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Paper Session II-B - Solid State Oxygen Sensor Development

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SOLID STATE OXYGEN SENSOR DEVELOPMENT

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ABSTRACT
To anticipate future long-duration mission needs for life support sensors, we explored the feasibility of using thin-film metal-oxide semiconductors. The objective of this task was to develop gas sensors for life support applications which would be suitable for long-duration missions. Metal oxides, such as ZnO, SnO$_2$, and TiO$_2$ have been shown to react with oxygen molecules. Oxygen lowers the metal oxide's electrical resistance. Critical to the performance is the application of the oxide in a thin film on an inert substrate: the thinner the film, the more readily the oxygen penetration and hence the more rapid and sensitive the sensor. Metal oxides are not limited to oxygen detection; rather, oxides offer detection and quantification applications to the complete range of gases of interest, not only for life support systems, but for propellants as well.

After a preliminary assessment of various metal oxides, we chose ZnO as the active sensory element for oxygen - the most critical near-term need for life support sensors. Our results to date are that we:

- Verified that metal oxides respond linearly to oxygen concentration
- Experimented with deposition techniques for a thin film of ZnO
- Determined the appropriate operational parameters by which ZnO could be used to measure oxygen in concentrations from 10% to 30%
- Selected a conceptual design suitable for proof of concept
- Developed techniques to fabricate the prototype sensor compatible with integrated circuit and microelectronic packaging

Subsequent work will optimize the ZnO properties, refine prototype design and fabrication, and install and test the sensors in the KSC Plant Growth Chamber.

INTRODUCTION

There is a need for a reliable, lightweight oxygen sensor for advanced life support systems. Current oxygen sensors, such as those in the Space Shuttle Orbiter, are potentiometric cells with a solid electrolyte. These cells exhibit insufficient lifespan for missions in excess of 30 days. Furthermore, electrochemical cells degrade over time, requiring frequent re-calibration. These electrochemical cells are currently changed out every few days, and require refurbishment on the ground. Additional drawbacks of current systems include: bulkiness and a continuous...
drift due to the saturation in the electrolyte and the change in reference electrode potential.

The use of metal-oxide semiconductor thin films as oxygen detection devices offers an alternative approach. In this report, we present results on material development and characterization, the oxygen sensing characteristics, and the design of a miniature solid state heater in order to realize a integrated solid state oxygen gas sensor. Future directions are also outlined based on these results.

It has been well known since 1962 that these oxides, such as ZnO, SnO₂ and TiO₂ can react with oxygen molecules which are chemisorbed on the surface by electron transfer. The depletion of mobile electrons from the lattice lowers the material's electrical resistance which can be used to monitor the oxygen (or other gases) concentration. The chemisorption process is temperature sensitive. Within these oxides, there are different mechanisms occurring at various operating temperatures.

In order to satisfy the requirements for space mission applications, the oxide material of choice must have a low to medium operating temperature range, to minimize power use and maximize longevity, and the entire device be patterned into a miniaturized integrated solid state package. Moreover, the response is preferably linear in the oxygen concentration range of interest: 10% to 30%. Other issues such as selectivity and long term stability are also important.

Based on these considerations, and after a suitable literature search, we choose ZnO thin film to be the active sensing material. The ideal operating temperature for ZnO is between 250°C to 300°C when oxygen gas and ZnO interact according to the so-called "chemisorption" mechanism. During this process, electrons near the ZnO surface are depleted by chemisorbed oxygen molecules to form O₂⁻ - the electrical resistance of the ZnO increases linearly with the oxygen concentration. At high temperatures (above 300°C), oxygen vacancy diffusion inside the lattice dominates: the diffusion process is very slow and results vary. At temperatures lower than 250°C, ZnO has insufficient thermally activated electrons and therefore the chemisorption process is too slow to be practical. Thus, we must heat the ZnO to between 250°C - 300°C and maintain this temperature for proper sensor function.

