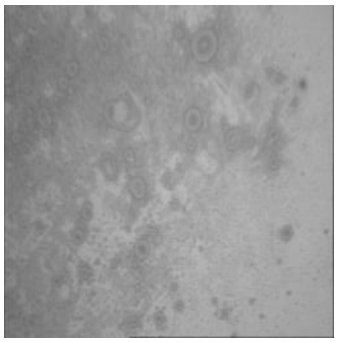

Fig 2 d

Fig 2 Dip coated Films heated to 500ºC

Severe cracks at edges and spotty pattern throughout. Dip coated samples showing both cracked and uncracked regions after heat treatment.

Fig 3 Conventional polishing machine for spin coating the films at low rpm

Fig 4 Fabricated Spin Coater working with motor running at max 19000 rpm

Fig 5 a. as-prepared Sol

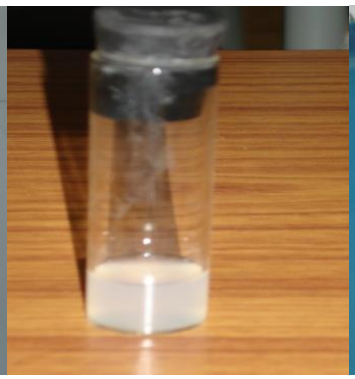

Fig. 5 b. sol aged for 24 hrs

Fig. 5 c. sol aged for 48 hrs

Table 1: Chemicals used for processing

Name of Chemical	Formula	Make	Mol wt	Vol used
Tin(IV) Chloride	SnCl4	LOBA chem	260.50	4 ml
Propane 1 ol	C3H8O	Sd-Fine chem	60.10	36 ml
Propane 2 ol	C3H8O	Lab Rasayan	60.10	24 ml
Acetone	(CH3)2CO	FINAR chem	58.08	-
Water	H2O	Double distilled	-	36 ml
Glass Substrate	Borosilicate	-	-	-

Table 2: The temperature and heat flow during processing

S.No	Temperature (°C)	Heat flow (W/g)
1	55.56	1.261
2	95.16	1.602
3	119.93	2.515
4	133.37	3.761
5	149.63	4.467
6	172.97	3.743
7	192.77	2.786
8	219.64	2.217
9	261.37	1.469
10	295.31	1.126
11	384.42	1.336
12	409.88	1.071
13	484.84	0.5708

IV. RESULTS AND DISCUSSIONS

The results obtained from the experimental investigation during preparation of SnO2 thin films are outlined and discussed in this chapter. The results mainly consist of the conditions under which crack free films were obtained and the path ways to obtain these films are discussed. The results also highlight the formation of sol and its transformations in resulting SnO_2. The significant characterization method employed is optical microscopy with differential scanning calorimetry and UV-Visible spectroscopy.

4.1 Preparation and Composition of the SnO_2 Sol

The ideal reaction taking place during the mixing of isopropyl alcohol and anhydrous tin chloride is

$SnCl4 + 4ROH \rightarrow Sn(OR)_4 + HCl$

However, complete alkoxide formation does not take place and only partial replacement of chloride resulting in partial alkoxide formation to SnClx (OPr) 4-x . The high cost, commercially available tin alkoxides eliminate chlorine completely. But the chlorine is mainly entrapped in the partial alkoxide and will form the sol. Taking in to consideration the addition of propane-1-ol, the solution should be better represented by the formula given SnClx (OPr) 4-x.PrOH. Like many reaction of water and chlorides, this formation also generates heat like acid base reactions. This is the primary reason, why the solution need to be cooled after the addition of proane-1-ol to $SnCl_4$ in the first step of sol formation. Further, when mixture containing proane-1-ol and water is added to the partial Sn-alkoxide, the hydroxide formation will be initiated as per the following reaction:

SnClx (OPr) 4-x + y $H_2O \rightarrow$ SnClx (OH) y (OPr) 4-x-y + yPrOH

If the mean number of unhydrolyzed Sn-Cl bonds is 2, a sol may result consisting of poorly branched SnO_2 particles and/ or linear chains. When the hydrolysis is very much limited, it will allow only the formation of monomers without long chain reactions. If the long chins were to present, a condensation reactions take place with the extension of 3-D network of the sol as shown

R4 yrSn (OH) y + R 4-s Sn (OH)s $\rightarrow$ R4 yr (OH) y-1 Sn-O-Sn R4-x (OH) s-1 + H_2O

Where R indicates the groups different from OH and is strongly hindered for low value of y.

Usually these type of condensation reactions are favoured by the increased hydrolysis as a result of increased water ratio or by the increased temperatures. The latter was observed during aging of the sols at high temperatures as shown in Table 2. Increased time of 48 hours had in fact resulted in a very thick sol that eventually formed in to a paste / powder. Similarly, the addition of amines / ammonia solution resulted in loss of organic network and formation of a precipitate in our experiments. Similar observations were also made by Epifani et al. The last step in sol formation of adding water isopropyl alcohol mixture would only stabilize and complete hydrolysis. The stirring after each of these additions only ensures that the reaction is uniform although.

V. CONCLUSIONS

The result of dip coating is the formation of non uniform and thick films that had usually cracked after thermal treatment at 500^{o}C. Due to the absence of any mechanized systems, the control of the film thickness is very difficult. There is no wonder that the films were non uniform and served only as the first step towards film preparation in assessing the wetability of the sol-substrate interface and their compatibility. To that extent, the experiments with dip coating have served their purpose.

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