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Novel processing of NASICON and sodium carbonate/barium carbonate thin and thick films for a CO_2 microsensor

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The use of chemical microsensors can be advantageous for the monitoring of gas species in efforts to accurately monitor environmental conditions, detect fires, and determine emissions. The microsensor described herein shows promise for use as a carbon dioxide sensor. Carbon dioxide levels are of particular concern for passenger environments, as a chemical signature of a fire, and as a combustion product.

This amperometric carbon dioxide microsensor was produced using microfabrication and micromachining techniques. Electron beam evaporation, sputtering, and thick film printing were used for deposition of the chemically active layers of the device—$Na_3Zr_2Si_2PO_{12}$ (NASICON) and Na_2CO_3/Ba_2CO_3. The deposition techniques used to deposit these materials were an important processing advance in this development endeavor. The films were incorporated into an amperometric, limiting current type sensor design with overall dimensions of 1.4 mm × 1.5 mm. The inclusion of this type of sensor in an array of differing sensors offers an advantage of high selectivity to analytes of interest.

1. Introduction

Accurate detection of carbon dioxide is of particular importance for environmental monitoring, fire detection, and engine exhausts. Air quality monitoring is important in an aircraft or spacecraft compartment or as part of a building ventilation system. Fire detection, again as part of an aircraft/spacecraft or building fire safety system, can be improved beyond the standard particle detection systems by concurrently monitoring for the chemical signature of a fire [1]. A suitable chemical signature to determine fire condition may be the CO/CO_2 ratio. Finally, control of a combustion process such as an engine or gas turbine generator can be improved as more information is known about the exhaust stream components, one of which can be CO_2.

A broad range of methods are available for detection of CO_2 concentration in a gas ambient. Infrared optical detectors are commonly used, but are relatively large and expensive and operable in a limited temperature range. Investigation of a variety of CO_2 sensitive materials and designs has been undertaken [2–9].

The sensors developed in this work are designed to be operated in amperometric mode. In this mode of operation, a voltage is applied across the NASICON electrolyte, and the current produced by the transport of ions through the NASICON is monitored. A diffusion barrier over the electrolyte limits the amount of reacting species that can reach the electrode/electrolyte interface, and the limiting current through the electrochemical cell can then be directly correlated to the bulk concentration.

Reduction of size and power required for ubiquitous use of solid-state gas sensors can be achieved through the use of microfabrication and micromachining techniques. These processes have been under development for the IC industry for decades and are now increasingly focused on the fabrication of microelectromechanical systems (MEMS). MEMS processing has enjoyed a great deal of success in the development of physical sensors and actuators, and this can be adapted to chemical sensor development. One of the key technical problems with adopting MEMS techniques to chemical sensors is the fact that the materials used have generally not been implemented in thin film applications.

This work focused on the development of processing techniques for NASICON and sodium/barium carbonate that fit within the framework of silicon-based microfabrication and micromachining. A general platform for an amperometric chemical sensor was previously developed [10] and methods for depositing films of NASICON and sodium/barium carbonate for CO_2 sensitivity were developed here.

Previous work on thin film deposition of NASICON material has been limited, likely due to the relatively

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complex stoichiometry of the material and concerns about contamination from sodium. Sputtering of NASICON films of varying stoichiometry has been reported by Ivanov [7] and Lang [8], while pulsed laser deposition (PLD) was investigated by Izquierdo [11].

The sensing mechanism of the NASICON/carbonate system for CO_2 detection is based on sodium ion conduction through the NASICON and CO_2 sensitivity provided by the carbonate. The number of free sodium ions for conduction controls the current flow through the electrochemical circuit, and the number of free sodium ions changes based on the equilibrium between sodium carbonate and its dissociation products, Na_2O and CO_2. The overall reactions governing the operation of the NASICON-based sensor in this work are as follows:

$$2\mathrm{Na}^+ + \frac{1}{2}\mathrm{O}_2 + \mathrm{CO}_2 = \mathrm{Na}_2\mathrm{CO}_3 \qquad (1)$$

$$\mathrm{Na}_2\mathrm{O} = 2\mathrm{Na}^+ + \frac{1}{2}\mathrm{O}_2 \qquad (2)$$

Sodium carbonate is formed by reaction of CO_2 with sodium (in the form Na_2O). Equilibrium is established between the Na_2CO_3 and CO_2, as the carbonate is produced by the reaction and consumed by dissociation (forming Na_2O and CO_2). A mixture of sodium carbonate and barium carbonate was used for the suppression of water vapor effects [12].

