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High Temperature Oxygen Sensor Using Ion Beam Sputtered YSZ Film

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이온빔 스퍼트한 YSZ 막을 이용한 고온 산소센서

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Summary

A micromachined silicon-based high temperature oxygen sensor operated in the amperometric mode is developed. Yttria-stabilized zirconia(YSZ) is used as a solid electrolyte. A two electrode electrochemical sensor has been developed. This sensor has some advantages as simple structure and small power consumption compare to the conventional three electrode ones. The sensor can be operated at up to 800℃ and requires about two watts to heat the sensor to 700℃ by using an internal heater. The design, processing and experimental results of this high temperature oxygen sensor will be discussed.

Introduction

Calcia- and yttria-stabilized zirconia have been used as a solid electrolytes for high temperature gas sensors for the monitoring of O_2, CO, H_2 and others. Over the years, high temperature oxygen electrochemical sensors have been fabricated using calcia- and yttria-stabilized zirconia and operated in either the potentiometric or amperometric mode(Kimura et. al., 1986, Logothetis and Hetrick, 1986). Each mode of operation has its advantages and disadvantages. For instance, the potentiometric oxygen sensor is relatively simple in construction and in requirements of measuring equipment. Yet, the potentiometric sensor output is governed by the Nernst equation that exhibits a semi-logarithmic relationship between sensor output and oxygen activity(concentration). This limits the sensitivity

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and the detecting range of the sensor. On the other hand, the amperometric oxygen sensor shows a linear relationship between sensor output (current) and oxygen concentration. Yet, the amperometric sensor requires a well-defined, highly reproducible surface area of the sensor electrode Microfabrication technology is a reasonable mean to accomplish this. Amperometric oxygen sensors using yttria-stabilized zirconia have been reported (Makovos and Liu, 1991), and thick film metallization techniques are used in that development.

In this study, an oxygen sensor is produced using silicon-based microfabrication and micromachining techniques. An ion beam sputtered yttria-stabilized zirconia (YSZ) thin film is used as the solid electrolyte. On-chip heater and temperature detector are adopted for the on-site heating and temperature sensing. The design, processing and testing results of this sensor will also be discussed.

Design and Fabrication of the Oxygen Sensor

Fig. 1. shows a mask pattern of an oxygen sensor including a heater, a temperature detector and sensing elements. An n-type (100), 300μm thick silicon wafer is used as the substrate. A 5000 Å thick silicon dioxide layer is grown to provide electrical insulation. On-chip temperature sensor and heater are incorporated in this design. Both the heater and temperature sensing elements employ a thin-film platinum resistance structure. The overall size of this oxygen sensor is 2.6㎜×3.5㎜.

Fig. 2. shows a cross-sectional structure of the high temperature oxygen sensor by using micromachining techniques and lift-off method (Wu et. al., 1993). The electrode elements of this oxygen sensor are also platinum films. The

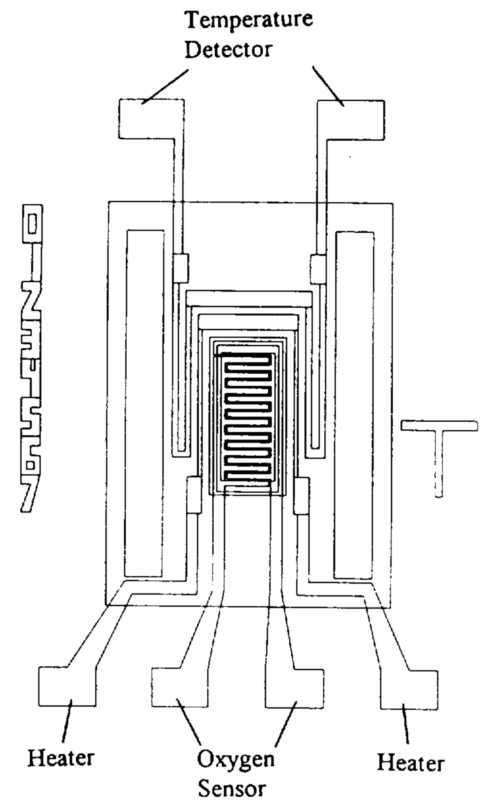


Fig. 1. A mask pattern of the high temperature oxygen sensor including a heater and temperature detector. The overall size of the oxygen sensor is 2.6㎜×3.5㎜.

