STUDIES IN SEMICONDUCTING METAL OXIDES
IN CONJUNCTION WITH SILICON
FOR SOLID STATE GAS SENSORS

Progress Report
for Period April 1, 1977 - September 30, 1979

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ABSTRACT

This report addresses itself to a fundamental investigation of SnO_2 and ZnO thin films with emphasis on their use in solid state gas detection.

Methods of thin film preparation, described here, include the chemical vapor deposition (CVD) technique for SnO_2 films and the radio frequency sputtering technique for SnO_2 and ZnO films.

The use of Auger electron spectroscopy, (AES), transmission electron microscopy, (TEM) and xray diffractometry, (XRD) in the analysis of these films is reported. Careful selection of the most useful films are made by applying these techniques to the films prepared here.

The electrical stability and gas sensitivity response of rf sputtered films are studied in detail. Information regarding the mechanisms involved in gas detection are also presented. Some preliminary device structures using these films along with well-established techniques for planar processing are also reported.

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156 words

SECTION I

OUTLINE OF REPORT

1. Introduction

This is a report on the use of semiconducting metal-oxides in conjunction with silicon for solid-state gas sensors. The project was funded for a period of thirty months by a grant from the Department of Energy (DOE) under contract number EE-S-02-77-4346 and was carried out by an interdisciplinary group of investigators at Carnegie-Mellon University, Pittsburgh. The principal aim of this program is to develop portable solid-state devices capable of detecting any one of several pollutant, toxic and inflammable gasses in the environment at the ppm level.

The promise of semiconducting metal-oxides as suitable candidates in the field of gas detection was recognized in a workshop at Brookhaven National Laboratories several years ago¹. The objectives of the conference were to stress the need for a portable gas-monitoring device which could be sensitive, selective, stable and reproducible on exposure to gases of interest. Such devices were deemed necessary in health-effect studies in order to help legislation on environmental regulatory decisions^{2,3}.

The work reported herein is for the entire period of this research (April 1, 1977- September 30, 1979). The contents of this report serve to outline the progress on the oxides of tin, SnO_2 , and zinc, ZnO , that hold promise as base materials for gas sensors. It aims at an understanding of the mechanisms involved in the preparation and characterization of the material; at an understanding of the electron exchange between

the bulk and surface when the gases to be detected are sorbed (i.e. adsorbed or absorbed) onto the surface; and at the understanding of the current transport of charge carriers in the material. The details of prototype devices that have emerged from this work are also disclosed. Sensitivity to CO and H₂S at the ppm levels is easily obtained. The publications that have appeared on these topics appear in the appendix.

Section II explores the techniques for SnO₂ thin film deposition carried out in our laboratory. These are the chemical vapor deposition (CVD) and the radio frequency sputtering (RFS) methods. The RFS technique forms our main emphasis to date, and has been studied in somewhat greater detail than the CVD process.

Analytical characterization of the material (structure, composition, morphology, etc.) is reported in Section III. We report on the use of Auger electron spectroscopy (AES), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and x-ray diffractometry (XRD) as applied to our films. Such a study is deemed necessary both in the control of film deposition, and in reliability studies to be reported later.

Section IV discusses the gas response of SnO₂ to O₂, H₂ and H₂S. It provides phenomenological details of our experimentation, and some explanation and discussion of these observations.

Section V is a discussion on the preparation and electrical characterization of ZnO films, prepared by the RFS technique. This is followed by a discussion on the gas sensitivity observed on these films in Section VI.

Section VII closes with a discussion of the final devices that have been developed by us.

The specific contributions of this work are:

1. A semi-quantitative understanding of the thermodynamic analysis for the deposition of SnO_2 thin films from the vapor phase.
2. A correlation of the various analytical characterization techniques used to study SnO_2 films, with a major contribution in the use of Auger electron spectroscopy.
3. A dramatic stabilization of rf sputtered films of SnO_2 by adjusting the sputtering environment.
4. A detailed insight into effects on conductivity of off-stoichiometric defect mechanisms in SnO_2 and a means of measuring the same.
5. A semi-quantitative understanding of surface reactions with the semiconductor, mainly the role of oxygen ions.
6. A detailed insight into the correlation of the properties of ZnO thin films with variations in the preparation conditions, such as substrate temperature, power levels, etc.
7. Emergence of sensitive films and integrated device structures capable of detecting 10 ppm levels of trace gases, and providing a possibility of being the portable devices envisaged in this program.

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SECTION II

PREPARATION TECHNIQUES FOR SnO_2 THIN FILMS

1. INTRODUCTION

In the last few years, a large number of papers on tin dioxide, SnO_2 , have appeared in the literature, emphasizing the use of this material in the form of thin films. An important commercial application is in the manufacture of antifrost windshields (as Nesa glass)¹.

The use of this transparent semiconducting oxide as a front contact to photovoltaic devices has received widespread acceptance in recent years. The material possesses the unique properties of good electrical conductivity and high optical transparency over the visible spectrum², both of which are desirable in the manufacture of solar cells.

From the literature, it is evident that there exist a large number of fabrication techniques for SnO_2 thin films. The purpose of of this section is to report on two of these methods, namely the chemical vapor deposition (CVD) process, and the radio frequency sputtering (RFS) technique used in the preparation of the oxide. Current emphasis in the fabrication of SnO_2 films lies with the RFS method. It must be clearly stated, however, that the shift in emphasis should not be interpreted as the superiority of one technique over the other in general. The main reason for the changeover lies in the application of the oxide as a material for solid-state gas sensors.

2. FILM DEPOSITION TECHNIQUES

2.1 The Chemical Vapor Deposition Technique

The most promising techniques discussed in the literature for the deposition of SnO_2 films may be categorized into five broad groups:

- (a) reactive sputtering of tin;
- (b) vacuum deposition of tin or its compounds;
- (c) dc glow discharge methods;
- (d) thermal oxidation of an organometallic solution;
- (e) growth of films by gas phase hydrolysis of stannic chloride SnCl_4 , or of other volatile tin compounds.

The use of reactive sputtering for the formation of closely controlled film thicknesses has been recently reported in a study of solar cells². The SnO_2 layer is formed by sputtering a tin target at dc voltages of 1000-3000V and currents of 10mA. The working gas is a mixture (1:1) of oxygen and argon at 10^{-2} Torr.

In connection with solar cell studies, a method has been investigated in which tin or some of its compounds are evaporated onto a cleaned silicon surface. The wafer is then subjected to a set of post evaporation treatments, yielding tin oxide-silicon junctions that are rectifying in nature^{4,5}.

The dc glow discharge method has been reported by Sabnis⁶ for growing antimony doped films. However, to the best of our knowledge, this technique has not found practical use in thin films.

The thermal oxidation process is the basis of the Nesa technique and finds extensive commercial use, such as in the manufacture of Nesa glass.

The last method, the hydrolysis technique, has been used widely in the formation of single crystals and films of the oxide. The reaction of stannic chloride with water vapor may be represented by the equation:

This section presents a thermodynamic analysis of the above reaction and some of our experimental results. The thermodynamic analysis evaluates the effects of parameters associated with the deposition process and is of assistance in the control of the same. In the next section, the RFS process is discussed.

Figure 1 is an illustration of the experimental setup. The reaction vessel is a quartz tube of 6.5 cm diameter, 12 cm length, modified to provide two gas inlets and the inverted funnel arrangement as shown. High purity liquid SnCl_4 is obtained from Alfa Ventron Corp., Massachusetts. Dry nitrogen is the carrier gas for the SnCl_4 which is heated in a bubbler to 25°C . The flow rate of the carrier gas is typically 75 cc/min. A second bubbler contains water heated to 35°C with oxygen as the carrier gas. A flow rate of 150 cc/min is typical. An inverted funnel arrangement is used to ensure that the reaction is confined to a narrow region of the tube. The substrates are placed in this region on a thin quartz boat which rests on the furnace tube floor. The deposition proceeds on an effective area of 98 cm^2 , part of which belongs to the substrates. The winding of the furnace yields a uniform temperature profile across the deposition area as determined by an alumel-chromel thermocouple. HCl vapor which is the main by-product of the reaction, is neutralized in a sodium bicarbonate solution at the furnace outlet.

At constant temperature and pressure, the change in the Gibbs

Fig. 1 Apparatus for the growth of SnO_2 films using the CVD technique.

1. Quartz tube	2. Oxygen inlet	3. Water	4. Nichrome heater
5. Nitrogen inlet	6. SnCl_4 solution	7. Quartz boat	
8. Electric furnace	9. Thermocouple	10. Sodium Bicarbonate solution	

free energy of a system undergoing reaction (1) may be written as⁷:

$$dG = \sum_{i=1}^4 \mu_i dn_i \quad (2)$$

where μ_i is the chemical potential of the component i and dn_i is the change in the number of its moles. The dn_i 's are related by the mass balance equations:

$$\frac{dn_{\text{SnO}_2}}{+1} = \frac{dn_{\text{HCl}}}{+4} = \frac{dn_{\text{SnCl}_4}}{-1} = \frac{dn_{\text{H}_2\text{O}}}{-2} = d\lambda \quad (3)$$

where λ is called the progress variable of reaction (1). Equation (2) may then be rewritten:

$$dG = \Delta G \cdot d\lambda \quad (4)$$

with

$$\Delta G = (\mu_{\text{SnO}_2} + 4\mu_{\text{HCl}} - \mu_{\text{SnCl}_4} - 2\mu_{\text{H}_2\text{O}}) \quad (5)$$

Equilibrium is reached when the Gibbs free energy reaches a minimum ($dG=0$), consequently, when $\Delta G=0$.

It is convenient to introduce the quantity ΔG° :

$$\Delta G^\circ = (\mu_{\text{SnO}_2}^\circ + 4\mu_{\text{HCl}}^\circ - \mu_{\text{SnCl}_4}^\circ - 2\mu_{\text{H}_2\text{O}}^\circ) \quad (6)$$

which is the value of ΔG when all the reactants and products are in their standard states. Values of ΔG° at temperatures ranging from 300 to 1500 °K are listed in Table I. They were obtained from reference [8] by standard techniques. Subtracting equation (6) from (5) introduces the differences $\mu_i - \mu_i^\circ$ which is readily related to the activity or to the partial pressure of i . At equilibrium:

$$\Delta G^\circ = -RT \ln K \quad (7)$$

where:

$$K = \frac{P_{\text{HCl}}^4 a_{\text{SnO}_2}}{P_{\text{H}_2\text{O}}^2 P_{\text{SnCl}_4}} \quad (8)$$

Values of K are deduced from equation (7) and are also listed in Table I .