2. Experimental

The sensors in this work were batch-fabricated and incorporated into a generic silicon-based electrochemical sensor platform. Photolithography was performed using a positive photoresist (Shipley 1818) and a contact mask aligner (Karl Suss MJB-3). The minimum line width for the patterned films was 6 microns. The device structure consisted of a silicon wafer with low stress silicon nitride deposited by chemical vapor deposition. The wafer was wet etched with tetramethyl ammonium hydroxide (TMAH) to reduce the thermal mass of the sensor. An integrated heater and a resistive temperature detector (RTD) were produced using lift-off techniques and consisted of sputtered platinum over a thin layer of titanium metal for improved adhesion. These elements were isolated from the sensing layers by electron beam evaporated aluminum oxide. The thin film NASICON was deposited on the alumina layer and platinum electrodes were then sputtered to provide electrical contact. Finally, the sodium/barium carbonate layer was deposited over the NASICON and platinum electrodes. A cutaway view of the device is shown in Fig. 1.

2.1. NASICON deposition

Deposition of NASICON was carried out using electron beam evaporation and sputtering from NASICON target material. The target material was obtained through samples from previous research [13] and commercially through Superconductive Components, Inc. (Columbus, OH). Electron beam deposition of the NASICON was performed at NASA Glenn Research Center in Cleveland, OH using an e-beam evaporation system manufactured by Denton Vacuum Systems, (Moorestown, NJ). The standard deposition conditions for the deposition were a beam voltage of 8 keV in an atmosphere of 1.4×10^{-4} torr (1.87×10^{-2} Pa) of pure oxygen. Beam current and deposition times were varied in order to obtain a rate of approximately 2 nm/s and a total film thickness of about 400 nm.

Sputtered films were deposited in a sputter system manufactured by Denton Vacuum system with a US Gun RF magnetron sputter gun. A 3” diameter target of NASICON was obtained from Superconductive Components for these depositions. The film was sputtered in a 50/50 argon/oxygen plasma at a total pressure of 3.5 millitorr. Deposition rates for sputtered NASICON were very low, and the extended time required for this deposition was not found to be compatible with lift-off patterning. Cooling of the substrate could allow lift-off patterning of the NASICON.

2.2. Carbonate deposition

Two methods for the deposition of a sodium carbonate film compatible with the microsensor platform were explored for this research. Thick film printing with an “ink” consisting of finely ground sodium/barium carbonate powder and sputtering the film with a sodium/barium carbonate target obtained commercially (Superconductive Components, Columbus, OH) were performed.

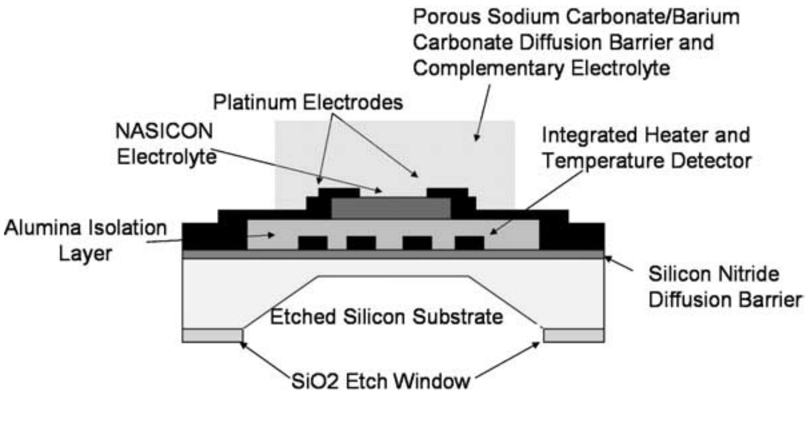

Figure 1 Cutaway diagram of CO_2 sensor.

For the thick film printing, $BaCO_3$:Na_2CO_3 powder with a 1.7:1 molar ratio was obtained from a previous study [13]. This powder was mixed and ground with tetraethyl orthosilicate (TEOS) and heptanol forming a paste for thick film printing. Use of a mechanical mixer/grinder to form the paste resulted in reasonably consistent and well defined patterns. Excess solvent resulted in spreading of the carbonate beyond the desired pattern while low levels of solvent resulted in an "ink" that could not be applied by the screen printer. The carbonate was treated for ∼36 h at 110°C and subsequently at 450°C.

Sputtered carbonate films were deposited using RF power in conditions similar to that described for the NASICON sputtering. As with the NASICON sputter process, the sputtered films were very slow to deposit and tended to overheat the substrate.

