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

Progress Report
for Period April 1, 1977 - March 31, 1978

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April 1978

The U.S. Energy Research and Development Administration
under Contract No. EE-77-S-02-4346

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ABSTRACT

ZnO films have been reproducibly grown using chemical deposition and radio-frequency sputtering techniques. These films are polycrystalline or amorphous, but are stable, uniform and lend themselves to material characterization by Auger and X-ray analysis techniques, and electrical measurements. SnO_2 films have been reproducibly grown by chemical vapor deposition, vacuum deposition and radio-frequency sputtering techniques. These films are also polycrystalline or amorphous, and lend themselves to material characterization and measurements. By vacuum deposition techniques, Si-SnO_2 heterojunctions have been grown, which exhibit good rectification properties. An original thermodynamic analysis of the growth of SnO_2 by a chemical vapor deposition technique based on the reaction between SnCl_4 and H_2O has been developed and submitted for publication. $\text{Pd-SiO}_2\text{-Si}$ Schottky barrier diodes exhibiting excellent rectification properties have been successfully fabricated. A formalism has been established for the analysis of the behaviour of these devices in the presence of H_2 , H_2S and CO . The ZnO films grown by chemical deposition have proven to be sensitive to CO and CH_4 . Sputtered ZnO films are sensitive to O_2 and H_2 . SnO_2 films grown by chemical vapor deposition are not very sensitive to gases. Sputtered films, however, are very sensitive to H_2 and H_2S . The $\text{Pd-SiO}_2\text{-Si}$ diodes are extremely sensitive to H_2 , H_2S and NH_3 , and, under certain conditions, to CO . A microprocessor data processing system has been developed incorporating gas sensors in the presence of a variety of gases and gas mixtures.

I. INTRODUCTION

This is a progress report of work at Carnegie-Mellon University on "Studies of Semiconducting Metal Oxides in Conjunction with Silicon for Solid State Gas Sensors". The work herein reported is for the period April 1, 1977 - March 31, 1978.

Section II of this report establishes conventional energy bands in a semiconductor as a basis for discussion and interpretation of electronic processes and surface conductance in the semiconducting metal-oxides. This general outline is followed in Section III with specific studies on ZnO thin solid films carried out in our research, highlighting film preparation and deposition by a chemical deposition technique and Radio Frequency (RF) sputtering. This Section also includes a characterization of electrical and physical properties of the films. Section IV describes work on deposition and characterization of SnO_2 films by chemical vapour deposition and RF sputtering techniques. Section V is a comprehensive report of the development and device modeling of metal-semiconductor Schottky barrier diodes. This section includes characterization of surface reactions on the metal and develops reaction rate parameters for a $\text{Pd/SiO}_2/\text{Si}$ Schottky barrier diode. The following three Sections VI, VII, and VIII report specific gas sensitivity figures for ZnO, SnO_2 and $\text{Pd/SiO}_2/\text{Si}$ devices, respectively. The role of a few common dopants in improving sensitivities and selectivities is highlighted. The final section of the report deals with a data acquisition system developed by us, and its application to our own devices as well as to commercially available devices. An elaborate microcomputer controlled system allows for detailed measurements of transient responses to changes in the thermal and ambient parameters, and it provides a convenient means for evaluating the mechanisms of response of materials and devices by evaluating the different time constants involved in the processes.

II. BACKGROUND

Current research at Carnegie-Mellon University on solid state gas detection is concerned with studies of semiconducting metal oxides and metal-semiconductor devices in conjunction with Si. Impetus for this work resulted from an assessment in 1975¹ which recommended a fundamental study of specific metal oxide systems which show promise as possessing the most potential for long term development as useful materials. The original objectives for this research appear in Appendix I. We are interested in obtaining quantitative information about the physics and chemistry of these materials with respect to elucidating physical and electronic properties that are influenced by chemisorption of gases. A review of the literature has shown a plethora of empirical theories and conflicting interpretations of data^{2,3}. Up to the present time our work has dealt specifically with the following materials: ZnO, SnO₂, and group VIII metals, all in conjunction with Si. This report will outline the results of our investigations on each of these systems up to now and define the intentions for meeting the objectives of Appendix I.

When studying electronic processes in semiconductor materials such as those above, the band model is a useful basis for interpretation and discussion. Band theory states basically that energy values for an electron in an ordered crystal are grouped as a function of energy into bands. This theory also conveniently yields a model for the study of the influence on electronic properties of impurities distributed in the bulk. In addition to the allowed levels, discrete energy levels in the energy gap exist which correspond to electrons localized at impurities or defects. For example, in zinc oxide these levels may arise from excess zinc atoms located interstitially in the lattice². The ionization energy for these atoms is such that at room temperature most are singly ionized donating electrons to the conduction band and making zinc oxide an n-type semiconductor.

Surface adsorption is characterized into two categories: physical adsorption and chemisorption. Physical adsorption originates from van der Waals polarization type interactions which usually involves a low heat of adsorption. Noble gas adsorption is an example. Chemisorption is, in contrast, characterized by strong chemical bonding accompanied by the liberation of large amounts of heat. Physical adsorption, by nature, will not effect the space charge region of the semiconductor but the surface dipole moment will influence the electron affinity. On the other hand, the charge associated with a chemisorbed adatom will effect space charge layers in the semiconductor surface. The process of charge transfer is essential in the basic model of equilibrium chemisorption. Figure I illustrates the band diagram for n-type zinc oxide^{2,5}. The electrostatic potential, ψ , measured from an arbitrary zero has the value of ψ_0 in the bulk and ψ_s at the surface of the semiconductor. ψ_s is a measure of the band bending, which is dependent on surface conditions. We consider adsorbed ions with energy levels corresponding to electrons localized at the surface in the form of oxygen acceptors which trap electrons from the surface. For the case of oxygen, two acceptor type levels may be present². We neglect here the possibility of impurity levels introduced as a result of sample preparation or defects in stoichiometry. Electrons are trapped on the acceptor levels because these levels are lower in energy than levels for interstitial zinc in the semiconductor introducing a potential barrier at the surface. Assuming that this barrier is produced by ionization of donor impurities in the semiconductor, Poisson's equation can be used to determine the potential distribution in the semiconductor resulting from the equilibrium adsorption. The amount of band bending in the neighborhood of the surface can be determined by integration of Poisson Equation subject to suitable

Fig.1 Energy levels in n-type ZnO for equilibrium adsorption of an acceptor gas, O_2 . references 2 and 5.

boundary conditions. This is usually a formidable task. A reasonable assumption is to approximate the space charge region in the bulk of the semiconductor by a rectangular distribution, i.e., the concentration of ionized impurities, N_d , is a constant. Then Poisson's equation becomes

$$\nabla^2 \psi = \frac{q N_d}{k \epsilon_0}, \quad (1)$$

where q = electronic charge.

k = dielectric constant of the semiconductor.