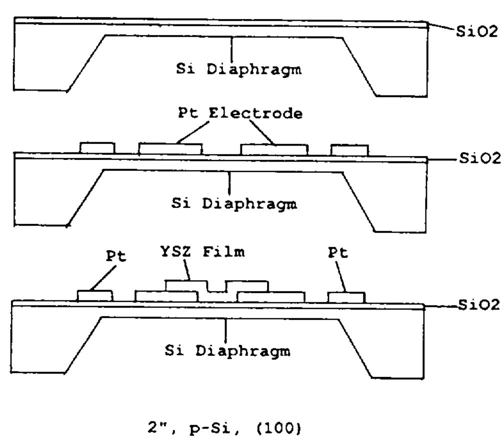


Fig. 2. A cross-sectional structure of the high temperature oxygen sensor by using micromachining technique and lift-off method.

thickness of the platinum film in all these sensor elements is 5000 Å. The yttria-stabilized zirconia film is prepared by using an yttria-zirconia target (composition : Zirconium Oxide-Yttria stab. 5-10 wt% Y_2O_3, Kurt J. Lesker Co., Claiton, PA) and the film is deposited by ion beam sputtering technique. Table 1 shows ion beam sputtering conditions for the platinum and the YSZ films. The deposition angle in this table is the angle between target and substrate. The thickness of the film deposited is about 5000 Å. The porosity of the films deposited are affected by the deposition angle. The films deposited by 45 degree is less dense than 0 degree.

Table 1. Ion beam sputtering conditions for the platinum and the YSZ (yttria-stabilized zirconia) films

	Pt	YSZ
Deposition Angle	45 degree	45 degree
Working Pressure	2E-4 torr	2E-4 torr
Ar/O_2 Ratio	Pure Ar	9% O_2
Power	1kV, 15mA	1kV, 15mA
Deposition Rate	25A/min	9-12A/min
Substrate Temperature	no heating	no heating
Plasma Clean	yes	no
Beam	focussed	focussed

Fig. 3. is the ESCA results of the deposited YSZ films. Analysis of the deposited zirconia film shows the yttria content to be approximately 8 mol% that is within the original yttria composition of the target. And also the analyzing results of the surface and the bulk of the YSZ films show the same composition. This means that the deposited YSZ film has a uniform composition within the film. All patterns acomplished in this fabrication process are well defined by a lift-off technique.

Because yttria-stabilized zirconia will only become ionic conductive at 600℃ or above, the sensor must be heated to that temperature. In order to minimize any significant mass heat loss, as well as the power consumption of heating the sensor, the backside of the silicon wafer is selectively removed by chemical anisotropic etching using an EPW (ethylene-diamine pyrochatechol water). This reduces the total thickness of the silicon wafer from 300μm. This thickness is controlled by a p^+ etching stop. The

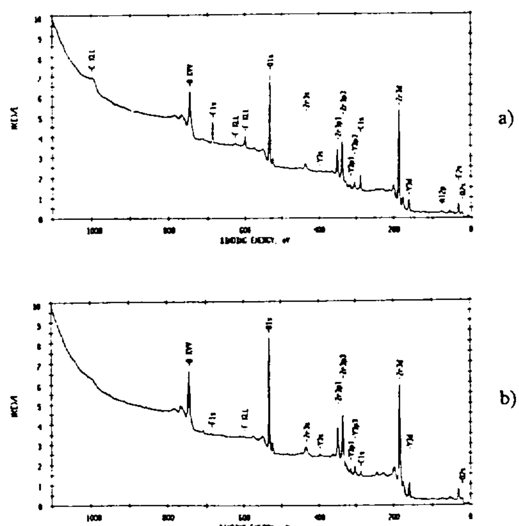


Fig. 3. ESCA spectra of the YSZ films, a) as deposited, b) after sputter etching about 500 Å.

overall size of this oxygen sensor is 2.6mm×3.5 mm. The diced sensor is mounted on a ceramic flat-pack, and gold lead wires and ceramic spacers are used for the proper connections and heater insulation, respectively. Especially, a high temperature ceramic adhesive (Ultra-Temp 516, Aremco Prod., Inc.) is used as an adhesive for the sensor package.