In the "chemisorption" regime, the resistance change (i.e. sensitivity) can be optimized by the doping density of the film, its thickness, and exposed surface area. For large resistance change, films with small thickness, large exposed area, and low electron density are most desirable. These material parameters are easily adjustable by using the Pulsed Laser Deposition technique to grow ZnO thin films. Finally, the temperature range of interest is sufficiently low that it can be achieved by micro-filament heaters.

MATERIAL DEVELOPMENT

The key issue in growing high quality ZnO films is the ability to incorporate sufficient oxygen into the lattice to maintain its stoichiometry. While traditional thin film growth techniques such as Chemical Vapor Deposition and Sputtering are commonly used, we find that Pulsed Laser Deposition offers the most advantage and flexibility in fulfilling this requirement. This
novel technique employs a pulsed high energy UV laser as an external power source for evaporation and deposition.

The growth using Pulsed Laser Deposition was carried out in 0.02 torr of oxygen background pressure to provide a reactive environment. Typical growth rate was 1 micron/hr. Sapphire, silicon, quartz plate, and silicon wafers with metal film for electrical contact were used as substrates. Under a laser fluence of 2J/cm² to ablate an undoped ZnO target, we were able to grow ZnO films at a temperature as low as 25°C. ZnO films grown at room temperature are transparent with 82% transmission and an absorption edge at 3840Å wavelength. Structurally, it is preferentially c-axis oriented as shown in the X-ray diffraction pattern in Figure 1.

For comparative purposes, the oxygen sensing properties of films grown at different temperatures were measured and compared. In addition, we were also able to control the electron density in the ZnO film by introducing nitrogen into the lattice substitutionally. Undoped ZnO films are n-type due to the presence of oxygen vacancies. The electron carrier density is between $10^{18}-10^{20}$ cm⁻³. In nitrogen doped ZnO films, electron density is reduced by compensation. This is significant as the resistivity of the doped films is 3 to 6 orders of magnitude higher than the undoped samples. Clearly, this has important implications for sensor sensitivity.

SENSOR PROPERTIES MEASUREMENT

After a film is grown, we patterned a pair of Au/Ti interdigitated electrodes by photolithographic lift-off technique. The ratio of the total length of the electrode to the spacing distance between the two electrode is about 100:1. Electrodes are surrounded by a guard ring biased at ground potential to reduce spurious noise. Thin gold wires are attached to the electrode pads by silver paste for electrical measurement. The sensor is mounted on a inconel holder whose temperature can be regulated up to 700°C with an accuracy of ±0.5°C.

The resistance of the ZnO thin film was measured by applying a constant voltage across the electrodes while measuring the current flow. The test chamber has a capacity of only 3 liters to facilitate rapid gas purging. Oxygen and nitrogen gases are introduced through
mass flow meters and well mixed in a T-shaped tube filled with glass grit. During the measurement, the test vessel was wrapped tightly with aluminum foil to eliminate any photoconductive effect.

Figure 2 shows the response of a 1.2 micron thick ZnO film at 275°C to an injection of oxygen into nitrogen to achieve a 20% Oxygen/80% Nitrogen mixture. The film was grown at 175°C. The response time, defined as the time required to achieve 95% of the final constant value, is about 270 seconds (4.5 minutes). It does not vary considerably within the studied temperature range from 250°C to 300°C. The rate limiting step is believed to be the diffusion of oxygen along the grain boundary to be chemisorbed at the active surface site. This suggests that the response time can be shortened by reducing the thin film thickness.

In order to speed up response time, we tested a film grown under identical conditions but with a thickness of only 5000Å, it shows a shorter response time of only 155 seconds (2.58 minutes). The response time can also be shortened by nitrogen-doping into the ZnO film. Figure 2 compares the response time between a nitrogen-doped ZnO film and an undoped film. The nitrogen-doped film, although twice the thickness as the undoped film, shows a faster response: 92 sec (1.53 minutes). A plausible explanation is that the introduction of low concentration levels of nitrogen atoms to substitutionally replace the oxygen atoms in the lattice. This replacement can cause internal stress because of the different atomic radii of the two species. The stress enhances the rate of diffusion of oxygen along the grain boundary. Further investigation out to optimize the film thickness and nitrogen doping level with respect to improve the response time is needed.