Because SnO_2 is pure, its activity, a_{SnO_2} , is equal to 1. We also note that:

$$p_1 = \frac{n_1}{n_g} P \quad (9)$$

where n_g is to the total number of moles in the gas phase and P is its pressure. In the conditions of our runs, P is equal to 1 atmosphere and equation (8) becomes:

$$K = \frac{n_{\text{HCl}}^4}{n_{\text{H}_2\text{O}}^2 n_{\text{SnCl}_4} n_g} \quad (10)$$

Let us identify by a prime ('), the concentrations of the various species at any given time before reaction (1) proceeds. For the experimental conditions described in section (3), we have:

$$p'_{\text{SnCl}_4} = \frac{n'_{\text{SnCl}_4}}{n'_{\text{N}_2} + n'_{\text{SnCl}_4}} = 0.0326 \quad (11a)$$

$$p'_{\text{H}_2\text{O}} = \frac{n'_{\text{H}_2\text{O}}}{n'_{\text{O}_2} + n'_{\text{H}_2\text{O}}} = 0.0473 \quad (11b)$$

and

$$n'_{\text{O}_2} / n'_{\text{N}_2} = 2 \quad (11c)$$

Selecting $n'_{\text{N}_2} = 1$ mole as a relative basis for our calculations, the number of moles n_i at equilibrium are related to the equilibrium value of the progress variable λ by the mass balances:

TABLE I

Temperature dependences of the Standard Gibbs free energy change and equilibrium constant associated with the reaction:

<u>T(°K)</u>	<u>ΔG°(kcal)</u>	<u>K</u>
300	2.22	0.024
400	0.87	0.333
500	-0.54	1.73
600	-2.02	5.59
700	-3.56	13.44
800	-5.16	26.87
900	-6.80	47.46
1000	-8.50	76.62
1100	-10.24	115.7
1200	-12.02	165.8
1300	-13.84	228.6
1400	-15.69	304.6
1500	-17.57	395.0

$$n_{\text{SnO}_2} = \lambda \qquad n_{\text{HCl}} = 4\lambda \qquad (12a)$$

$$n_{\text{SnCl}_4} = 0.0326 - \lambda; \qquad n_{\text{H}_2\text{O}} = 0.0946 - 2\lambda \qquad (12b)$$

$$n_{\text{N}_2} = 1; n_{\text{O}_2} = 2; \qquad n_g = 3.1272 + \lambda \qquad (12c)$$

Consequently, equation (10) yields:

$$K = \frac{(4\lambda)^4}{(0.0326 - \lambda)(0.0946 - 2\lambda)^2(3.1272 + \lambda)} \qquad (13)$$

Numerical solutions for λ yield the deposition rate (moles of SnO_2 per mole of N_2) at various temperatures. The growth rate of the film may then be deduced from the flow rate of N_2 , the molar volume of SnO_2 and the area on which the film is deposited. The reaction may be studied further by allowing for several ratios of the initial concentrations of water vapor to tin chloride:

$$B = n'_{\text{H}_2\text{O}}/n'_{\text{SnCl}_4}. \quad \text{The results are described in Fig. 2.}$$

The results of the calculations presented in Fig. 2 show that although the growth rate of the deposit increases with both temperature and the ratio B, this increase levels off at high values of T and B. Recently, Ghoshtagore⁹ found, experimentally, that in the range 753 to 1080°K and for values of B larger than 4 the growth rate was practically independent of the water vapor concentration. Our calculations are in agreement with this observation.

Figures 3 through 6 show representative films grown in our laboratory using the CVD apparatus, for several different temperatures. For the films in Figs. 3, 4 and 5, the B ratio is held close to 3. The corresponding experimentally observed growth rates at each of these temperatures appear in Fig. 2.

Fig. 2 Equilibrium deposition rate (nm/min) of thin films of SnO_2 as a function of temperature, and with B ($n_{\text{H}_2\text{O}}/n_{\text{SnCl}_4}$) as a parameter. The bars around each experimental point represent the variations in thickness of films prepared at these temperatures.

The film shown in Fig. 3 was produced in 10 minutes at 600°K, with a growth rate of 150 nm/min. The film is clear but exhibits iridescence fringes as a result of variations in uniformity. It is n-type semiconducting in nature with trace impurities of chlorine (as revealed by the Auger electron spectroscopy (AES) technique, discussed later) acting as a possible dopant. Sheet resistivity is of the order of 80-100 ohms/square, and can be modified by post deposition techniques.

Figure 4 is a film produced at 800°K with a growth rate of 180 nm/min. The film is beginning to show a spiked growth characteristic. Resistivities for these films are around 1 Kohm/square.

Figure 5, a film prepared at 1000°K, illustrates large grain sizes. The film growth is around 200 nm/min, but the oxide is virtually insulating in nature.

Figure 6 is an illustration of a film grown at 800°K but with a lower amount of reactants. A more uniform deposit of smaller grain size is obtained. The partial pressure of the SnCl_4 in the gas stream was reduced by cooling the bubbler of liquid SnCl_4 to 0°C. A similar technique has been described by Tabata¹⁰. The growth rate is around 50 nm/min. Our calculations for these conditions again show that the observed growth rate closely approximates the theoretical equilibrium deposition rate yielded by the above equations.

2.2 The Radio Frequency Sputtering Technique

The apparatus for the RFS process consists of a Perkin-Elmer three-target sputtering system, equipped with power splitting facilities (Randex Model 2400-6J). The RF power supply is coupled to the anode (substrate) - cathode (target) assembly through a tunable impedance

Fig. 3: SnO_2 film on Si.
 $T = 600^\circ\text{K}$, 10 mins.
deposition time (x5000)

Fig. 4: SnO_2 film on Si.
 $T = 800^\circ\text{K}$, 10 mins.
deposition time
(x5000)

Fig. 5: SnO_2 film on Si.
 $T = 1000^\circ\text{K}$, 10 mins.
deposition time (x5000)

Fig. 6: SnO_2 film on Si.
 $T = 800^\circ\text{K}$, 10 mins.
deposition time,
source limited growth
(x5000)

matching network. The output of the RF generator is limited to 1 KW power at a fixed frequency of $13.56 \text{ MHz} \pm 2 \text{ KHz}$. The sputtering is performed in a plasma composed of high purity (five 9's) argon and/or oxygen mixtures in dynamic equilibrium within the system. A total pressure of 25mTorr (1 Torr=132 Pa) during the sputtering process is typical. A He closed cycle cryopump routinely provides a base pressure of 5×10^{-7} Torr prior to a sputter; residual impurity gases are thus kept to a minimum in the background. The target, from which the films are deposited, is made by sintering a 7.5 cm pressed sample of SnO_2 . The powder used in making the sample is of high purity (99.99%) and was obtained from Alfa Ventron Corporation, Massachusetts.

Table II summarizes the data for the deposition parameters that were used in the preparation of the films reported here. The substrates are placed on a water cooled table, and a chromel-alumel thermocouple is used to monitor the temperature rise during the deposition. A maximum temperature of about 100°C was recorded in all our experiments. Depending on the composition of the mixture in the sputtering chamber, the time for the deposition is varied in order to keep the film thickness around $6000 \text{ \AA}$. The curves in Fig. 7 illustrate the rate of deposition of SnO_2 films in a plasma of pure oxygen and pure argon for a power level of 500 W.

The higher deposition rate in pure argon is expected in view of the greater mass of this ion in comparison to that of oxygen.

For a mixed environment, the deposition rate falls in between the above rates.

The analytical characterization of these films is reported in the next chapter.

Fig. 7 SnO_2 deposition rates in pure argon and pure oxygen plasmas. The power applied to the target is 500W.

TABLE II

DEPOSITION PARAMETERS FOR SnO_2 FILMS

Power level	500W
Substrate-target distance	7 cm
Substrate temperature	100°C
Plasma composition	Ar/ O_2 mixture for samples 2-5
Target	SnO_2 disc 7.5 cm diameter
Dark shield opening	5 cm diameter

3. CONCLUSIONS

From the foregoing, it is concluded that the growth of thin films of SnO_2 from the hydrolysis reaction between SnCl_4 and H_2O proceeds essentially under equilibrium conditions. Good agreement is observed between theory and experiment, allowing the prediction of growth rates as a function of the input reactant ratios and temperatures. the deposition rate is a sensitive function of the temperature, T , and the ratio, B , of H_2O to SnCl_4 but levels off at large values of the two parameters, in agreement with the experimental results of other studies.

Increasing temperatures, however, leads to uneven films with large grain sizes, and causes a decrease in the conductivity of the material.

Smooth transparent films with a sheet resistivity of 80 ohms/square are obtained at 600°K with a growth rate of 150 nm/min. Even lower conductivities are possible by incorporation of dopants within the film although such studies have not been conducted in depth in our laboratory.

Somewhat lower deposition rates are obtained with the RFS technique. However, as will become evident in the subsequent chapters, this is a versatile technique that permits control over the thickness and resistivity of the material being deposited. We have observed a remarkable change in the resistivity of as-sputtered films of similar thicknesses, merely by changing the oxygen content within the sputtering ambience.

Films prepared in a plasma of pure oxygen show low sheet resistance, and are more stable than films prepared in other atmospheres.

Analytical characterization of these films reveal the grain size to be around 200 Å. Debye-Scherrer rings are obtained from a diffraction analysis indicating the polycrystallinity of the films. These films form the backbone of all our further studies.

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SECTION III

ANALYTICAL CHARACTERIZATION TECHNIQUES

1. INTRODUCTION

Until a few years ago, the solid state engineer was concerned mainly with the bulk properties of semiconductors. Very often these materials existed in the form of single crystals, and the characterization techniques were relatively straightforward. The recent shift to polycrystalline and amorphous combinations of single, binary, ternary and even quaternary compounds has brought with it a bewildering host of characterization tools.

The choice of any particular technique is often dictated by a number of considerations. In the case of thin films, this includes considerations of the area and depth of sampling, the sensitivity of the instrument and the number of detectable elements. Frequently, however, the ultimate decision is made according to the financial constraints imposed by these instrumental techniques. Table I lists the features of some of the common equipment in use today.

The purpose of this chapter is twofold. First, it provides a background on the analytical methods employed in our studies of SnO_2 films. These include Auger electron spectroscopy (AES), x-ray diffractometry (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Second, we present the results obtained from an application of these techniques to thin films of SnO_2 . The

TABLE I

SURVEY OF METHODS FOR SURFACE AND THIN FILM ANALYSIS ¹

Method	Probe Diameter μm	Sampling Depth Atomic Layers	Optimum Detection Sensitivity (ppm atomic)	Reproducibility (%)	Coverage of Elements	Special Features
Ion Probe Microanalysis	1-300	10-1000	0.1-100	<u>+2</u>	Nearly Complete	Semi-quantitative, three-dimensional conc. profile
Auger Electron Microscopy	25-100	2-10	0.01-0.1%	<u>+20</u>	Nearly complete	Semi-quantitative, three-dimensional conc. profile
"SAM" Scanning Auger Microanalysis	4-15	2-10	0.1-1%	<u>+20</u>	Nearly complete; No H, He	Semi-quantitative, three-dimensional conc. profile two dim'l auger images
"XPS", Xray Photoelectron Spectroscopy ("ESCA")	10	2-10	0.1-1%	<u>+20</u>	Nearly complete No H, He	Semi-quantitative, valence states

details of TEM, SEM and XRD techniques will only be touched upon since a large amount of information exists on them in the literature. The AES technique, however, has gained prominence only in the last few years, and will be discussed at some length. It is here that we have made some of our contributions to the literature.

2. AUGER ELECTRON SPECTROSCOPY

The Auger effect, discovered as early as in 1925, bases itself on the interaction of a primary excitation with the electronic shells of an atom. Briefly, an electron (or ion or photon) incident on a solid surface ionizes an atom by removing a tightly bound electron, thereby rendering the host atom in an active state. The atom may now return to its initial ground state by emitting a photon (an effect known as fluorescence); alternatively, it may impart its excess energy to another electron in a loosely bound state causing it to be ejected away from the atom (Fig.1). This electron is known as the Auger electron, and possesses a definite energy depending on the atom from which it was ejected.