ϵ_0 = permittivity of vacuum.

Integration of (1), using as boundary conditions $\psi = \psi_s$ at the surface and $\frac{d\psi}{dx} = 0$ at $x = x_0$ (the width of the space charge region), yields

$$\psi_s = \frac{q^2 N_d x_0^2}{2k \epsilon_0} \quad (2)$$

This can be related to the concentration of chemisorbed oxygen ions, N_a , as follows

$$N_a = x_0 N_d, \quad (3)$$

if each adsorbed oxygen ion accepts only one electron and each donor impurity gives up only one electron. This simple model excludes the possibility of diffusion of the surface species into the surface layers as well as diffusion of bulk impurities to the surface. The background above is relevant to both ZnO and SnO_2 devices, and it is useful to establish the character of the physical properties of the material before and after chemisorption, particularly the surface conductance of the films. In these two instances we are referring to conductance of the film as influenced by gas chemisorption.

In another family of devices incorporated in this report, the Schottky Barrier Diodes, the surface potential and space charge regions alluded

in equations (1), (2) and (3) refer to the potential and space charge region of a semiconductor, silicon for example, used as the base of a metal semiconductor diode. The metal constitutes the gas sensitive portion of the device, and changes introduced in the metal by adsorption of gases in it affect the properties of the semiconductor underneath the metal film. The electrical property of interest affected by gas adsorption in the metal is not the surface conductance of the semiconductor, however. Rather it is the current flowing through the metal semiconductor diode.

III. STUDIES OF ZnO

Shown in Fig. I is the band edge diagram for zinc oxide. The bandgap determined by optical adsorption techniques is found to be about 3.2 eV⁶. We have used the TSC method⁷ of generating activation energy data for undoped polycrystalline samples and have found E_a to be a few hundredths of an eV. ZnO assumes a hexagonal wurtzite structure shown in Fig. II. Each Zn cation is surrounded by four O anions situated at the corners of a nearly regular tetrahedron, and each anion is surrounded by four cations. The bond is partly ionic. Its electronegativity difference is plotted in Fig. IV. The crystal is noncentrosymmetric and exhibits a polar c-axis.

Methods of depositing uniform thin films of ZnO for gas detection are: vacuum deposition⁸, chemical deposition developed by Safety in Mines Research Establishment (SMRE)⁹, thermal oxidation, and Radio Frequency Sputtering (RFS)¹⁰. Vacuum deposition uses an e-beam technique but has drawbacks because the sublimation is accompanied by decomposition of the compound. Annealing in air makes possible changing the film resistance but this is difficult to control. High temperature thermal oxidation has not been investigated. It has been our experience that the SMRE and RFS techniques are the only methods available for controlled reproducible deposition

Unit cell of the crystal structure of SnO_2 . Large circles indicate oxygen atoms and the small circles indicate tin atoms.

Fig. II

Figure III

Figure IV

of thin films of doped ZnO. ZnO is doped with various III-VI compounds and certain elements from groups VIII and VIIA. Both the SMRE and RFS techniques lend themselves to controlled doping.

Of the two methods, the SMRE one is the best understood at this time. Characterization of material prepared using this technique, with some modifications introduced by us, has given considerable insight into the gas sensitivity and response mechanisms and has lead to appropriate dopants. The RFS method is being used to improve the uniformity of very thin films in conjunction with Si. We have recently established in our lab for this purpose a Randex 2400 6-J series multi-target RF Sputtering System. Features included in this system are variable power splitting, which permits sputtering from more than one target making possible doping of the ZnO from high purity target material, low temperature deposition, good film adhesion to many different kinds of substrates, and target etch cleaning modes to minimize contamination.

Targets are prepared by three techniques, (1) Hot pressing of the powder produced by the SMRE technique or any high purity undoped or doped polycrystalline powder into 3 inch disks, then sintered, (2) SMRE deposition onto glass disks, (3) reactive sputtering from a pure Zn target in an O_2 ambient. Film thickness is determined by a Sloan Tallysurf stylus. Film stoichiometry is identified by glancing X-ray diffraction and TEM.

In connection with methods (1) and (2), targets of 1.5% Pd doped (1% Cl) ZnO have been sputtered in a partial pressure of O_2 . We observe that the resultant films do not contain the same concentration of dopants as the targets. Auger and the X-ray analysis of the obtained films indicate that Pd and Cl do not appear in the sputtered film. We believe that the $ZnO_{1-x}PdCl_x$

complex is sputtered as a molecule or group of molecules (aggregate) but that the properties of the deposited film are subject to reactions in the gas phase and at the substrate surface. The fact that the final films are Pd and Cl deficient may likely result from a complex interaction of several of the deposition parameters such as substrate temperature and Ar and O_2 partial pressures (which determine in part the mean free path of the sputtered molecule). Substrate temperature is maintained low by a tuning network to minimize reflected RF power to the substrate and cooling water to ensure a substrate temperature less than 200°C . We have observed that methods (1) and (2) will not be as useful as hoped for the deposition of doped ZnO films from doped targets prepared by the SMRE technique. It appears that controlled doping will result from a multi-target process.

In connection with method (3), we have been able to demonstrate that reactive sputtering of ZnO films is possible. The stoichiometry has not been completely characterized as yet. We intend to prepare thin films ($1000\text{\AA}$) of doped ZnO for use as a gas detection material using the RFS system. Recommendations for sample preparation are based on the recent observations of sputtered films. We have observed that the catalytic activity of doped ZnO is dependent both on the availability of conduction electrons from group III-VI (Ga_2O_3) and group VIIA (Cl) donors and the presence of an activator metal such as group VIII (Pd). Unfortunately, sputtering from SMRE targets following methods (1) or (2) results in films deficient in these two elements. A multi-target process will be used to study sputtered films of ZnO doped with Ga_2O_3 (1%) and Pd (1%).