Experimental Results and Discussion

1. Experimental procedure and equipment

Fig. 4. shows calibration characteristics of an on-chip platinum temperature detector. In this experiment, the detector is placed in a quartz chamber inside a tube furnace with a set of thermocouple to measure an active temperature. The measured temperature range is between 700K and 1200K. The temperature response of the platinum film resistor on the chip is fairly linear and stable. The platinum film shows temperature coefficients of 100$m\Omega$/K at the temperature below 1070K and 65$m\Omega$/K at the temperature above that. So these can be used for the calibration of the temperature detector.

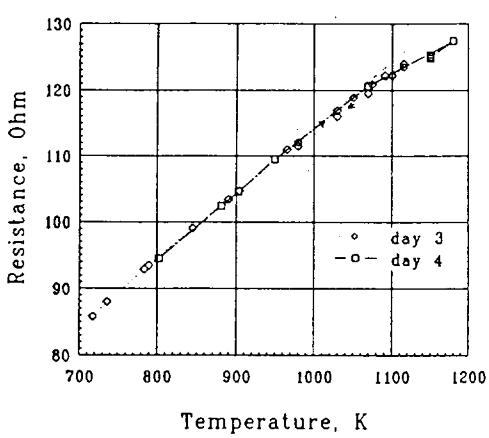


Fig. 4. Calibration characteristics of an on-chip platinum temperature detector.

Fig. 5. shows a gas flow and measurement systems for the high temperature oxygen sensor. The total flow rate of a supplied gas is between 200~500cm^3/min that do not affect significantly the sensor response time (Makovos and Liu, 1991). The mixing ratio of the supplied gases were controlled automatically according to the specified individual flow rates or mole fractions. In this experiment, the total flow rate was maintained constant at 225cm^3/min for an experiment. Over the range of the flow rates used, the gas in the tube could be assumed to be at chemical euqilibrium at temperature above 1000K (Makovos, 1989). A measurement system is composed of a potentiometer (model 273, Princeton Applied Research Corp., Princeton, NJ) and a personnel computer to analyze the data being measured.

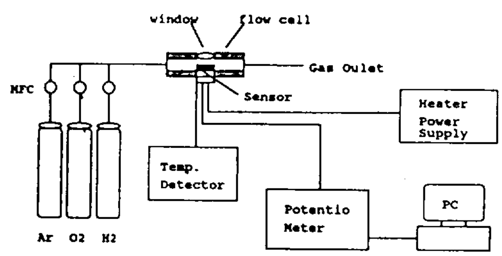


Fig. 5. Gas flow and measurement systems for the high temperature oxygen sensor.

2. Results and discussion

Preliminary evaluation of the on-chip heater is accomplished using the measurement system in Fig. 5. at the air atmosphere. The result shows that heating the sensor up to 700℃ with a total power of approximately 2 watts indicates that the sensor is a truly low mass, low power driven device. This depends on the level of heat insulation of the sensor package. The light emission from the heater can be observed during the measurement at the temperature above 600℃.

The sensor's response to the oxygen presented has been evaluated. In this evaluation, the sensor is placed inside quartz chamber using a furnace heating instead of using an on-chip heater. A known quantity of oxygen is premixed with helium using a MFC system from 0 to 18mol% and then fed into the quartz chamber. Ameperometric measurements are then made when the system has reached a stable operating temperature 1150K.

Fig. 6. shows a typical cyclic voltammetric response of an oxygen sensor. The magnitude of the current at various points between the potential scan limits of -0.52V and +0.32V were appreciably influenced by the oxygen content of the gas phase, but had a non-zero value even in the absence of oxygen. Stable voltammograms were usually obtained within 5 minute after the change in the gas composition entering the quartz tube.

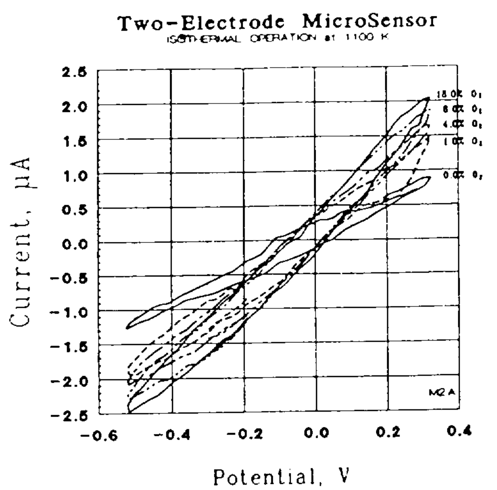


Fig. 6. A cyclic voltammetric response of a high temperature oxygen sensor at 1100K in the atmosphere of He and O_2 at the indicated levels. Potential scan limits -0.52 and +0.32V.