Numerous papers describe the factors which must be taken into account in calculating the energies of the Auger electrons¹⁻⁶. It is well agreed that if the primary beam excites an electron from the A level to the B level, and thereupon liberates an electron from the C level, then as a first approximation:

$$E_{ABC}(z) = E_A(z) - E_B(z) - E_C(z) - \Delta E_C(z) \quad (1)$$

where $\Delta E_C(z) = \Delta z E_C(z+1) - E_C(z)$, and z refers to the atomic number.

Fig. 1 Schematic illustration of the $K-L_1, L_{2,3}$ Auger process. The electron energy levels are measured with respect to the Fermi level. (After Chang⁵)

Chung and Jenkins⁶, show that the case E_{ABC} and E_{ACB} , although indistinguishable by quantum mechanical considerations (since the initial and final states are identical in both cases), result in different values of the electron energies when equation (1) is used. To overcome this difficulty, they suggest an averaging technique:

$$E_{ABC}(z) = E_A(z) - E_B(z) - E_C(z) - \Delta z' [E_B(z+1) - E_B(z)] - [\Delta z' E_C(z+1) - E_C(z)] \quad (2)$$

where $\Delta z'$ is a parameter that must be adjusted to the experimental data. For transitions other than of the type KLL a good value for this parameter is $1/2$ ⁶.

For a transition of the type ABV where V is the valence level referred to the Fermi level, equation (3) becomes:

$$E_{ABV}(z) = E_A(z) - \frac{1}{2} [E_B(z) + E_B(z+1)] - E_V \quad (3)$$

while for transitions of the type AVV the equation is

$$E_{AVV}(z) = E_A(z) - 2E_V \quad (4)$$

Energies of various Auger transitions (in tin) computed from equations (2) to (4) are presented in Table II, along with the spectroscopic observations from the spectra of Fig. 2. The energy levels for the ground state of each element was obtained from reference [7]. The Auger plots were obtained from high purity specimens of Sn (99.999), SnO (99.99) and SnO₂ (99.99) from Alfa Ventron Corporation. Pure MgO crystals were used as the O₂ reference as outlined in [7].

Auger spectra may be analyzed quantitatively by expressing the Auger current from an electron transition ABC of the jth element $I_j(ABC)$

TABLE II

AUGER TRANSITIONS AND SPECTROSCOPIC OBSERVATIONS
FOR Sn PEAKS IN Sn, SnO AND SnO₂

Auger Transition Levels	E _{cal} eV	E _{observed} eV		
		Pure Sn	Sn in SnO	Sn in SnO ₂
N _{4,5} ^{VV}	20	15		
M ₅ N ₁ N _{4,5}	313	312	310	306
M ₄ N ₁ N _{4,5}	321	320	318	313
M ₅ N _{2,3} N _{4,5}	364	363	362	359
M ₄ N _{2,3} N _{4,5}	372	412		
M ₅ N _{4,5} N _{4,5}	430	426	423	419
M ₄ N _{4,5} N _{4,5}	438	433	431	426
M ₅ N _{4,5} ^V	456	456	452	448
M ₄ N _{4,5} ^V	464	464	460	457

Fig. 2 Reference Auger spectra from high purity Sn foil (a) SnO powder (b) and SnO₂ powder (c).

as a product of a number of factors. These include the concentration of the j th element x_j , the average electron escape depth, ionization cross-section, surface roughness, etc. among others⁵. Since little is known about each of these parameters, it is convenient to denote I_j (ABC) as:

$$I_j \text{ (ABC)} = I_j^{\circ} \text{ (ABC)} x_j f(x_j) \quad (5)$$

where I_j° (ABC) denotes the standard Auger current of the j th element and equals I_j (ABC) when $x_j f(x_j) = 1$. Here $f(x_j)$ is a concentration dependent factor varying linearly with x_j . Because of the uncertainty involved in each of the above-mentioned factors that contribute to the Auger current, an empirical approach is often applied to express the concentration of one component in a binary system. This takes the form:

$$x_1 = I_1 / (I_1 + I_2 \beta) \quad (6)$$

in which β is a relative sensitivity factor given by:

$$\beta = \frac{I_1^{\circ} f(x_1)}{I_2^{\circ} f(x_2)} \quad (7)$$

If we assume the Auger current I_j to be a linear function of x_j so that $f(x_j) = 1$, and use the values of I_j° for the Sn peak at 426 eV, and the oxygen peak at 510 eV, x_{Sn} is computed to be 0.50 for SnO, and 0.40 for SnO₂. The former is in perfect agreement with the stoichiometric ratio while the latter is somewhat high. If, however, we relax the restriction on $f(x_j)$, and compute β from the data for SnO, x_{Sn} may then be calculated for SnO₂. Such an analysis yields a value of x_{Sn} in SnO₂ to be 0.35, in fair agreement with the stoichiometric ratio of 0.33. We also note from the available data that the ratio of the Sn to O₂ peak heights is around 1.64.

In addition to the detection of elements, AES also provides information about the chemical states of the various species. This is obtained from the shifts in the peak positions, brought about by the binding energies in the material^{4,5}. From the curves in Fig. 2 we resolve a shift of about 3 eV for the SnO peaks, and about 6 eV for those of SnO₂.

3. TEM, SEM AND XRD STUDIES

As mentioned in Chapter 2, tin oxide crystallizes in the tetragonal rutile structure of 6:3 co-ordination⁸. Each tin atom is at the center of six oxygen atoms located approximately at the corners of a regular octahedron, and every oxygen atom is surrounded by three tin atoms placed at the corners of an equilateral triangle. Lattice parameters for the unit cell are $a=b=4.737 \text{ \AA}$, and $c=3.185 \text{ \AA}$. The angles $\alpha=\beta=\gamma=90^\circ$ ⁹. The symmetry of the structure is $p4_2/mmm$ ¹⁰. From geometric considerations, the Bragg angles for this material is given by¹¹:

$$\theta = \sin^{-1} \left\{ \frac{1.5405}{2} \sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{b^2}} \right\} \quad (8)$$

Table III compiles the information on d-spacings, Bragg angles and interplanar distances for the oxide. The most intense peak is in the (110) direction.

In the next section, we present the results from our analytical characterization of the thin film prepared at CMU.

4. ANALYTICAL CHARACTERIZATION OF SnO₂ THIN FILMS

The details of the RF sputtering technique have been outlined earlier. Briefly, film deposition is carried out in a Perkin-Elmer three target system (2400-6J) on 6mm x 6mm quartz substrates,

TABLE III

DIFFRACTION SPECTRUM DATA FOR SnO_2

$d(\text{\AA})$	$I/I_0(\%)$	$2\theta(\text{degrees})$	(h k l)
3.35	100	26.605	110
2.644	80	33.889	101
1.765	65	51.804	211
2.369	25	37.980	200
1.675	18	54.798	220
1.439	18	64.760	112
1.415	16	66.010	301
1.498	14	61.928	310
1.215	12	78.766	321

Structure: Tetragonal $a=b= 4.738 \text{ (\AA)}$
 $c= 3.188 \text{ (\AA)}$

as well as on substrates coated with a thin layer of amorphous carbon. (The carbon layer provides the possibility of taking the films off the substrate for electron microscopy studies). The sputtering is performed in a plasma composed of high purity argon-oxygen mixtures at a total pressure of 25mTorr (1 Torr $\sim$ 132 Pa) in the system. The target used for the purpose is made from hot-pressed SnO_2 powder. The forward RF (13.56 MHz) power applied to the target is around 500 Watts; the typical temperature rise of the substrates, during deposition, is around 100°C . The film thickness is around $400 \text{ \AA}$.

The films prepared by the above technique are characterized by several complementary methods for information regarding the grain size, the structure and the composition. Some of these are:

(a) Morphology

Films are studied for their grain size using transmission electron microscopy (TEM). The sample preparation for such studies is fairly elaborate, requiring the selective etching of a wedge in $\langle 100 \rangle$ oriented silicon.

Electron microscopic investigations show (Fig. 3) continuous films, in most cases, consisting only of one layer of crystallites. The diffraction pattern (Fig. 5) gives indication of a continuous distribution of fine crystalline material. No preferred orientations are discovered in these films. Dark field imaging (Fig. 4) with the first ring of the SnO_2 diffraction pattern (110), allows further study of some of the crystals in greater detail. The analysis shows these to contain a high density of twins and stacking faults. The crystallite size varies between 80 and $250 \text{ \AA}$, with the majority of these in the range of 200 and $250 \text{ \AA}$ in diameter. These figures are typical of all our films.

Fig. 3 Bright field TEM image of 400 Å thick SnO₂ films prepared by rf sputtering

Fig. 4 Diffraction pattern for the film in Fig. 3

Fig. 5 Dark field TEM image of the film in Fig. 3. Twin boundaries and stacking faults are clearly visible.

Powder Diffraction Spectrum

(a) SnO_2 target

Fig. 6(a) XRD on SnO_2 target used to prepare thin films by the sputtering process. The numbers refer to Bragg angles (2θ)

(b) Structure

All films are further studied for their structural information by means of a conventional x-ray diffractometer. The observed peaks agree well with those of pure SnO_2 as defined in the ASTM card 21-1250. Figure 6b, a plot from the x-ray diffractometer, was obtained on one of the samples and is typical of our films. The broadening of the peaks is thought to be caused by a strain in the lattice due to the preparation conditions. The plot of Fig. 6a shows the corresponding peaks for the SnO_2 target used in all depositions.

(c) Composition

Elemental composition on the films is obtained by means of Auger Elemental Spectroscopy (AES). The Auger peaks for SnO_2 are compared with those of the individual elements, Sn and O_2 to provide an estimate of the composition in the material. Both experimental and theoretical considerations for the ratio of the Sn peak at 430 eV to the O_2 peak at 510 eV in SnO_2 , show this to be around 1.60. The theoretically derived ratios are based on the Auger transitions of the type ABC, ABV and AVV, using the equations of reference [6]. Here A,B,C represent energy levels below the Fermi level, while V is the energy of the valence band also referred to the Fermi level. Figure 7 shows a typical Auger spectrum for SnO_2 films. We also observe a shift in the above Sn line by about 6.5 eV. As outlined earlier, chemical shifts in the Auger spectrum are indicative of the binding energies in the material, which, our observations suggest, are comparable to the energy of formation of SnO_2 ($\sim 128 \text{ kcal} = 5.6 \text{ eV}$ at 300°K)⁵. These results have not appeared elsewhere to the best of our knowledge.

(b) Sputtered Film

Fig. 6(b) XRD on sputtered SnO_2 film. The widening of the peaks is due to strain in the lattice from the preparation conditions.

The films, for the most part, show an oxygen deficiency. Auger analysis of CVD films, reported in detail in the master's thesis of this author, show the presence of large amounts of chlorine. This fact probably accounts for the films' high conductivities since the incorporation of chlorine in an oxygen site within the crystal lattice liberates an electron to the conduction band, i.e., chlorine acts as a dopant.