We obtain the activation energy for ZnO from σ vs. $1/T$ curves. ZnO doped with 1% Ga_2O_3 shows an increase in the specific conductivity with Ga substituting as a donor for the Zn. Catalytic activity of these films is observed not to differ dramatically from the undoped extrinsic ZnO ($N_d = 5 \times 10^{15} \text{ cm}^{-3}$). The influence of semiconductivity on catalytic

activity is a complex and ill understood subject. The concept has been used by others to explain the mechanism by which poisons and activators operate³. However, in quite a few instances a change in conductivity resulting from impurity doping does not seem to influence the catalytic activity of the material. We intend to investigate in more detail the aspects of the relationship between semiconductor as expressed in contemporary solid state theory in connection with the mechanism of catalytic activity occurring on the metal oxide surfaces of interest to our overall project.

ZnO films deposited by the SMRE technique are polycrystalline with average grain size of 0.5 microns. The dc measurement of resistance of non-single crystal material is often dominated by the intergranular contacts so that measured values provide little information about the bulk material. In addition, the errors arising from rectifying contacts and thermal emf's which may develop across the sample must be reckoned with. To elucidate these effects, ac resistance measurements at high frequencies were performed. We observed that the resistance decreases as the frequency increases. This points to an electrical model for the SMRE films which should incorporate an effective intergranular capacitance in parallel with an intergranular resistance, and this in series with an equivalent resistance of the single crystal, as shown in Fig. V.

The change in conductivity of zinc oxide when exposed at elevated temperatures to various ambients is most probably affected not only by surface adsorption but also diffusion of the gas species into the bulk or perhaps diffusion of bulk impurities or interstitial Zn to the surface. For example, with high concentration of oxygen, interstitial Zn may diffuse to the surface and form ZnO leaving less conduction electrons in the material. For low concentrations just the opposite may occur. Oxygen at the surface may dissociate and Zn diffuse interstitially into the

(a)

(b)

Fig. V (a) Simplified 2 dimensional electrical model for polycrystalline ZnO. The dc conductivity, σ , and changes in σ due to chemisorption are determined by intergranular contacts between small ($0.5\mu\text{m}$ avg.) hexagonal crystals (SMRE)

(b) $\log \sigma$ vs. $\log f$ for undoped polycrystalline ZnO.

bulk. We intend to perform more carefully a few key experiments with the polycrystalline films eliminating as many parameters as possible so as to study for a particular doping scheme and gas ambient the mechanism of response versus temperature.

IV. STUDIES OF SnO_2

Thin films of SnO_2 have been deposited in the laboratory using three different techniques. To wit: (1) Chemical Vapor Deposition using the hydrolysis reaction between SnCl_4 and H_2O , (2) RF Sputtering of SnO_2 , and (3) Vacuum Deposition Techniques.

The Chemical Vapor Deposition technique is based on the hydrolysis reaction between Stannic Chloride and Water vapor:

A complete thermodynamic analysis of the above reaction shows that the Gibb's free energy for the system is positive at temperatures above 462°K (189°C); the reaction thus proceeds in the forward direction above this temperature. From the thermodynamic analysis, kinetic behaviour is predicted for deposition of SnO_2 from the vapor phase on a substrate. At lower temperatures transfer across the substrate-vapor interface of the reactants governs the reaction. At higher temperatures diffusion in the gaseous phase or diffusion of gaseous reactants across the boundary layer are the controlling mechanisms. High flow rates can be used to increase the diffusion of reactants across the boundary layer. Turbulent flow is desirable to insure intimate mixing of the reactant gas stream.

Accordingly, the apparatus for the growth of SnO_2 films consists of two bubblers stocked with H_2O and SnCl_4 , with O_2 as the carrier gas for the former and N_2 for the latter. The bubblers are heated by means

of nichrome heaters wound directly on the glass cylinders.

The hydrolysis reaction itself is carried out in a small hot zone of a quartz tube which has two entry ports on one side for the vapors of SnCl_4 and H_2O . The H_2O vapors are led through an inverted funnel arrangement placed 1" away from the boat carrying the substrates. Such an arrangement minimizes prereaction between the reactant gases. The quartz tube is heated by means of an electric furnace. Uniform thin films are^{11,12} obtained when the temperature is 325°C .

RF Sputtering of SnO_2 films is carried out in the Perkin-Elmer 2400J system. The target is a disc of SnO_2 prepared by pressing the reagents obtained from commercial vendors at a pressure of 10 tons. The pressed disc is then allowed to sinter at $1150\text{--}1200^\circ\text{C}$ for a period extending over 12 hours. High percentages of dopants are incorporated within the disc to ensure that the final film contains these dopants to 1% levels. The fact that the film does not contain the dopant in the same proportion as the target material is partly due to the difference in sputtering rates of different materials.

A typical deposition of thin films is carried out in an ambient of argon and oxygen. The operating pressures are typically around 15 Torr, with 11% of this due to the oxygen. It has been found that the films so produced are $2000\text{\AA}$ thick when deposition times are in the order are 10 minutes. The films are probably polycrystalline or even amorphous, but further experimentation is needed to confirm this. Typical conductivities are much lower than the films produced by the CVD technique and the two reasons that at present seem to explain this are, (a) absence of Cl in the RFS films and/or (b) tin deficiency, as pointed out by the Auger Elemental Spectroscopy technique.

The vacuum deposition technique is the basis of formation of Si-SnO₂ heterojunctions. In this technique, crystals of stannous chloride SnCl₂·xH₂O are evaporated onto a clean silicon surface through a mask of molybdenum. The evaporation is carried out at a pressure of 3x10⁻⁷ mm of Hg. The silicon wafer is then subjected to an oxidation step in which the SnCl₂ is converted to SnO₂ as per the reaction:

The oxidation is carried out at a temperature of 510°C, with a flow of oxygen at 300 cc/min., and takes about 15 minutes for completion. Silver paste is used as an ohmic contact to the SnO₂ while a thin layer of Sb/Sn evaporated and diffused into the silicon back surface ensures an ohmic contact there. The junction thus formed is found to be rectifying in nature. The direction of forward bias is a positive polarity on the SnO₂ layer. Fig.6a shows the device, and Fig.6b shows a plot of the I-V characteristics. Note that the junction degrades with time possibly due to the reduction of SnO₂ by the silicon, ie.,

This might then impose a severe restriction on the operation of such a device.