The values of the current as a function of the mole fraction of oxygen in the gas at the two selected potentials is shown in Fig. 7. The plotted values were sampled at the decreasing potentials in the cathodic region and at the increasing potentials in the anodic region. A linear relationship between the sampled current and the logarithm of the oxygen mole fraction over the

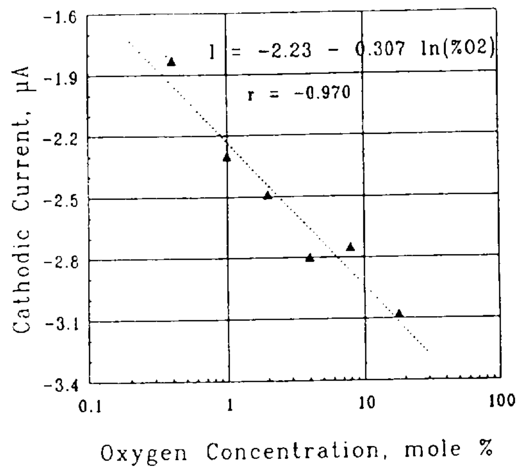
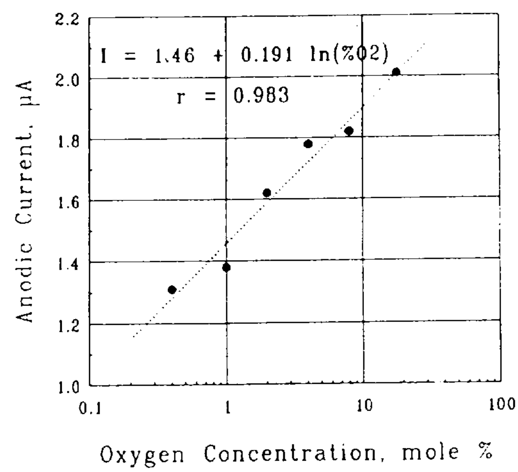


Fig. 7. a) The calibration data collected at the indicated potentials under the conditions described for Fig. 6. for volumetric gas flow rate of 225㎤/min. Relationship between cathodic current vs. oxygen concentration at 1150K in the furnace.



b) Relationship between anodic current vs. oxygen concentration at 1150K in the furnace.

oxygen concentration of 0 to 18mol% at 1150 K (877℃) is demonstrated.

The cyclic voltammetric investigation of the high temperature oxygen-helium system showed that the current sampled at a chosen value of potential is a reliable indicator of the oxygen concentration in the helium. Basically the oxygen sensor made in this experiment is consist of two electrode electrochemical gas sensor compared to other's (Kletz et. al, 1983). So the sensor has following advantages, simple structure and small power consumption. Now the experiment to evaluate the high temperature oxygen sensor using the on-chip heater is being made.

Further extended evaluation of the sensor's performance in terms of temperature effects, operational life and reproducibility will be carried out in the near future.

Conclusions

In summary, a micromachined, solid electrolyte amperometric oxygen sensor has been produced using microfabrication technology and micromachining techniques. The performance study of the high temperature oxygen sensor showed a reliable response. Basically the oxygen sensor made in this experiment is consist of two electrode electrochemical gas sensor compared to the other's. So the sensor shows a simple structure and consumes a small power as advantages.

This device is a low mass, low energy driven device and shows promise in various industrial applications.

Acknowledgment

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〈국문초록〉

이온빔 스퍼트한 YSZ 막을 이용한 고온 산소센서

전류구동형 모드에서 동작하는 마이크로머시닝기술을 이용한 실리콘을 기초로한 고온 산소센서를 개발하였다. 이온빔 스퍼트한 이트리아로 안정화된 지르코니아(YSZ) 막을 고체전해질로 이용하였다. 종래의 삼전극 시스템 전기화학센서와 다른 이전극 시스템의 센서를 개발함으로서 보다 간단한 구조와 소모전력이 작은 장점을 얻었다. 내장된 히터를 이용하여 센서의 온도를 약 800℃까지 올릴 수 있으며, 약 2와트 정도의 전력으로 700℃까지 센서의 온도를 올릴 수 있었다. 이러한 고온 산소센서의 설계, 제조 공정 및 실험결과를 다루기로 하겠다.