In the next chapter, we discuss the electrical characteristics of our films. Their gas sensitivity response is also presented, along with a macroscopic explanation for the observed sensitivity.

5. CONCLUSIONS

Thin films of SnO_2 , 400 Å in thickness, prepared by the radio frequency sputtering technique, have been studied in detail for information regarding their structure, morphology, grain size and composition. In this context, the most useful analytical tools are x-ray diffractometry, scanning and electron microscopies, and Auger electron spectroscopy, respectively.

The results so obtained, show the films to consist of a fine layer of crystallites, with an average grain size of 200 Å. They are polycrystalline in nature, and exhibit defects such as twins and stacking faults. Auger analysis shows these films to consist of tin and oxygen. When compared to the spectrum obtained from stoichiometric samples, all films exhibit a deficiency in the cation sublattice (i.e., a large number of oxygen vacancies are to be expected).

CVD prepared films contain chlorine, perhaps as a by-product of the reaction from which they are prepared. Scanning electron microscope studies of these films (shown in Chapter 3), reveal large grain sizes.

Reproducibility is a definite problem, since the process is very sensitive to changes in any one of the large number of operating parameters such as temperature, flow rate, etc. Furthermore, the presence of chlorine makes it very difficult to control film property, and often masks out the gas response of the material. We have found the RFS technique to be more reproducible in the preparation of these films, and, as far as we are able to ascertain, they are free from impurities. Accordingly, the next chapter will be devoted to the results of electrical characterization on RFS films.

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SECTION IV

ELECTRICAL CHARACTERIZATION TECHNIQUES

1. INTRODUCTION

Electrical conductivity in undoped samples of tin dioxide, SnO_2 , is known to be due to electrons arising out of a deviation from stoichiometry in the material composition. These deviations are caused either by oxygen vacancies or by tin interstitials, both of which act as donors^{1,2}. In the former case, a $1/6$ dependence of resistivity on the oxygen partial pressure is expected for doubly ionized oxygen vacancies. For tin interstitials, however, the variation in resistivity follows a $1/5$ dependence.

Defect reactions in undoped SnO_2 samples may be described in terms of the Kroger-Vink notations³. Thus for oxygen vacancies we have:

Here V_o'' denotes a doubly ionized oxygen vacancy, while $\text{V}_\text{o} \cdot$ is a singly ionized vacancy. The mass action law applied to the above yields:

$$K_1 = [\text{V}_\text{o}''] [e]^2 p_{\text{O}_2}^{1/2} \quad (4)$$

$$K_2 = [\text{V}_\text{o}''] [e] / [\text{V}_\text{o} \cdot] \quad (5)$$

$$K_3 = [\text{V}_\text{o} \cdot] [e] / [\text{V}_\text{o}] \quad (6)$$

Charge neutrality conditions within the material dictate that:

$$[e] = [V_o^\bullet] + 2 [V_o^{\bullet\bullet}] \quad (7)$$

From equations (4), (5) and (7), one readily has:

$$[e]^3 = \frac{K_1}{p_{O_2}^{1/2}} \left[2 + \frac{e}{K_2} \right] \quad (8)$$

In accordance with the results of reference [2] wherein it is concluded that $[V_o^{\bullet\bullet}] \gg [V_o^\bullet]$ equation (8) yields:

$$[e] = (2 K_1)^{1/3} p_{O_2}^{-1/6} \quad (9)$$

Assuming the electronic mobility to remain constant, equation (9) becomes:

$$\sigma = K'_1 p_{O_2}^{-1/6} \quad (10)$$

which is the familiar 1/6 rule referred to earlier. In all these equations, the K's are equilibrium constants.

It may be mentioned that for the other case i.e. $[V_o^\bullet] \gg [V_o^{\bullet\bullet}]$, a 1/4 dependence of the conductivity is expected.

Some of the above ideas have indeed been verified by electrical measurements for single crystals of the oxide^{2,4}. However, little is known at the present time about the defect mechanisms in polycrystalline films. This, perhaps, is due to the complications introduced by intergranular potential barriers, which arise out of stoichiometric differences between contacting grains⁵. Our observations of twin boundaries and stacking faults merely add to the complexity of the problem. A semiquantitative approach on this topic is described in the appendix.

In this chapter, we report on the use of electrical and analytical techniques to explain some of the dramatic results obtained on RFS films. The first half of the chapter deals with routine studies of films prepared in various gas ambients within the sputtering system. Careful selection of the films are made from these tests. Finally, we report on their gas sensitivities to oxygen and hydrogen.

2. ELECTRICAL CHARACTERIZATION OF SnO_2 FILMS

Electrical studies are carried out in two steps for all films. The first step, performed at room temperature, is designed to provide a rough estimate of the resistivity of the film before any gas tests are conducted.

Figure 1 shows the resistivity of the as-sputtered SnO_2 films as a function of the oxygen content [%] in the sputtering system. The resistivity value of the films prepared in pure argon tends to drift around and is not typical. However, the nature of the remaining portion of the curve in this figure has been confirmed by us on several occasions.

An Auger depth study was conducted on two of the films, one prepared in pure oxygen, and the other in a 50% oxygen environment. Figures 2 and 3 show, respectively, the Auger spectra and the depth profile of the tin and oxygen concentrations in the film. As can be seen, the film prepared in pure oxygen has a uniform concentration extending from the surface to the bulk; however, the other film shows a lower Sn/O_2 ratio for the surface, indicating that the surface is richer in oxygen than the bulk. The curvature in the figure for the first few angstroms of the material further indicate a variation in film composition.

Fig. 1 Variation of room temperature resistance of as-sputtered SnO_2 films as a function of the oxygen percentage in the sputtering plasma

Fig. 2 Auger spectra for rf sputtered samples
 (a) pure oxygen sputtered film
 (b) 1:1 oxygen: argon sputtered film. In each figure, a spectrum of the surface [1] and of the bulk [2] ($\sim 1500 \text{ \AA}$) is shown

Fig. 3 (Auger depth analysis) Concentration profiles of Sn and O₂ in as-sputtered films prepared in a plasma of 100% (●) and 50% oxygen (■). The slope of the curves is due to a drift in the recording equipment.

We decided to test the electrical stability of these films by heating them at 250°C in synthetic air. Both TEM and AES were used in the analysis of their composition and structure before and after the heating.

The curves in Fig. 5 show the change in film resistance (change in resistance, ΔR /initial resistance, R_i) as a function of time. As can be seen, the best stability is exhibited by films sputtered in pure oxygen.

Figures 3 and 4 show a depth profile of the Sn and O₂ concentrations in samples prepared with 50% and 100% O₂ in the sputtering plasma. The former is the concentration used by many researchers.

The results of Fig. 3 are obtained on unheated samples, while Fig. 4 shows the corresponding results on specimens that had been heated.

All depth spectra are measured by sputtering through successive layers with an argon ion beam attachment. Earlier work, conducted here and elsewhere^{6,7} have shown that there is no appreciable reduction of the oxide under the prolonged ion bombardment.

From Figure 3 we conclude that films prepared in pure oxygen possess a uniform composition extending from the surface to the bulk. For the other film, however, this is not true. When compared with the Auger spectra obtained from a stoichiometric SnO₂ sample, it is found that both these films are oxygen deficient.

Figure 4 illustrates that the main changes in sample composition, due to heating, occur in the first few layers (~ 400 Å). Further, the Sn/O₂ ratio for the surface layers is lowered, indicating a decreasing concentration of oxygen vacancies in this region. Consequently, the conductivity of this region is appreciably lowered. In both

Fig. 4 As in Fig. 3, but for films heated at 200°C in air for a few hours. Note the changes in the first $400 \text{ \AA}$ of each film

Fig. 5 Showing the change in resistance vs. time for sputtered films heated in air. The numbers correspond to the preparation conditions in Fig. 1.

these films, the bulk oxygen concentration is also increased, although the change for the film sputtered in pure oxygen is somewhat lower.

TEM studies on specimens heated from 10 minutes to 70 hours at a higher temperature ($\sim 350^{\circ}\text{C}$) show little change in the grain size or structure of the film. Thus morphological changes in the material may be ruled out.

Because the films prepared in 100% oxygen in the sputtering ambient show the best stability, we have confined our attention to devices made by this process.

3. GAS SENSITIVITY TESTS

The films prepared by the above technique are studied in detail for their response to oxygen and to hydrogen. The former is useful in an elucidation of chemisorption processes while the latter yields information regarding the mechanisms involved in gas detection. Such tests are carried out both at sub-atmospheric pressures.

The sub-atmospheric tests are carried out in a vacuum system that can be pumped down to 2×10^{-6} Torr. The volume of the system is such that 1 cc of a known gas at STP causes a partial pressure of 20 μm . Electrical feedthroughs provide a means of studying the devices (Fig. 5).

Measured parameters for a typical test are the ambient gas pressure, film resistance, heater current and the time intervals at which the measurements were taken.

The device itself is in the form of a square 6 mm x 6 mm in size. Aluminum stripes serve as ohmic contacts (Table I). The film is 6000 Å thick. The choice of resistance as a measurement parameter arises out of the phenomenological observations in these films viz:

TABLE I
OHMIC CONTACTS TO STANNIC OXIDE (SnO_2)

Reference Number	Investigator	Sample	Material Used
13	Kohnke (1962)	Natural Stannic Oxide Crystals	Indium-Gallium Amalgam (0°C and above)
14	Loch (1963)	Polycrystalline bars $0.5 \times 0.5 \times 5$ cms	Spring Contacts, Pt
15	Sinclair and Peters (1963)	Polycrystalline films (reactive sputtering)	Silver Paste fired @ 500°C (finely divided silver and 8 w/o glass in Amylacetate and cellosolve acetate)
16	Marley and Dockerty (1965)	Single crystals $< 574^\circ\text{K}$	Indium metal applied ultrasonically. Necessary to "form" contacts electrically (Hall)
17	Morgan & Wright (1966)	Single crystals	4 probe measurement with platinum paste (current) and voltage probes were pressure contact of fine platinum wire
18	Kajimaya and Furukawa (1967)	SnO_2 heterojunction	Silver paste
19	Van Daal (1968)	Polycrystalline tablets	Pt - Au paste Ag - In alloy Ag - Sn mixture
4	Fonstad & Rediker (1971)	Schottky diode Au-SnO_2 Hall samples $< 625^\circ\text{K} (325^\circ\text{C})$	Indium as ohmic contact to SnO_2 Indium was used for current contacts on the bar end. Four voltage probes .05mm dia. gold wires
20	Fillard & J.C. Manificier (1970)	SnO_2 -Si hetero-junctions	Silver paste or vacuum deposited Ag film
21	General Monitors (1973)	Thin films	Pt or Au (Noble metals)

a change in the ambience causes a change in the film resistance.

Figure 6 is the result of tests performed in an ambience of oxygen. The sample had been heated for a few minutes at the indicated temperature, in vacuum, prior to the introduction of oxygen.

The curves of Fig. 7 show the dynamic response of the detector to hydrogen. Each curve is generated by first allowing the sample to come to equilibrium in a known background concentration of oxygen. Note that the hydrogen partial pressure remains constant in this experiment.