V. STUDIES OF METAL SEMICONDUCTOR SCHOTTKY BARRIER DIODES

In a metal-semiconductor Schottky barrier diode the barrier to carrier flow at the interface is a strong function of the surface state density of the semiconductor itself. Ideally, the barrier produced depends only on the difference of the electron affinity of the semiconductor and the position of the Fermi level which determines the work function of the metal. It has been well established¹⁴ that several metals including Pd,

Fig. VIa (i) The SnO_2/Si n-n heterojunction device geometry.
(ii) The proposed band diagram for the heterojunction.

Fig. VIb I-V characteristic of SnO_2/Si heterojunction over 24 hours.

Pt, and Ni adsorb and dissociate gases such as H_2 and O_2 . It has also been established that in the case of H_2 the adsorbed molecule is ionized donating two electrons to the metal and the ion is absorbed and diffuses into the metal. The donated electrons result in an increase in the Fermi level that is uniformly distributed throughout the bulk.

We began exploring this phenomena with several metals used as contacts to various semiconductor substrates observing changes in reverse leakage current density as a result of changes in barrier height upon exposure to different gases. Our early research explored barrier height changes of Pd and Pt on group IV and group III-V semiconductors that could be conveniently doped n or p type in the hope of developing a detector that would be sensitive to both donor and acceptor type vapours, such as H_2 , which donate electrons when ionized, and acceptor type vapours, such as O_2 , which donate holes when ionized. Our original model proved to be incomplete but considerable information was obtained from the study.

Barrier heights of metal-semiconductor contacts can be loosely divided into two groups as far as the semiconductor is concerned: 1. Barrier heights for covalent semiconductors, group IV and group III-V, are observed not to be strongly dependent on the metal Fermi level and thus are effectively a function of the particular semiconductor alone. This is a consequence of the high density of surface states characteristic of these semiconductors. For most semiconductor surfaces of this group the peak density of surface states lies at approximately one-third of the bandgap from the valence band edge. 2. Barrier heights for the more ionic semiconductors are observed to be much more strongly dependent on the position of the Fermi level in the metal and depend both on the semiconductor and the metal together. This system behaves as if the surface state density is essentially zero resulting in a barrier height that is more

ideally related to the difference in metal work function and semiconductor electron affinity. This we explain by invoking the fact that surface states are very close to the band edge and the Fermi level at the junction can move over a large range in energy. As far as gas detecting properties are concerned, a change in the Fermi energy of the metal for a large concentration of gas would give rise to a larger change in barrier height if an ionic semiconductor such as CdS is used rather than if a covalent semiconductor such as Si or GaAs is used. To illustrate this situation Fig.III shows plotted barrier heights measured by capacitance techniques for different metal-semiconductor contacts fabricated in our laboratory. The slope of the line gives an indication of the change in barrier height expected for a change in Fermi level in the metal. Fig.IV exhibits the slope from Fig.III versus electronegativity difference of the semiconductor compound. The choice of substrate was determined entirely by this surface index. Efforts with ZnS to form a suitable system with Pt or Pd were unsuccessful because the material could not be doped to less than about 5000 ohm-cm. In addition, the adhesion of the metal film to the substrate was extremely poor.

We used CdS to investigate several metals with a view toward correlating band theory and the periodic table with experimental observations. In reactions that involve the dissociation of H_2 , Pt is a very active catalyst whereas its neighbor in the periodic table, Au, is not. Both have similar crystal structures (fcc) and work functions. The difference in atomic size

is about the same as that for Pt and Ni, but Ni is observed to dissociate H_2 . It would seem that neither the crystal structure nor the work function play any major role in determining the catalytic activity for clean metal surfaces. One observes that the highest energy levels of

Pt, the d-band, is only partially filled whereas the d-levels of Au are filled. However, the d-levels of Pd, an active catalyst, are filled. The difference to be noted is that the magnetic susceptibilities, χ_m , are very different. For Pt and Pd, χ_m is very high, for Au χ_m is low. Other experiments¹⁵ by Dowden et al. measured activities for various metal alloys. It was shown for example in the Ni-Cu system that addition of small amounts of Cu to Ni decreased the hydrogenation activity of Ni. Addition of Cu changes the specific magnetization of the alloy and the d-band vacancies are filled to some extent by electrons from the Cu. Another example is the chemisorption of H_2 on W. Calculations involved show that only those W d-orbitals closest to the adatoms and having lobes directed towards the 1-s orbital of the H_2 atom make significant contributions to the bonding of hydrogen¹⁶. It would seem that by nature of the strong bonding involved in chemisorption that d-orbitals play an important role. We are using this approach to determine which metals may prove useful for gas detection devices operating between room temperature and 120°C .

Our early attempts to work with metal Schottky barrier diodes eventually culminated in focussing on a structure that has been proven to be extremely sensitive to H_2 . This structure is Pd/SiO₂/Si diode. The surface index of SiO₂ is unity. A 20Å layer of SiO₂ is provided to reduce the surface state density of Si so as to appear electrically transparent to carriers flowing across the junction. The band diagram for this system appears in Fig. VII. Researchers in the solar cell area have been interested in such an interfacial layer because it considerably increases the conversion efficiency of metal-semiconductor solar cells. One explanation¹⁷ is that surface states at the oxide-semiconductor interface shape the electric field in the semiconductor altering the I-V characteristic. An alternative explanation¹⁸ proposes tunneling through the thin oxide layer. When the oxide layer

Figure VII Band diagram for Pd/SiO₂/Si diode.

is sufficiently thin, large tunnel currents can flow. In the case of Si this is about $60\text{\AA}$. In the case of Pd the metal work function is such that the dominant component of diode current tunnels from the metal to the minority carrier energy band in the Si. This diode is called a nonequilibrium minority carrier MIS tunnel diode. Nonequilibrium refers to the fact that the tunnel current is greater than the rate of minority carrier generation in the Si. Such diodes have been shown to exhibit I-V characteristics which approach those of an ideal pn junction¹⁹. Upon exposure of the diode to H_2 the barrier height is lowered by two mechanisms; a dipole layer which is formed at the Pd/SiO_2 interface and, for large concentration of H_2 , an increase in Fermi energy. Because of the decrease in barrier height the diode becomes a majority carrier MIS device.