![Figure 2](image_url)

**FIGURE 2. Response of the electrical resistivity of various ZnO films to oxygen in a 20% oxygen/80% nitrogen mixture**

**SENSITIVITY**

Figure 3 shows the resistance of ZnO thin film as a function of oxygen concentration in an oxygen/nitrogen mixture at 275°C. For undoped ZnO, the sensitivity increases with the decrease in thickness. Since the thickness of the electron depleted layer occupies a larger fraction of the total thickness, sensitivity also increases with the decrease in electron carriers since the number of depleted electrons will account for a larger portion of the total electrons. This is reflected in the results showing that thin undoped ZnO film has a higher sensitivity than thick films while nitrogen doped ZnO film exhibits the highest sensitivity. A systematic study well be carried out to optimize the sensitivity by adjusting the nitrogen doping level.
FIGURE 3. Relative electrical resistivity R/R_o of various ZnO films vs. oxygen concentration in oxygen nitrogen mixture. (R_0 is the resistance of the film in the absence of oxygen)

In addition to basic performance characteristics, we also found that common gases such as CO_2 and NH_3 have no interference effect. Preliminary investigation on reliability shows that during the first 60 hours of operation, the sensors show some degradation. However, after the initial "burn in" period, they show excellent long term stability. The stability seems to be dependent on the crystallinity of the ZnO film.

MICRO-ELECTRONIC PACKAGING

For operational use, the entire sensor assembly will be miniaturized into a chip-sized solid state device with an integrated micro-heater and a built-in temperature sensor. The initial sensor characterization was carried out in an environmentally controlled chamber with a bulk heater. Of course, this assembly is impractical and not representative of life support applications.

To enable the assembly and realistic test of a miniaturized prototype, a photolithographic set of five masks has been designed. Fig. 4 shows the cross sectional view of this device.

FIGURE 4. Cross sectional schematic view of a miniature solid state oxygen sensor

The assembly of this prototype is anticipated for December 1993. The active element is at the center of a low stress and low thermal conductivity silicon oxynitride free standing film on a silicon substrate for thermal isolation. A meandering thin film nickel filament micro-heater and a resistive type temperature sensor will be deposited and patterned. The heater will then be covered by a SiO_2 layer for electrical insulation. This will be followed by the deposition and patterning of a pair of interdigitated Au electrodes aligned just on top of the heating element. Finally, ZnO film will be deposited on the interdigitated electrode. Each wafer is 8 mm x 8 mm in size and will be mounted on a 20 mm x 20 mm 20-pin header. Each wafer contains three identical gas sensor devices. Integral, triple-redundant cells will serve as a cross check to assure accuracy and inherent backup in case a
single unit failure. The active area of each device is only 0.5 mm x 0.5 mm. An estimate power consumption to achieve 300°C in such a small localized area is approximately 1.3 watts.

CONCLUSIONS

We have demonstrated the merits of using nitrogen-doped, thin-film ZnO for oxygen detection and measurement. This technique offers great promise not only for oxygen detection, but other gases. The response of thin-film ZnO is stable over time, a significant advantage over current oxygen sensors. Because of the relatively small size of our prototype sensors, distributed networks of low-weight, low power sensors can more accurately assess local environmental conditions than current sensors. Low power use and low weight are obvious advantages for space systems. All of these benefits offer a significant improvement in current life support systems control.

FUTURE WORK

1. We will continue to optimize the ZnO film properties, especially thickness and nitrogen doping level to improve sensitivity and shorten response time.

2. We will gain a better understanding the degradation mechanism during the initial "burn in" period. This has been speculated to be related to the crystalline quality.

3. Integrated solid state oxygen gas sensors will be fabricated and tested.

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