Tests at atmospheric pressure are conducted in a dynamic flow system. Oxygen and nitrogen are mixed outside the test chamber in proportions sufficient to create synthetic air, while the hydrogen concentration is varied by changing the flow rate. The result of such a test is shown in Fig. 8. The difference between these results and those obtained in Fig. 7 are borne out later.

The time dependence of conductivity of the sample can be derived by assuming a dilute system of oxygen surface states. This seems to be possible on grounds of the Weisz⁸ condition, which places a limit of 10^{12} chemisorbed surface ions. Since a crystal surface has between $10^{15} - 10^{16}$ (per cm^2) surface sites⁹, the assumption of little or no interaction between the chemisorbed species seems plausible in the early stages of the reaction. This is the basis of the Elovich¹⁰ equation.

Assuming that the rate of change in the chemisorbed density is related to the number of oxygen ions already present on the surface, we may write

$$\frac{d[O_2]}{dt} = \alpha e^{-\beta [O_2]} \quad (11)$$

Fig. 6 Oxygen tests on SnO_2 sample. The specimen was heated for 1 hr. at 600°K in a vacuum of 2×10^{-6} Torr before the tests. The temperatures and pressures are: 1. $400^\circ\text{K}/200\mu\text{m}$, 2. $500^\circ\text{K}/200\mu\text{m}$, 3. $600^\circ\text{K}/200\mu\text{m}$, 4. $500^\circ\text{K}/1000\mu\text{m}$, 5. $600^\circ\text{K}/1000\mu\text{m}$

Fig. 7 Fractional change in resistance of the SnO_2 samples as a function of time. The curves are generated at different temperatures and oxygen partial pressures as indicated. In each test the partial pressure of H_2 remains constant at $20\mu\text{m}$. The O_2 pressures are: 1. $200\mu\text{m}$, 2. 1 Torr, 3. 10 Torr, 4. 20 Torr, 5. 70 Torr, 6. 200 Torr, 7. 700 Torr

Fig. 8 Fractional change in conductance of SnO₂ sample as a function of H₂ concentration. The measurements are carried out in synthetic air at room pressure

Integration of equation (11) with the initial condition $[O_2] = [O_{2(o)}]$ at time $t = 0$ then gives:

$$[O_2] = 1/\beta \ln [\alpha\beta] t + \frac{1}{\alpha\beta} e^{\beta(O_{2(o)})} \quad (12a)$$

$$= 1/\beta \ln [(t + t_o) + \gamma] \quad (12b)$$

If we assume that the dominant charge transfer is such that each molecule of O_2 draws one electron from the bulk layers, then

$$[e] = [O_2] \quad (13)$$

The resistivity of the material at a fixed temperature may then be approximated by:

$$\rho(t) \propto [O_2] \quad (14)$$

with the implicit assumption that the mobility does not vary during the experiment.

From a combination of the above equations one has:

$$R(t) = A \log (t + t_o) + B \quad (15)$$

Here A and B are constants that depend on the temperature¹⁰, while t_o is an offset due to the initial conditions. Similar observations have been made by Matthews¹¹ et al., on sintered samples of SnO_2 . Figure 9, which is a plot of the data in Fig. 7, but on a semilog scale, endorses the above ideas.

The assumption that O_2^- is the dominant adsorbed species is valid only under certain temperature ranges. Studies of Electron Spin Resonance (ESR)¹² on ZnO surfaces indicate that the surface species go from $O_2^- \rightarrow O^- \rightarrow O^=$ with increasing temperatures. The transition is somewhat abrupt.

Fig. 9 The data of Fig. 6 replotted on a semi-log scale. The straight line nature of the plot indicates a surface reaction in accordance with the Elovich equation

An Auger analysis of the above sample both before and after this test, shows that the main changes on the film occur at the surface. The bulk is relatively unaffected.

Results of hydrogen tests bring out the role of surface reactions somewhat more clearly. A quasi-chemical reaction may be written between the adsorbed O_2^- species and the hydrogen as follows:

The sum of these is the reaction:

At equilibrium, the law of mass actions applied to the above yields:

$$K = \frac{[H_2O]^2 [e]}{[H_2]^2 [O_2^-]} \quad (18)$$

For low H_2 concentrations, the surface oxygen concentration O_2^- may be treated as a constant in (18). The stoichiometric ratios involved in [17] further suggest that:

$$[H_2O] = \frac{1}{2} [e] \quad (19)$$

From equations (17), (18), and (19) one has:

$$[e] \propto [H_2]^{2/3} \quad (20)$$

Again, assuming the mobility to remain constant, one arrives at the important result for the conductivity change as:

$$\frac{\Delta G}{G_i} = C [H_2]^{2/3} \quad (21)$$

where $\Delta G = G_{\text{final}} - G_{\text{initial}} = G_f - G_i$ and C is a constant.

Equation (21) can be modified for the case where the hydrogen molecules merely dissociate on the surface without any interaction with the adsorbed oxygen species. Under these conditions,

$$\frac{\Delta G}{G_1} = D [H_2]^{1/4} \quad (22)$$

Such a situation can arise when the number of oxygen atoms on the surface is small.

Figure 10 is a plot of the data of Fig. 7 on a log-log scale. We note that the slope of the curve is $\sim 1/4$, as suggested by equation (22).

Figure 11 similarly plots the data of Fig. 8 on a log-log scale. Again, the close conformity to equation (21) is brought out.

4. DISCUSSION

From a practical viewpoint, a detector is useful only if it is able to sense the desired trace gas in the presence of other background gases; in our case this background is air. However, from the foregoing it becomes apparent that any trace gases which react with the surface oxygen on SnO_2 can cause a change in the resistance of the material. Thus a means of achieving selectivity (and not only sensitivity) must be incorporated in an SnO_2 based device. At present, we have successfully used zeolite molecular sieves in our laboratory to discriminate between the effects of H_2 and H_2S on a commercial SnO_2 sensor operating in air (Taguchi sensor from Figaro Engineering Co., Japan). This is shown in Fig. 12. The zeolite sieve used for this purpose had a $3 \text{ \AA}$ pore size, thus blocking out the H_2S response from that of H_2 . Current research is aimed at exploring means of depositing the zeolite sieves in the form of thin films so as to be

Fig. 10 Log-log plot of the data in Fig.7. The slope of the curve suggests a dissociation reaction as in Equation (22)

Fig. 11 Log-log plot of the data in Fig. 8. The slope of the curve suggests an interaction of H_2 with the surface oxygen as in Equation (21)

Fig. 12 Showing the discrimination of the H₂ response from the H₂S response on a commercial detector. Curves 1 and 2 were obtained with the 3A zeolite sieve, while 3 was generated without any zeolite.

compatible with a planar device that is being developed. For other gases such as CO, similar filtration techniques are being tested. We would like to emphasize that the results presented in this chapter are merely a starting point in the investigation of thin film sensors. More work is needed before we have a full understanding of the mechanisms involved in the operating of these devices. The reliability of one such device shows promise of long term stability, but not enough data are available to us to report on the details at this stage.

5. CONCLUSIONS

The dependence of film resistivity on the oxygen concentration in the sputtering system has been noted in the study of SnO_2 films, and is commonly attributed to the variation in the number of oxygen vacancies within the crystal lattice¹. However, as is well-known, the conductivity of polycrystalline samples is dependent on the intergranular potential barriers, which, in turn, are related to the stoichiometric differences between the contacting grains⁵. The fact that the defect density in the observed films (even within each individual grain) is quite high, further gives rise to inhomogeneities in the current paths. Our Auger results suggest that for the film deposited in oxygen, the greater uniformity in material composition might be the main reason for the lower resistivity in the material. Similar Auger studies on the other samples showed that none of these possessed the uniformity of the film prepared in oxygen.

Heat treatment of these films showed that pure O_2 sputtered samples possessed the greatest electrical stability. TEM and AES investigations revealed almost no structural changes; however an increase in the

oxygen content was found.

The electrical sensitivity of these films to oxygen and hydrogen was tested. Conductivity measurements indicate that the observed sensitivity of SnO_2 to trace gases is probably due to an interaction of the gas with the chemisorbed oxygen ions already present on the surface of the oxide.

A means for providing selectivity between H_2 and H_2S , through the use of zeolite molecular sieves is discussed, and results on a commercial device are presented.

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SECTION V

PREPARATION AND ELECTRICAL CHARACTERIZATION OF ZnO FILMS

1. INTRODUCTION

Past investigations have shown that zinc oxide properties are significantly dependent on sample thermal history and method of preparation, particularly in the case of sintered specimens. The importance of surface effects in this material, due primarily to chemisorbed oxygen, has also been demonstrated. Therefore, measurements of properties of single crystal or sintered samples are not applicable to sputtered films. Because of the recent practical interest in ZnO sputtered thin films for surface acoustic wave¹ and solid-state gas sensing devices², and the unavailability of data for these films, the present investigation has been carried out.

Zinc oxide is an n-type ionic wide band gap semiconductor ($E_g = 3.2$ eV) having a wurtzite crystal structure. It is generally agreed that a non-stoichiometric excess of interstitial zinc, which occurs in undoped material, is responsible for the free electrons. The temperature dependence of the excess zinc concentration for ZnO in an ambient of air³ and zinc vapor⁴ have been determined by chemical analysis. Early electrical measurements on sintered specimens⁵ indicated the importance of heat treatment in determining conductivity and Hall mobility. Another study of sintered ZnO⁶ revealed that a single shallow donor model was unable to describe the temperature

dependence of the carrier concentration and suggested the possibility of deep-lying acceptor states. Hutson⁷ was the first to report comprehensive single-crystal electrical measurements. For most of his zinc-, lithium-, and hydrogen-doped samples, the data could be fitted by a single shallow donor model. The mobility temperature dependence could be described well by a combination of polar optical mode, acoustic mode, and ionized impurity scattering, with the fit being best between 200°K and 300°K. Later studies⁸ revealed donor band conduction at low temperatures (below about 50°K).

In contrast to the extensive literature for single-crystal and sintered specimens, few studies of the electrical properties of sputtered ZnO films have been reported^{9,10}. A number of authors have described characteristics of sputtered ZnO films in connection with surface acoustic wave applications¹¹. However, the emphasis has been on film morphology, which is important for these devices, and not on electrical properties. In the present work, the influence of applied sputtering power, sputtering ambient composition, and substrate temperature on film properties has been studied in detail. Film growth rate, optical transmission, grain size, resistivity, and Hall mobility have also been examined.

2. EXPERIMENTAL METHODS

For gas sensor applications, conductive ZnO films having well-controlled carrier concentration and grain size are required. A number of film deposition techniques, such as vacuum evaporation of ZnO source material, post-deposition oxidation of zinc thin films, and firing of an aqueous suspension of zinc oxide powder have been

investigated by us. However, none of these allows the ease of incorporation of dopants and process reproducibility of the radio frequency sputtering (RFS) process. (See Section II for a full description of the RFS process). Targets for this study were fabricated by pressing and sintering high purity ZnO powders; both an undoped and gallium doped target (5% Ga:Zn ratio) were used. Quartz substrates were used for electrical measurements, while glass microscope slides were employed in the optical transmission and growth rate experiments. The substrates could be maintained at 500°C during deposition by radiant heating.