Several papers^{20,25} describe the use of Pt and Pd MOSFET devices as smoke and H_2 detectors. The $\text{Pd/SiO}_2/\text{Si}$ device emerged from a model that was based on a bulk effect, but the excellent sensitivity to very small concentrations of H_2 must be attributed entirely to an interfacial effect. From capacitance measurements it is observed that a very small amount of H_2 results in a significant shift in the flat band voltage. The amount of H_2 dissolved in the Pd is far too small to result in a shift in the bulk Fermi level as proposed by Steele et al.²⁶. It is assumed that the adsorption sites at the Pd/SiO_2 interface are very similar to those at the Pd surface. With this model it is assumed that the concentration of hydrogen at the interface is in equilibrium with that on the Pd surface. This will be discussed in more detail later. The volume of adsorbed gas, v , can be related to the partial pressure of H_2 , $P_{\text{H}_{2g}}$, by a Langmuir isotherm of the form

$$v = v_m \frac{\epsilon P_{\text{H}_{2g}}}{1 + \epsilon P_{\text{H}_{2g}}} + \xi \frac{P_{\text{H}_{2g}}}{1 + \xi P_{\text{H}_{2g}}} \quad (7)$$

where v_m is the volume required to form a monolayer and ψ and ξ are constants related to adsorption and desorption rates. For very small concentrations such a model does not account for a bulk effect being of any significance.²⁷ In addition, photoemission experiments have identified a dipole layer at the Pd/SiO₂ interface. To wit, our model assumes that the change in barrier height is due to partial coverage by hydrogen ions forming a dipole at the Pd/SiO₂ interface as well as a contribution from a bulk change in Fermi level of the Pd for large concentration of H₂. The possibility that molecular H₂ diffuses along grain boundaries to the SiO₂ entering the oxide and perhaps the Si has been considered. Experiments with Al and Au contacts did not reveal any shift in the C-V curves or increase in the reverse leakage current of the diode. Several metals (Pt, Pd, Ni, and Fe) have been shown to dissociate and dissolve H₂ at room temperature whereas Al, Ag, and Au do not. Experiments with different contact areas have lead us to believe that the Pd/SiO₂ interface is uniform or pinhole effects, if any, in the oxide are uniformly distributed. The nature of the interface is currently being studied with the TEM.

We have also conducted experiments with CO. The device is sensitive to small amounts of CO in air only after the device has been previously exposed to H₂. Apparently CO is interacting with dissolved H₂ in the Pd which is not desorbed at room temperature. The oxidation of CO is reported to be activated at low temperatures in the presence of H₂.²⁸ Our experimental observations point to the following reaction

The role of the H₂ in the above reaction and the source of the new hydrogen sites in the Pd are not understood. Lundstrom²⁰ has observed a related anomaly with the oxidation of hydrogen peroxide. He proposes

the existence of silanol (Si-OH) groups to account for the more stable hydrogen sites. The nature of dissolved H_2 in Pd may be revealed by CPD and tracer experiments. We anticipate revealing results if the above technique is used to study adsorption phenomena on "real" Pd (and other metals) surfaces in different ambients. Earlier studies have always been performed on clean surfaces^{14,29} in high vacuum. Our work function studies reveal striking differences in the properties of the two surfaces.

Capacitance and current - voltage characteristics have been used to characterize the diode. On exposure to H_2 the C-V curve is shifted as shown in Fig.VIIIa. This shift corresponds to a change in the barrier height of the diode. The increase in capacitance is a result of the dipole layer at the Pd/SiO₂ interface. The magnitude of the discontinuity in potential associated with a perfect dipole layer is given as

$$\Delta = np/\epsilon_0, \quad (9)$$

where n is the number of aligned dipoles per unit area and p is the dipole moment of each dipole. The change in barrier height is a result of a change in affinity at the interface due to the layer of adsorbed dipoles. This is illustrated in Fig.VIIIb. The shift is independent of oxide thickness. The voltage shift, ΔV , is proportional to the dipole coverage, θ_d , at the Pd/SiO₂ interface and the bulk contribution, $\Delta\phi_w$.

$$\Delta V = \Delta V_{\max} \theta_d + \phi_w. \quad (10)$$

For small concentrations of H_2 the second term is negligible. ΔV is measured from a reference voltage V_{FBO} which is the flat band voltage of the diode extrapolated to zero hydrogen content. Adsorption and dissociation of H_2 on the Pd surface can be expressed as

where c_1 and d_1 are rate constants for the reaction and the g and sa

Room Temperature 5% H_2 in dry air

Figure VIIIa

Figure VIIIb Band diagram of Pd/SiO₂/Si a) before H₂
 b) after H₂ showing barrier height lowering
 due to dipoles at the Pd/SiO₂ interface.

subscripts refer to gaseous and surface adsorbed, respectively. Hydrogen atoms diffuse and are adsorbed onto the Pd/SiO₂ interface as well, i.e.,

The reaction rate constants c_2 and d_2 are much greater than c_1 and d_1 .

The hydrogen at the interface is considered to be in equilibrium with that on the surface. The expression which relates the time rate of change of adsorbed hydrogen is

$$\frac{d\theta}{dt} = c_1 P_{H_{2g}} (1 - \theta_s)^2 - d_1 \theta_s^2, \quad (13)$$

where θ_s is the fractional coverage of adsorbed hydrogen on the surface, which in turn is related to θ_d as follows

$$\frac{\theta_d}{1 - \theta_d} = \frac{c_2}{d_2} \frac{\theta_s}{1 - \theta_s}, \quad (14)$$

if c_2/d_2 is not unity. Our model considers this ratio to be unity. The steady state coverage of hydrogen atoms at the Pd/SiO₂ interface is then

$$\frac{\theta}{1 - \theta} = (c_1/d_1 P_{H_{2g}})^{1/2}, \quad \theta_s = \theta_d = \theta. \quad (15)$$

Combining (14) and (19) we write

$$\Delta V_{\max} = \Delta V [(c_1/d_1 P_{H_{2g}})^{-1/2} + 1]. \quad (16)$$

Plotting ΔV vs. $P_{H_{2g}}^{-1/2}$ and extrapolating $P_{H_{2g}}^{-1/2}$ to zero we obtain $\Delta V_{\max}$ as in Fig. IX. The slope of the line is $\sqrt{c_1/d_1}$. The temperature dependence of this parameter is used to evaluate the heat of adsorption for a H₂ molecule on the surface of Pd.

We are applying reaction rate theory to analyze data for many chemical reactions on the Pd surface. The goal is to use this device to monitor chemical reactions that involve production of H₂. To determine the true heat of adsorption of H₂ on Pd from the theory to be discussed later, experiments must be performed in an inert ambient. The temperature coefficient

Fig. IX

of $\sqrt{c_1/d_1}$ in a nitrogen ambient indicates the possibility of chemical reactions of the following nature

Techniques for establishing values for rate constants such as c_1 and d_1 would be very useful for studying more complex reactions as well as chemical poisoning. For reaction (11) the initial rate of change of θ is given as

$$\frac{d\theta}{dt} \Big|_{t=0^+} = c_1 P_{\text{H}_{2g}} \quad (18)$$

By observing the transient change in the flat band voltage, c_1 can be evaluated as shown in Fig X. We have from equations (10) and (18)

$$\frac{d\Delta V}{dt} \Big|_{t=0^+} = \Delta V_{\max} c_1 P_{\text{H}_{2g}} \quad (19)$$

The constant c_1 is then determined by plotting the slope of the graph of Fig. IX vs. $P_{\text{H}_{2g}}$ as in Fig. XI. Consider the following reaction as an example

We have observed that this reaction is irreversible at room temperature but entirely reversible above 120°C in air. An evaluation of c_4 as a function of exposure time to H_2S at room temperature may lend information about the mechanism of poisoning.

The model of reaction rate theory used to evaluate our observations applies, in the case of H_2 , to surface reactions on the metal, whereas our device measures hydrogen at the Pd/SiO_2 interface and, for large concentrations, in the bulk. The experimentally determined rate constants must be modified if the assumption of equation (14) is not valid. The following discussion follows the development of the theory found in several texts^{30,31,32}.

Figure X

Figure XI

The adsorption and dissociation of molecular hydrogen on the Pd surface via vacant adsorption sites, A_v , involves a transition energy state, H'' , as shown in Fig. XII.

with rate constants k_1 , the first step to the transition state, and k , the overall rate constant.

$$k_1 = \frac{[H'']}{[H_{2g}][A_v]^2} \quad \text{and} \quad k = \frac{[H_{as}^+]^2}{[H_{2g}][A_v]} \quad (22)$$

The temperature dependence of the rate constants is illustrated by replacing the state functions with their respective partition functions. Assuming Maxwell-Boltzmann statistics for the atoms in equilibrium which are partitioned among the different energy states the atoms have a distribution. Briefly, the partition function is made up of three components which represent the total energy of the atom; translational, rotational, and vibrational. Refer to reference 31 for details. We have then

$$k_1 = \frac{Z[H'']}{Z[H_{2g}]Z[A_v]^2} \exp[-q\psi_1/kT]$$

and

$$k = \frac{Z[H_{as}^+]^2}{Z[H_{2g}]Z[A_v]} \exp[-q\psi_0/kT]. \quad (23)$$

We have by definition that $c_1/d_1 = k$ such that

$$\sqrt{c_1/d_1} = \frac{Z[H_{as}^+]}{Z[A_v]Z[H_{2g}]^{1/2}} \exp[-q\psi_0/2kT]. \quad (24)$$

The theory predicts a temperature dependence for the experimentally determined rate constant depending on the choice of partition function used for the adsorbed hydrogen.

For immobile adsorbed hydrogen ³²

$$\sqrt{c_1/d_1} = \text{const } (T^{-7/4}) \exp[q\psi_0/kT^2], \quad (25)$$

Figure XII

and for adsorbed hydrogen that is free to move about on the Pd surface

$$\sqrt{c_1/d_1} = \text{const } (T^{-3/4}) \exp [q\psi_o/kT]. \quad (26)$$

Experiments by others²⁰ have shown that a model of immobile adsorbed hydrogen fits their own experiments more closely, which is surprising. From this theory the heat of adsorption ψ_o in eV can be evaluated. Remembering that the experimentally determined rate constant refers to hydrogen adsorption at the Pd/SiO₂ interface, the value of ψ_o refers to heat of adsorption at the interface.

In a similar fashion the temperature dependence of c_1 can be predicted. The initial rate of adsorption for the first step in expression (21) is

$$\frac{d\theta}{dt} = 2\nu Z[H''], \quad (27)$$

where ν is the vibration frequency of the transition state perpendicular to the surface. From equations (18) and (27) we have

$$c_1 = \frac{2\nu Z[H'']}{Z[A_v]^2 Z[H_{2g}]} \exp [-q\psi_o/kT]. \quad (28)$$

The temperature dependence here is dictated by the nature of the transition state. Experimentally determined values of c_1 can be used to calculate the activation energy ψ_1 . This holds for values of c_4 as well as in the case of our other example H₂S. Lundstrom has applied a similar theory to a fundamental study of hydrogen in argon and in air²⁰. We have used this approach to evaluate data for hydrogen in nitrogen and air, and H₂S in nitrogen and air.

What is needed now is to conduct careful studies of work function changes and gather adsorption data for real metal surfaces. This is going to be done by the Chemical Engineering group participating in the project. We believe the Pd/SiO₂ interface behaves very much like the exposed Pd surface in terms of the nature of the adsorption sites.