Optical measurements were performed with a Cary 14 Double Beam Spectrometer. Film thickness was determined with a commercial stylus profile measuring device. For resistivity and carrier concentration measurements, six-arm Hall specimens were produced by sandblasting through a metal mask. Pressure contacts were then made to evaporate aluminum pads. Measurements at other than room temperature were made in a metal dewar with the sample surrounded by a vacuum. Except near 100°C, the maximum temperature employed, no changes in electrical properties due to desorption of chemisorbed ions were detected. For Hall effect and conductivity measurements, a conventional D.C. technique was used.

3. EFFECT OF COMPOSITION OF SPUTTERING ATMOSPHERE ON GROWTH RATE, ELECTRICAL AND OPTICAL PROPERTIES.

(a) Film Growth Rate

The nature of the sputtering process for compound materials has not been well characterized, but it is believed that both individual atoms and aggregates of atoms are sputtered¹². In order to maintain

stoichiometry in the deposited film, it has been found necessary to mix a small percentage (10%) of oxygen with the argon sputtering gas. Properties of films sputtered in less than this percentage of oxygen are sensitive to atmosphere composition, while those sputtered in a greater percentage are not sensitive. The importance of ambient composition in determining film properties has been discussed previously¹⁰.

Figure 1a shows film growth rate vs. ambient composition and applied R.F. power. Addition of 10% oxygen is seen to reduce growth rate by 36%, while further increase to 100% oxygen results in an additional 13% reduction. This behavior is not due simply to the mass difference of the argon and oxygen atom, since a linear relationship between growth rate and percentage oxygen would then be expected. One possible explanation is that, in atmospheres containing less than 10% oxygen, individual zinc and oxygen atoms are sputtered, while in greater than 10% oxygen, larger aggregates are sputtered in addition to individual atoms. Ignoring differences in binding energy, the energy transfer from the sputtering ion to the ejected target material is greatest when the mass of the ejected particle equals that of the ion. This would result in a greater sputtering rate in the absence of oxygen.

Figure 1b shows the dependence of growth rate on applied R.F. power. In both 0% and 10% oxygen, an apparent threshold in power is seen below which sputtering does not occur. This behavior has been reported for D.C. sputtered SnO_2 ¹³. Nonlinearity is seen in both curves; however, it is most pronounced in the 10% oxygen curve. This would be expected if (as conjectured above) the 0% sputtering process involved transport only of individual atoms, while the 10% oxygen process involved sputtering of atoms and aggregates in various

Figure 1: (a) Dependence of deposition rate of undoped ZnO on applied RF power; (b) dependence of deposition rate and resistivity of undoped as-sputtered ZnO on argon-oxygen ratio of the sputtering gas.

proportions depending on applied R.F. power.

(b) Resistivity of Undoped Films

Films sputtered in less than 10% oxygen contain a high concentration of electrically-active defects, as shown in Fig. 1a. Assuming singly-ionized shallow donor defects, and a conductivity mobility of $5 \text{ cm}^2/\text{V-s}$, typical of values found in Hall measurements (Sec. 4b), films sputtered in pure oxygen have a carrier concentration of about $4 \times 10^{18} \text{ cm}^{-3}$, or 100 ppm atomic. Hagemark and Toren⁴ studied the solubility of interstitial zinc for single-crystals in equilibrium; the solubility was found to exceed 100 ppma for temperatures in excess of 1050°C . The degree of vibrational disorder of the surface of the growing film should in fact be equivalent to a very high temperature, since the mean energy of the impinging particles is several eV; therefore, the defect density seen in the sputtered films could be of the order of magnitude measured.

The conductivity of as-sputtered undoped films was found to be due in part to defects which annealed rapidly at 400°C . Films sputtered in pure argon and in a partial pressure of oxygen both showed a rapid resistance increase upon heating in air. The high final resistance values made quantitative study of this effect difficult, but an increase of greater than three orders of magnitude occurred for the pure argon films. The rate of diffusion of interstitial zinc at 400°C is too low to account for this annealing; in the solubility study⁴, two weeks were required to reach equilibrium between a mm size crystal and zinc vapor at 700°C . A more likely explanation for the 400°C resistivity increase is chemisorption of oxygen at surface oxygen vacancies.

(c) Optical Transmission

Figure 2 shows the optical absorption spectrum for single-crystal, powder, and sputtered ZnO. The 3700 Å absorption edge for the single crystal corresponds to a band gap of 3.2 eV. Powder and sputtered samples show absorption at photon energies below the band gap.

Van Craeynest et al.³ attribute the behavior of powder samples to F-centers associated with interstitial Zn, which is singly ionized below 750°C and doubly ionized at higher temperatures. Curve 1 of [3] represents powder cooled slowly in air from 1100°C and presumably containing a minimal amount of excess Zn. Curve 2 shows a sample quenched from 920°C containing excess Zn^{2+} centers. The sputtered films 1 and 2, sputtered in greater than 5% oxygen, show the same absorption band as powder specimen 2, although stronger in magnitude. The slight shift (0.08 eV) to lower photon energies in the curve for the Ga-doped film (#2) is due to photo-excitation of carriers to the Ga levels as opposed to the conduction band in the undoped sample. The film sputtered in pure Ar, however, shows a spectrum markedly different from the other sputtered or powder samples. The absorption edge at 6000 Å is associated with the electrically-active defects which anneal at 400°C, since the transmittance in the visible is increased with heat treatment at 400°C. It is reasonable that the surface oxygen vacancy concentration, responsible for the high conductivity and strong optical absorption, should be largest in this film.

4. EFFECT OF DEPOSITION TEMPERATURE ON ELECTRICAL PROPERTIES.

The results described in the following section are restricted to Ga-doped films, since these were found to have stable characteristics

Figure 2: Optical transmission spectrum of as-sputtered ZnO compared with single crystal and powder ZnO data. Sputtered film thickness is $1000 \text{ \AA}$. Data for single crystal and powder samples have been normalized to transmittance of sputtered films 1 and 2 at $7000 \text{ \AA}$.

and resistivities which facilitated measurement of the electrical properties. Substrate temperature can influence electrical characteristics through effects on grain size and doping concentration. Many polycrystalline films, including ZnO, are known to contain a high concentration of acceptor states in the grain boundary region; these states arise from point defects and departures from stoichiometry.

In films of small grain diameter, the effective free carrier concentration n_{eff} can become significantly smaller than the doping concentration because of trapping of carriers by grain boundary defects. This behavior, termed autocompensation¹⁴, has been modeled by simultaneous solution of Poisson's equation and the charge neutrality relationship in small spherical crystallites¹⁵. The trapped carriers in the grain boundary region give rise to potential barriers and mobility values which are much lower than single-crystal values^{16,17}. The second effect of substrate temperature, change in doping concentration, occurs because of loss of a volatile dopant during sputtering, and has been reported for CdSn_2O_4 ¹⁸.

Figure 3 shows that both grain size and doping concentration vary with substrate temperature. Grain size is seen to increase four-fold between 120°C (no radiant heating) and 480°C. A decrease in free carrier concentration of almost two orders of magnitude between 270°C and 480°C is found. Since the amount of charge trapped in the grain boundary region is smallest at highest deposition temperatures, the loss of dopant at high temperatures is seen to be the predominant effect of substrate heating.

Figure 4 shows the temperature dependence of carrier concentration and mobility in Ga-doped films, compared with single-crystal and

Figure 3: Grain diameter as determined by scanning electron microscopy (SEM) and carrier concentration of as-sputtered Ga-doped ZnO vs. substrate deposition temperature.

sintered sample measurements. Evidently the variation in doping level and grain size results in quite different behavior for samples deposited at different temperatures. The 270°C sample most closely approximates single-crystal behavior in temperature dependence of n_{eff} and μ_H , as well as magnitude of mobility in this temperature range.

In Fig. 5, the n_{eff} vs $1/T$ data are analyzed by plotting

$$\ln \frac{n_{\text{eff}}}{(N_D - n_{\text{eff}})N_C} \quad (1)$$

vs $1/T$, as was done by Hutson⁷. Here N_C is the conduction band density of states, calculated using an effective mass of $0.3 m_0$. N_D was estimated from the carrier concentration above room temperature. Although previous authors have varied N_D from this estimate to produce the best straight line fit to the data, such a procedure is not warranted here. The present discussion is concerned mainly with the slopes of the curves, which are insensitive to order-of-magnitude changes in the value assumed for N_D . The heavily doped 270°C sample shows a considerably lower slope than the other two samples and additionally a possible break in slope near room temperature. Although onset of degeneracy can lead to such a slope change, the 270°C sample is at most weakly degenerate. Modification of eq. (1) to reflect weak degeneracy^{7,19} does not significantly alter the curve. From the data, the level scheme shown in Fig. 5 is inferred, with the Fermi level in this temperature range lying between the upper two donor levels for the 270°C sample and just above the third donor level for the 350°C and 480°C samples. One or both of the upper two donor levels is due to Ga. The optical spectra of Fig. 2 indicate a shift toward lower energy of the absorption edge

Figure 4 (a): Carrier concentration of as-sputtered Ga-doped ZnO films vs. reciprocal temperature compared with representative data for single crystal and sintered specimens. Numbers adjacent to curves for the latter two materials correspond to designations of original articles. Sputtered film thickness is $2 \mu\text{m}$.

Figure 4. (b): Hall mobility for as-sputtered Ga-doped ZnO films compared with representative data for single-crystal and sintered specimens.

Figure 5: Analysis of carrier concentration data of Fig. 4(a) after the method of Hutson (ref. 7).

of the Ga-doped sample compared with the undoped sample. The shift could be due to transitions to the middle donor level, since the magnitude (~ 80 meV) is close to the 60 meV donor level measured.

Regarding the lower donor level, it is not possible from the present data to establish whether it is due to Ga or is present in the undoped film. The deep-lying acceptor levels which pull the Fermi level down in the less heavily doped samples are probably due to chemisorbed oxygen, which forms acceptor states 0.72 eV below the conduction band (20).

In the mobility plot (Fig. 4b), the 270°C sample shows a mobility value approaching that of sintered specimens, as well as a decrease with increasing temperature similar to the single-crystal and sintered specimens. The mobility fall off near room temperature in single-crystal ZnO is due to the predominance of polar optical mode scattering⁷. That the mobilities of the sintered and 270°C sputtered samples are similar to the single-crystal curves apart from an approximately constant factor suggests that the current flow in the first two is through material having the same electrical behavior as single-crystal ZnO. The scaling of the mobility in sintered and 270°C sputtered ZnO implies that the cross-sectional area of the current path in these specimens is smaller than the measured cross-sectional area of the specimen. This would be expected if the current flow is through narrow necks between adjacent grains, with the electrical properties of the necks and material within the grains being essentially the same as single-crystal ZnO.