VI. GAS RESPONSE OF ZnO FILMS

Deposition of doped and undoped ZnO by pyrolysis yields thin polycrystalline films with average grain size of 0.5 microns. Elemental analysis of impurity concentration is done using Auger and X-ray techniques. Conductivity and optical absorption spectroscopy are yielding information about the band diagram for this material and the influence of impurities on electrical properties such as mobility. Controlled crystal structure and improved gas sensitivity have been observed for ZnO films doped with Pd and Cl using $(\text{NH}_4)_2\text{PdCl}_6$ as the dopant source material in the modified pyrolysis scheme. Gas detection studies with undoped ZnO and ZnO doped with Pd and Cl have laid the groundwork for developing experimental procedures and a criteria for evaluating gas sensitivity.

ZnO films have demonstrated good sensitivity to CO and CH_4 at elevated temperatures in a reversible fashion. A temperature range for best sensitivity to CO has been established to lie within 350 to 450°C in both dry and 3% humid air. The response to CO is history dependent and in general, devices must be first heated to higher temperatures for a short time and then operated within the above range. ZnO devices exhibit long term irreversible deterioration in terms of sensitivity due to sulphur and carbon contamination. This has been confirmed with Auger analysis. Experimental observations point to both an electronic behavior as well as an active sites contribution for gas sensitivity. ZnO is doped n-type with group VII and III-VI compounds. Group VIII metals are used to lower the activation energy of chemisorption reactions. Early results with sputtered films incorporating the doping schemes show better sensitivity than with polycrystalline films and in the case of Cu doping, some degree of selectivity between CO and CH_4 has been observed. Sputtered films are characterized

by TEM and elemental analysis. We are in the early stages of parameterization but have demonstrated good film adherence to many substrates and controlled doping.

Gases of interest with the ZnO system are CO and CH₄. The geometry and apparatus for testing these materials is identical to that outlined for SnO₂. Within the temperature range stated for CO, doped films of ZnO exhibit per cent changes of resistivity as large as 50% in dry air for CO concentration of 1000ppm. Humidity has been shown to reduce sensitivity in this temperature range slightly. Response to 5000ppm CH₄ in this temperature range is enhanced greatly by use of group VIII dopants. For films doped with 2% Pd changes in resistivity as large as 70% have been observed in dry air. In general for doping schemes that do not include group VIII impurities, the sensitivity range for CH₄ detection requires a minimum temperature in the range of 500°C. Some degree of selectivity is observed between the two gases in the lower temperature range for films that do not contain group VIII impurities but these films do not show the same degree of sensitivity. Recently it has been observed that Cu doping improves the sensitivity to CO in this temperature range improving selectivity.

Sputtered films of undoped and doped ZnO are sensitive to O₂ concentration in an irreversible fashion in the temperature range of 350 to 450°C. O₂ acts as an acceptor gas reducing the conductivity of the ZnO. Films doped with group VIII metals show a very high degree of sensitivity to H₂ over the temperature range. A change of 2 orders of magnitude of resistance for 100ppms H₂ is typical and fully reversible.

VII GAS RESPONSE OF SnO_2 FILMS

The films prepared by the CVD technique have a planar geometry. The films are thus tested by a four-probe station, and the unit is housed in a vacuum system. The range of films tested vary from thick insulating films to transparent conducting films on various substrates. However, the results of gas sensitivity leaves a lot to be desired. Fig. XIII shows the response curves for one typical set of thick films. One reason for this poor response might be due to the fact that the planar geometry, and the testing method limit the temperatures of operation to 350°C or so. This is definitely a low temperature when compared to the melting point of SnO_2 (1800°C).

The films prepared by RF technique are the most promising of all films tested to date. The geometry of the substrates used, however, is not planar; instead, it consists of a hollow alumina cylinder onto which the oxide film is sputtered. Two contacts are then provided to this film by means of a silver epoxy. The contacting wire is made of Platinum. A heater is inserted into the cylinder, and provides the necessary heat to the film. The whole unit is mounted on a TO-5 header. Fig. XIV shows the device. Fig. XV is a plot of the gas response of these films versus ppm concentration, at a constant temperature. The device is very sensitive to H_2 and H_2S (not shown). However, the sensitivity to CO and CH_4 is not as dramatic. This might then provide a selective device to distinguish between the gases. A resistance versus temperature study of one such device in air shows a minimum. It is hypothesized that this might result from the semiconducting nature of the film and its response to oxygen chemisorption as two competing mechanisms.

Fig. XIII Concentration studies in background of N_2 at $1000 \mu m$ (1-1) for SnO_2 films prepared by CVD.

OXYGEN: 2-2: 7%, 3-3: 44%, 4-4: 88%, 5-5: 93%.

R-R: Resistance measurement
H-H: Heater current

Fig. XIV Typical geometry for a Gas Sensor.

The heterojunctions prepared from crystals of SnCl_2 were tested in various ambients for gas response studies; tests were carried out at room temperatures and at temperatures around 100°C . However, little can be said about the results at this stage. The main drawback with this device is the rapid degradation of the junction (mentioned earlier). However, studies are being planned for extremely thin SnO_2 layers, such that the device may be used as a surface effect device.

VIII GAS RESPONSE OF $\text{Pd/SiO}_2/\text{Si}$ DEVICES

Room temperature sensitivity to H_2 of this device is very good. 1ppm H_2 in dry air is easily detected and the operating range extends into the area of 10,000ppm where the characteristic saturates. The optimum temperature for H_2 sensitivity has been established at 120°C for a few tenths of 1ppm. Water vapor reduces the sensitivity to H_2 at room temperature. Operation of the device at elevated temperatures improves the sensitivity. The device can be used at temperatures as high as 150°C . The device is also sensitive to gases which dissociate on the Pd surface and produce H_2 within the above temperature range. H_2S and NH_3 are two such gases. Response times for these two gases are determined by the time associated with dissociation of the gas species on the surface whereas response time for H_2 alone is immediate.

The response to H_2S is observed to be reversible at elevated temperatures in air. Room temperature exposure or exposure in an ambient devoid of oxygen results in an irreversible deterioration of the sensitivity. However, devices exposed in this manner still show good sensitivity to H_2 .