The 350°C and 480°C samples have considerably lower mobilities at any temperature than any of the other samples and moreover have strongly increasing mobilities with temperature. The slope cannot be due to ionized impurity scattering, since this process is of comparable

or larger magnitude in the heavily-doped sample (270°C). Rather, the slope is indicative of a mobility controlled by intergranular potential barriers due to trapped impurities. From the thermionic emission formula, the barrier mobility may be written¹⁶

$$\mu = \frac{e \langle v \rangle}{N_1 kT} e^{-\phi_b / kT} \quad (2)$$

where $\langle v \rangle$ is the mean thermal velocity of carriers, N_1 is the number of barriers per unit length along the current path, and ϕ_b is the potential barrier height. The exponential temperature dependence of μ_H is seen for both lightly-doped samples, the slightly greater slope of the 480°C sample indicating a larger barrier height. Seager and Castner¹⁷ have theoretically and experimentally studied potential barriers in epitaxially-grown polysilicon films. It was found that at low doping levels, the barrier height approaches $(E_C - E_A)$, the acceptor energy with respect to the conduction band edge. Above a certain doping level which depends on the trap density, the potential barrier was found to go to zero. This is evidently the case for the 270°C film. The barrier height for the 480°C sample is 0.14 eV, which is considerably less than $(E_C - E_A)$ for chemisorbed oxygen. Possible reasons for this difference are: (i) the carrier concentration of the 480°C film is not low enough to reach the limiting value for ϕ_b ; (ii) the donors are non-uniformly distributed throughout the grains, giving rise to an electric field in opposition to the field due to the grain boundary charge. The latter possibility was avoided in ref. [16] by doping the silicon through neutron transmutation. Further experiments using less heavily doped films are in progress.

5. CONCLUSIONS

The properties of sputtered zinc oxide films in certain cases is strongly dependent on deposition conditions. In particular, as-sputtered films deposited in less than 10% oxygen show increased growth rate, markedly increased optical absorption in the visible region, and a higher free carrier density than films sputtered in greater than 10% oxygen. The optical absorption and donor defects, which anneal at 400°C in the oxygen deficient films, were attributed to surface oxygen vacancies. Films sputtered in greater than 10% oxygen possess optical absorption similar to that seen in zinc-rich powder ZnO and attributed to F-centers formed by zinc interstitials. For films sputtered in an adequate oxygen concentration, properties are insensitive to precise ambient composition. Gallium doping was found to produce a slight shift in the absorption edge.

Substrate temperature affects grain size and doping concentration of the Ga-doped films, with the latter effect being of primary significance. Substrate temperature control provides a convenient means for varying the carrier concentration by more than two orders of magnitude for films sputtered from one target. Analysis of the temperature dependence of the carrier concentration revealed at least three donor and one acceptor levels. The trend in the mobility data is similar to that reported for polysilicon. The mobility in samples doped in the range 10^{18} cm^{-3} appears to be controlled by intergranular potentials barriers, while samples doped to greater than 10^{19} cm^{-3} do not have barriers. The latter films, as well as sintered samples, show a mobility temperature dependence similar to single-crystal ZnO but scaled down by a constant factor.

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SECTION VI

GAS SENSITIVITY IN RF SPUTTERED ZnO THIN FILMS

1. INTRODUCTION

Chemisorption and charge transfer processes on RF sputtered ZnO thin films can result in appreciable changes in electrical characteristics, and may be characterized by conductivity measurements.

The thin films discussed here appear particularly attractive for sensing hydrogen containing molecules, which when dissociated on the detector surface produce hydrogen, and reducing gases such as CO, which can interact with ionized adsorbed oxygen on the oxide surface. Gas sensitivity of ZnO thin films to H_2 and CO in O_2 - N_2 mixtures is reported here.

2. EXPERIMENTAL RESULTS

Details of the preparation of Ga-doped ZnO thin films have been outlined in Section V. As discussed earlier, these films possess stable electrical properties when cycled in various ambients and through varying temperatures. For gas sensitivity experiments, films were deposited with substrate temperature as a variable parameter in an O_2 -Ar plasma of 25 mT with 11 atomic % O_2 . A deposition rate of 22 nm/sec was used to produce films 2 μ m thick on quartz. Pd was introduced into some of the Ga-doped ZnO films by variable power splitting (VPS).

Figure 1 illustrates the change in resistance of the film following a change in the O_2 partial pressure in the test chamber. The response

time constant, τ , defined as $1/e$ times the final stable resistance value, has been observed to vary inversely with temperature. Furthermore, the response time for a decrease in $[O_2]$, corresponding to oxygen desorption, is longer than oxygen adsorption. In general, the temperature dependence of τ can be used to calculate the activation energy of adsorption/desorption process. However, for these films at elevated temperatures τ is on the order of the response time of the test apparatus which has been estimated to be about 90 seconds, and depends on the gas flow rates used. For this reason, we lack confidence in interpreting the temperature dependence of τ of these samples. Nevertheless, we can conclude that the approximate response times estimated for the films operated at elevated temperatures appear adequate for detector applications.

In addition to the general shapes of the response curves, the noise signal is of interest. This noise signal has been observed to vary in amplitude and frequency in different gas ambients, which we attribute to being induced by chemisorption. The signal is quiet in pure ambients such as N_2 or O_2 , but appears noisy in a mixture of the two. The inset of Figure 1 illustrates observed recordings in different atmospheres. The phenomenon has not been investigated in detail, but in some samples the effect appears to be both temperature and ambient dependent.

The responses of samples to other gases of interest are shown in Figs. 2 and 3. Figure 2 illustrates the sensitivity of the film to several hundred ppms of hydrogen in air. It is also evident that the response to hydrogen is non-linear. Figure 3 shows a response curve for 233 ppms of CO in air.

Figure 1: Measured resistance vs. time for changes in O_2 - N_2 ambient. Total flow rate maintained at 10 CFH. Chemisorption oscillatory signals are shown (1) pure O_2 (2) air (3) pure N_2 .

Figure 2: Measured resistance vs. time of ZnO film exposed to several concentrations of hydrogen in air. Recording illustrates reproducibility of the response.

Figure 3: Measured resistance vs. time for a ZnO thin film exposed to 233 ppm CO in air.

Figure 4: Temperature response of ZnO thin film to 500 ppm H_2 in air.

Figure 4 illustrates the temperature dependence of sensitivity of two representative samples to H_2 in air. The increase in sensitivity of one sample over the other and the shift of this curve to lower temperatures is attributed entirely to the catalytic properties of Pd in the film. The data of Fig. 4 fits a straight line dependence for $[H_2]^{1/2}$. For practical applications, determination of the hydrogen concentration is reduced to determining the constant of proportionality by calibration. The square root dependence suggests a chemical process involving adsorbed oxygen ions on ZnO:

The reaction rate constant for the process is

$$K = \frac{[H_2O] [\bar{e}]}{[H_2] [O]} \quad (2)$$

For dilute concentrations of hydrogen, the concentration of adsorbed oxygen, $[O^-]$, remains a constant. Furthermore, $[H_2O] = [\bar{e}]$ and eqn. (2) yields:

$$[\bar{e}] = K' [H_2]^{1/2} \quad (3)$$

The measured change in conductance is proportional to $[\bar{e}]$. Therefore, we have the result,

$$\Delta G \sim [H_2]^{1/2} \quad (4)$$

Figure 5: Conductance change vs hydrogen concentration for several ZnO thin films.

However, the temperature dependence of sensitivity suggests that more than a simple hydrogen dissociation process is responsible for the observed behavior.

Sensitivity versus temperature for 111ppms of CO is plotted in Fig. 6. The upper curve illustrates once again how a small addition of Pd increases the sensitivity and shifts the temperature dependence. The latter region of sensitivity was not investigated in detail. The inflection may suggest the presence of two or more energy levels associated with the O^- species on the Ga-doped ZnO surface. It is observed in all Ga-doped samples and may be a topic for further study.

The temperature dependence of the sensitivity of these films to H_2 and CO is of particular interest for the following reason. We note that for either gas, the bell shaped curves in Figs. 5.15 and 5.17 occur at almost identically the same temperature of 320°C. The presence of Pd in the film increases the film sensitivity and shifts the curve to lower temperatures. Specifically, addition of Pd results in an overall increase in sensitivity to H_2 of a factor of 1.3 and a shift in temperature of about 15°C. For CO, the overall increase in sensitivity is a factor of 2.56, or about twice that of H_2 , with an identical temperature shift. The greatest increase in sensitivity to H_2 resulting from addition of 1 atomic % Pd occurs at 315°C and is a factor of 2.25. The most substantial increase in sensitivity to CO after addition of Pd occurs at 300°C and is a factor of 27.5, and order of magnitude greater compared to H_2 for the data in these two figures.

This striking result suggests that the features of the temperature dependence of sensitivity may be used to discriminate between the gases.

Figure 6: Sensitivity is plotted as a function of temperature for a Ga-doped ZnO thin film deposited onto a heated substrate (480°C) and for the same film incorporating 1% Pd. The gas is 111 ppm CO in air.

3. CONCLUSIONS

Samples of RF sputtered ZnO films are sensitive to H_2 and presumably to a number of other gases containing hydrogen such as H_2S and NH_3 . Sensitivity is also exhibited to CO. In later cases, the levels of sensitivity are in the ppm range.

The presence of gallium and palladium to the film yields the desirable features of good electrical stability and increased sensitivity of the material to CO and H_2 . In the next section, we report on prototype gas sensing devices which may be used for sensitivities as low as 10 ppm.

SECTION VII

DEVICES AND DISCUSSION

1. INTRODUCTION

The results of the previous chapters demonstrate the feasibility of using SnO_2 and ZnO thin films for the detection of gases at 100 ppm levels. The conductivity change at this concentration, however, leaves a lot to be desired. In this chapter, we present the results on integrated devices designed to overcome the limitation on sensitivity. The first half of the chapter is thus devoted to the development of the IC device.

In the second half of the chapter, we outline some of the work that might be used to advantage in this field, and present a summary of the entire report.

2. DEVICE FABRICATION

Figure 1 illustrates a planar device developed here. Briefly, it consists of a SnO_2 resistor coupled to a bipolar transistor on one chip. The SnO_2 serves as a base bias resistor for the transistor, and modulates the base current input upon exposure to trace gases. A practical realization of the device presents several problems, chief of which is the incorporation of a heater (needed to operate the SnO_2 detector) and the bipolar transistor on the same chip. The development follows several steps.

A computer simulation of the temperature distribution on the device was first carried out. The symmetry of the device (Fig. 2) reduces the problem to two dimensions. Although this greatly simplifies the analysis, the number of variables that exist even at this stage

Fig. 1 Illustrating the concept of the gas sensing device under development. The SnO_2 serves to modulate the base current and, hence, the output V_{out} on exposure to a trace gas

Fig. 2 Computer simulation of the temperature distribution of the device shown in the upper half of the figure.

precludes a closed form analytical type of solution.

In carrying out the numerical analysis, the assumption is made that the free surfaces of the chip are essentially adiabatic. This represents a worst case analysis since, in reality, there is some heat loss by convection even at this temperature¹. A finite difference technique is then easily applied to determine the temperature distribution on the device. Care must be taken to determine the position of the node to which the finite difference equation is applied. For a typical interior node A (Fig. 2), the temperature $T(I,J)$ is obtained through an application of Fourier's law of heat conduction:

$$\sum q_{ij} = 0 \text{ which gives}$$

$$\theta_{i,j} = \frac{(k\theta)_{i,j-1} + (k\theta)_{i-1,j} + (k\theta)_{i,j+1} + (k\theta)_{i+1,j}}{k_{i,j-1} + k_{i-1,j} + k_{i,j+1} + k_{i+1,j}}$$

where $\theta = (T - T_1)/(T_2 - T_1)$ with T_2 = heater temperature

T_1 = reference temperature

Table I shows the equations that apply to the various nodes in the simulation. The results of the analysis are also described in Fig. 2.

From the results we note that a back plane metallization below the transistor provides sufficient cooling to prevent the device from going into thermally induced breakdown. Figure 3 is an exploded version of our device. The heater is made by silk screening techniques in which a resistive ink is squeezed through a blue-poly mask onto alumina substrates. The substrates are then heated at 700°C for a few minutes. SnO_2 films deposited on oxidized silicon substrates are then attached to the heaters by means of a high temperature epoxy. The entire structure is mounted on a TO-5 header. The heaters possess a resistance of about 75 ohms and exhibit very good electrical stability.

TABLE I

FINITE DIFFERENCE EQUATIONS FOR THE NODES OF THE DEVICE

GEOMETRY SHOWN IN FIG. 2

Type of Node	Equations for θ (ij)
Left Hand Top Corner	$\theta_{ij} = \frac{k_{i,j+1} \theta_{i,j+1} + k_{i+1,j} \theta_{i+1,j}}{k_{i,j+1} + k_{i+1,j}}$
Interior	$\theta_{ij} = \frac{k_{ij-1} \theta_{ij-1} + k_{i-1,j} \theta_{i-1,j} + k_{ij+1} \theta_{ij+1} + k_{i+1,j} \theta_{i+1,j}}{k_{ij-1} + k_{i-1,j} + k_{ij+1} + k_{i+1,j}}$
Left Surface	$\theta_{ij} = \frac{k_{i+1,j} \theta_{i+1,j} + k_{i-1,j} \theta_{i-1,j} + 2k_{ij+1} \theta_{ij+1}}{k_{i+1,j} + k_{i-1,j} + 2k_{ij+1}}$
Top Surface	$\theta_{ij} = \frac{k_{ij-1} \theta_{ij-1} + k_{ij+1} \theta_{ij+1} + 2k_{i+1,j} \theta_{i+1,j}}{k_{ij-1} + k_{ij+1} + 2k_{i+1,j}}$
Right Hand Top Corner	$\theta_{ij} = \frac{k_{ij-1} \theta_{ij-1} + k_{i+1,j} \theta_{i+1,j}}{k_{ij-1} + k_{i+1,j}}$
Right Surface	$\theta_{ij} = \frac{k_{i+1,j} \theta_{i+1,j} + k_{i-1,j} \theta_{i-1,j} + 2k_{ij-1} \theta_{ij-1}}{k_{i+1,j} + k_{i-1,j} + 2k_{ij-1}}$
Bottom Surface	$\theta_{ij} = \frac{k_{ij-1} \theta_{ij-1} + k_{ij+1} \theta_{ij+1} + 2k_{i-1,j} \theta_{i-1,j}}{k_{ij-1} + k_{ij+1} + 2k_{i-1,j}}$

Fig. 3 Exploded view of the device fabricated in our laboratory

Current research is aimed at a more sophisticated approach to the device structure.

3. Pd/ZnO SENSORS FOR H_2S

As discussed earlier in Section VI, ZnO films show good hydrogen sensitivity, with concentrations of 10 ppm easily detected. Current efforts are aimed at exploiting this sensitivity in the detection of a gas of greater interest, namely hydrogen sulfide. The operating principle of the ZnO-based hydrogen sulfide detector is similar in certain respects to that of the Pd/SiO₂/Si Schottky barrier diode (SBD). In both cases, the H_2S molecules dissociate into atomic hydrogen and sulfur at the surface of a Pd thin film. The H atoms readily diffuse through the Pd and are detected by an underlying sensor element. In the case of the SBD, the element is the interface between the Pd and Si, with the very thin SiO₂ layer serving only to "tie-up" intrinsic surface states in the Si. In the ZnO device, detection is accomplished through reaction of atomic hydrogen with chemisorbed oxygen at the ZnO surface, causing a donation of electrons back to the ZnO conduction band and consequent decrease in resistance of the ZnO film. The advantages of the device under development are: first, the ZnO films have shown greater hydrogen sensitivity than the SBD devices; this coupled with greater stability, is expected to show better performance than the SBD device. Secondly, the parameter monitored in the new device, namely resistance, is more easily measured than junction capacitance or reverse leakage current, which are monitored in the SBD.

The proposed geometry for the ZnO hydrogen sulfide detector is shown in Fig. 4. The device is basically a layer structure with the

TOP VIEW

CROSS-SECTIONAL VIEW

Figure 4: 1. Substrate 2. Underlying metal film
3. Contact to underlying metal film
4. Insulating film (SiO_2 or other suitable insulator)
5. Overlying palladium film 6. Zinc oxide film
7. Contact to overlying palladium film
8. Window in insulating film

ZnO film sandwiched between a metal film and thin outer Pd film.

A SiO_2 layer with an etched window serves to define the sensitive area and to prevent unwanted electrical contact between the two metal films.

We have spent considerable time in preparing the necessary artwork and photolithographic masks needed for the fabrication of the device.

Presently, we are in the process of fabricating all the ancillary elements of the device: the underlying metal film, the SiO_2 layer with a window, and the outer Pd film. The SiO_2 has been deposited using a standard silane process, and the other elements are patterned through standard photolithographic techniques. With the perfection of these procedures, ZnO is incorporated into the devices by sputtering through a metal mask.

4. DISCUSSION

From the contents of this manuscript it may be seen that some progress has been made in the field of thin films sensors. We have made contributions in the areas of preparation, characterization and operation of these devices; we were also among the first to point out the role of oxygen in the operation of these detectors². It is our belief, however, that the progress in the field has been somewhat slow. This is due, mainly, to the large number of unknowns that exist even at this point. Some of these are:

1. Lack of a detailed understanding of the exact nature of the chemisorbed O_2 species on the free surfaces and the grain boundaries of the material.
2. Lack of an understanding of the role of grain boundaries in altering the current transport in the oxide.

In light of what has been said, we would like to stress a fundamental approach to some of the above topics for future work. In this context, the important points are:

1. Use of Electron Spin Resonance (ESR) techniques to study the adsorption mechanisms of oxygen on SnO_2 crystals and films.
2. Adaptation of the bicrystal growth techniques to the preparation of SnO_2 crystals so as to be able to study the effects of grain boundaries on current flow.
3. Effect of certain additives (not dopants) such as palladium and gold in increasing the chemisorption sites for O_2 .

The use of ESR in identifying surface species has been known for quite sometime now. It is used extensively in the field of organic chemistry³. The instrument could prove invaluable in a study of O₂ adsorption on free surfaces. By an adaptation of the technique for the growth of bicrystals (developed by the Center for Joining of Materials), one could look at adsorption of oxygen along grain boundaries of preselected angles. The same technique could prove of great use in understanding the role of grain boundaries in electrical transport of charge carriers. A total time of 12-18 months should prove adequate.

4. CONCLUSIONS

This report has addressed itself to a fundamental study of SnO₂ and ZnO thin films with a view to using them in solid state gas detection. Methods of thin film preparation and characterization have been developed and used in the interpretation of the gas sensitivity of the material. Of the several methods available to the experimenter for SnO₂ film deposition, we have studied the chemical vapor deposition and the radio frequency sputtering techniques in detail. The CVD technique produces a faster deposition rate, but is extremely sensitive to the several operating parameters such as gas flow rates, substrate temperatures and input reactant ratios. A large amount of chlorine has been found in these films. Reproducibility is a problem unless all operating parameters are held constant. The technique does not require high skill for operation.

In contrast, the RFS technique is somewhat more sophisticated, but does require skilled handling. This is, however, a very versatile technique and permits great control over the film thickness and properties. A remarkable variation in the resistivity of as-sputtered

films spanning about five orders of magnitude has been obtained by controlling the sputtering ambient within the system.

Several methods have been used in the analytical characterization of the material. The use of Auger electron spectroscopy and transmission electron microscopy has provided insight into the composition, structure and stability of all films. For the sputtering conditions described in Chapter 3, the resultant films are polycrystalline and have a wide range of grain sizes. Most crystallites are about 200 Å in size. Twin boundaries and stacking faults are observed in the entire film. Films sputtered in an ambient of oxygen show a uniform composition extending from the surface to the bulk. This is not true of films prepared in other atmospheres, and very often we have found them to contain a higher amount of oxygen in the first 400 Å from the surface than the bulk. The oxygen sputtered films also possess the greatest stability. X-ray diffractometry shows all films to be strained.

We have also conducted extensive annealing tests on these films. Our Auger and TEM studies suggest that all changes in resistivity may be attributed to changes in composition rather than the structure. This is the key point in film stability.

Electrical conductivity methods have been employed in the study of the defect structure and the gas sensitivity response of the oxide. Kinetic tests conducted in a high vacuum system have shown the existence of a large number of oxygen ions on the surface. Further tests with hydrogen reveal the observed gas sensitivity of the material to be due to an interaction of the trace gases with the chemisorbed oxygen ions.

A prototype of the portable gas sensor capable of sensing ppm levels with good signal amplification has also been reported. Further research to enhance the density of chemisorbed oxygen ions is being conducted. The use of zeolite molecular sieves in planar form is being explored in order to achieve the necessary selectivity before the device can be successfully marketed.

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APPENDIX:

The following is an updated list of publications

1. G.N.Advani, Y.Komem, A.G.Jordan, D.J.Leary and R.L.Longini: "Studies of SnO_2 as a Material for Gas Detection", presentation² at the 153rd Meeting of the Electrochemical Society, Seattle, Washington, May 21-26, (1978); Recent News Paper # 37.
2. A.G.Jordan, D.J.Leary, G.N.Advani and J.O.Barnes: "Studies of Semiconducting Metal-Oxides in Conjunction with Silicon for Solid State Gas Sensors", Invited talk at the Symposium on The Development and Usage of Personal Monitors for Exposure and Health Effect Studies, January 22-24, (1979), Environmental Protection Agency, Research Triangle, North Carolina.
3. G.N.Advani, A.G.Jordan, C.H.P.Lupis and R.L.Longini: "A Thermodynamic Analysis of The Deposition of SnO_2 Thin Films from the Vapor Phase", Accepted for Publication in Thin Solid Films, April (1979)
4. G.N.Advani, P.Kluge-Weiss and A.G.Jordan: "Analytical Characterization of SnO_2 Thin Films", Accepted for Publication in Materials Science and Engineering, May (1979)
5. G.N.Advani and A.G.Jordan: "Thin Films of SnO_2 as Solid State Gas Sensors", Accepted for Publication in Journal of Electronic Materials, June (1979)
6. G.N.Advani and A.G.Jordan: "Stability of SnO_2 Thin Films Used for Photovoltaic Devices", Submitted to the journal of Solar Energy, June (1979)
7. G.N.Advani, P.Kluge-Weiss, A.G.Jordan and R.L.Longini: "Oxygen Vacancy Diffusion in SnO_2 Thin Films", (in preparation)
8. G.N.Advani, A.G.Jordan, P.Kluge-Weiss and R.L.Longini: " SnO_2 Solid State Gas Sensors", (in preparation)
9. J. O. Barnes, D. J. Leary and A. G. Jordan: "Relationship Between Deposition Conditions and Physical Properties of Sputtered ZnO ", submitted to the Journal of the Electrochemical Society, August (1979).