This device has also shown a peculiar sensitivity to CO at room temperature. The device will respond to several hundred ppm CO only after previous exposure to large amounts of H_2 . After exposure to H_2 ,

Fig. XV Response to H_2 for films prepared by RFS.

the device fully recovers its original characteristics. Exposure to CO results in a change in the device characteristic which recovers in a few seconds. Continued exposure to CO has no effect on the characteristic. This phenomenon is outlined more clearly in a previous section of this report. Use of this anomaly would find limited applications, because of the fact that previous exposure to H_2 is required for CO sensitivity.

IX. ELECTRONIC DATA PROCESSING

The thrust of work to date has been two pronged; firstly, the development of a test apparatus for automated control of a clean gas system and secondly, the use of the system for investigation of the basic mechanisms of chemisorption and detection of gases by thin-film metal-oxide sensors.

A clean gas system was constructed of stainless steel and glass. It allows the production of known concentrations of pollutant gases at atmospheric pressure down to one part per million. The system allows controlled mixing, injection, and dilution of any combination of air, oxygen, nitrogen, hydrogen, methane, carbon monoxide and argon. This gas apparatus can house up to sixteen gas detectors.

The detectors are monitored and controlled by a data acquisition system consisting of two microcomputers in tandem. One computer monitors the resistance of sixteen sensors simultaneously, measuring to 5% resistances which, owing to the power law nature of semiconductor devices, may vary over five orders of magnitude. It also provides real-time control of sensor temperatures so that as temperatures are modified resistances can be reliably measured. Typical time constants for response to a change in temperature range from several seconds to several hours. Data collection can occur every second, providing sufficient resolution to capture the most rapid dynamic behaviour of the detectors. The computer is programmed to control experiments which typically last several hours, obviating the need for constant operator attendance.

A second microcomputer receives data from the first and permanently stores it on disk. Statistical analysis, curve fitting, and parameter identification are the major duties of this computer. Using a high-level

language, BASIC, the raw data can be fit to models of device behaviour immediately at the end of data collection, giving low turn around time to an experiment from conception to completion.

Testing has focused on commercial gas detectors (Taguchi gas sensors, manufactured by Figaro Inc.) due to their availability in large numbers and their reproducibility. These are sintered tin oxide detectors similar to some of those being produced in house. In addition testing is done on our own in house detectors to determine their sensitivity to various gases and to provide direction to their further development. These detectors are primarily thin films of variously doped zinc oxide and tin oxide.

For these detectors experiments are devised to elicit the basic mechanisms of chemisorption, surface catalysis and detection of gases. These experiments fall into two broad classes: measurement of the dynamic response of sensor conductance to temperature change in various gases, and measurement of conduction at different concentrations of oxidizing or reducing gases at constant temperature.

The dynamic response to temperature change depends on adsorption/desorption phenomena as well as surface migration and chemical equilibria changes in the metal/oxide and oxygen/reducing gas reactions. Each of these mechanisms exhibits characteristic time constants. Experiments are designed to separate the various effects. By observing the rapid flash desorption times we determine chemisorption energies while longer time constants reveal changes in the metal-oxide stoichiometry. It appears that different heats of chemisorption of different species of gas will provide a means of producing gas selectivity by manipulating temperatures and/or surface doping levels. Results of flash desorption experiments will appear in a forthcoming paper.

The response of conductivity to low partial pressures of reducing gases at constant temperature is measured and is being fit to models for the appropriate surface catalysis. A major obstacle to the use of semiconductor sensors has been their highly nonlinear response to gas concentrations. Once the nature of this response is understood, however, a synergistic cooperation of detector and microcomputer may enable their widespread use.

X. CONCLUSIONS

To date we have successfully demonstrated techniques for deposition of thin solid films of SnO_2 and ZnO in doped and undoped form on a variety of substrates. These films show promise of good sensitivity to many toxic and flammable gases of interest. The use of proper doping materials has resulted in an increase in gas sensitivity in some cases and, in general, provide a means for improving selectivity as well. Characterization of these films is providing an understanding of the role of chemisorption and bulk diffusion mechanisms on carrier mobility and device conductivity. In short, we are well on our way to fulfilling the goals as outlined in Appendix I in terms of material characterization and device feasibility of deposition and/or growth on conventional semiconducting materials such as silicon.

In addition to conducting studies of semiconducting metal-oxides, we developed a highly sensitive metal/oxide/semiconductor diode sensitive to very small concentrations of gases, such as H_2S and NH_3 , which liberate H_2 when dissociated at the metal surface. Work on this device has laid the experimental and processing groundwork for metal-oxide materials in conjunction with silicon to produce heterojunction and field effect device structures. Some preliminary studies of these systems have already been performed.

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COMPLIANCE WITH CONTRACT REQUIREMENTS
AND PLAN FOR WORK DURING THE REMAINDER OF THE CONTRACT

The work reported is in compliance with contract requirements. During the time, April 1, 1977 - March 31, 1978, the principal investigator, A.G. Jordan, has spent 20% of his time working on the project. The other investigators have spent their times working on the project as follows: C.L. Bauer, 10%, T. Fort, 10%, R.L. Longini, 10%, D. Tuma, 20%. During the remainder of the current term, all investigators will spend their times working on the project as above.

A paper entitled "A Thermodynamic Analysis of the Deposition of SnO_2 Thin Films from the Vapor Phase" by G.N. Advani, A.G. Jordan, R.L. Longini, D.J. Leary has been submitted for publication in the Journal of Thin Solid Films. A reprint of the manuscript is presented in Appendix II.

As amply documented in this report, substantial progress has been made on the project during the first year since its inception on April 1, 1977. Much of the work has concentrated on the preparation of materials and devices, and on preliminary characterizations and rough measurements of devices' response to a variety of gases of interest. During the remainder of the term, (April 1, 1978 - September 30, 1978), work will continue on improving fabrication techniques for devices which have already proven feasible (concentrating on the most promising ones), on performing more careful measurements of devices response to gases of interest, on characterizing materials using powerful analytical techniques, and on understanding the surface chemistry involved in the chemisorption processes taking place in the devices. The latter two tasks will bring the expertises of C.L. Bauer (in materials characterization) and T. Fort (in surface chemistry) to more closely bear on the device preparation, modelling and analysis conducted by A.G. Jordan and R.L. Longini. In addition,

the work conducted by D.Tuma on electronic data processing (using commercial devices so far) will focus on the devices fabricated in our laboratory.