2.3. Gas sensing

CO_2 sensitivity and response time were tested at NASA Glenn Research Center using a chamber with a heater stage and electrical probes. Gas concentrations were regulated by mass flow controllers. The device was heated to 425°C and the applied voltage across the sensing electrodes was 1.25 V.

3. Results and discussion

3.1. NASICON film

The films resulting from these depositions were analyzed using an X-ray Photoelectron Spectroscopy (XPS) system (VG Scientific). The results of the analysis are shown in Table I and reflect that the e-beam evaporated NASICON tended to be low in zirconium but high in sodium. Some evidence of residual zirconium dioxide in the target material was also noted. In no case was the theoretical stoichiometry of $Na_3Zr_2Si_2PO_{12}$ achieved. The relatively large difference in melting/boiling points might explain the preferential evaporation of sodium over zirconium. The low zirconium content was somewhat improved by aggressively increasing the beam current (letter D in Table I), but this resulted in a composition that appeared to be low in silicon.

The sputtered film showed a very different composition, with much less sodium present but unusually high levels of silicon. The raw powder from previous work appeared very low in zirconium, but this might be a result of sodium preferentially migrating to the surface of the grains of powder used in the XPS analysis. The exact composition of the commercially obtained evaporation and sputtering material was not analyzed.

TABLE I Composition of NASICON films and powders (at%)

		Na	Zr	Si	P	O	Source
Raw powder	A	22	2	9	7	59	Sawayda
Evaporated	B	11	5	12	7	65	Sawayda
Evaporated	C	25	5	7	8	56	Superconductive
Evaporated	D	21	9	5	3	62	Superconductive
Sputtered	E	4	8	19	1	68	Superconductive
Theoretical		15	10	10	5	60	N/A

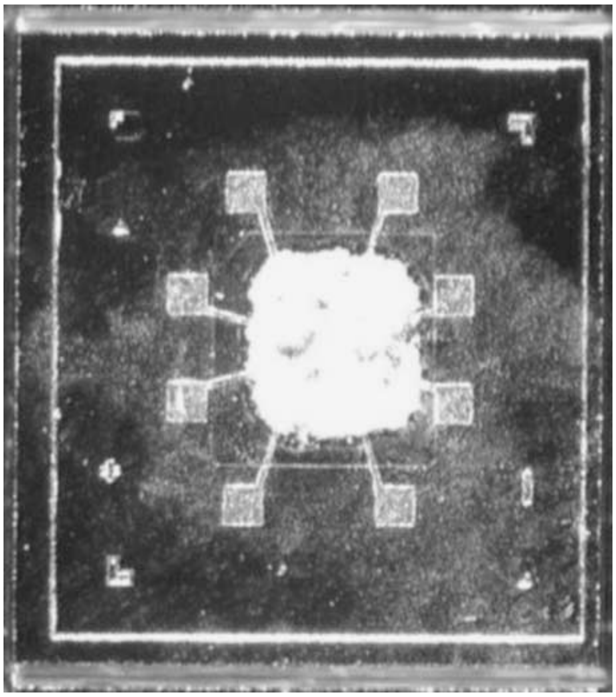

Figure 2 Micrograph of fabricated CO_2 sensor with evaporated NASICON and thick film printed sodium/barium carbonate, approximate dimensions are 1.4 mm × 1.5 mm.

3.2. Sodium/barium carbonate film

The thick-film printed carbonate film is shown in Fig. 2. Thick film printing produces films about 20–30 microns thick, but due to the fragility of the carbonate, this could not be verified with a surface profilometer. This was an order of magnitude thicker than any of the thin films used for other layers. Examination of the film under a microscope showed it to be porous and grainy.

Sputtering of the sodium/barium carbonate film generated difficulties parallel to that of NASICON sputtering. Long deposition times tended to overheat the photoresist, making lift-off difficult. In addition, the sputter target cracked after a few depositions in spite of relatively low power application (<70 W RF) and the target's copper backing plate. The films were also not very close to the desired stoichiometry, as seen in Table II. As with sputtered NASICON, sodium levels were significantly lower than desired. While the target was not tested under XPS for comparison, one explanation for the low sodium content is that the sodium ions were more easily deflected away from the surface of the substrate as they traveled through the magnetron plasma, resulting in low sodium content in the film.

TABLE II Composition of sodium/barium carbonate sputtered films (at%)

	Na	Ba	O	C
Sputtered	5	16	65	14
Sputtered	7	18	59	16
Stoichiometric	14	12	56	19

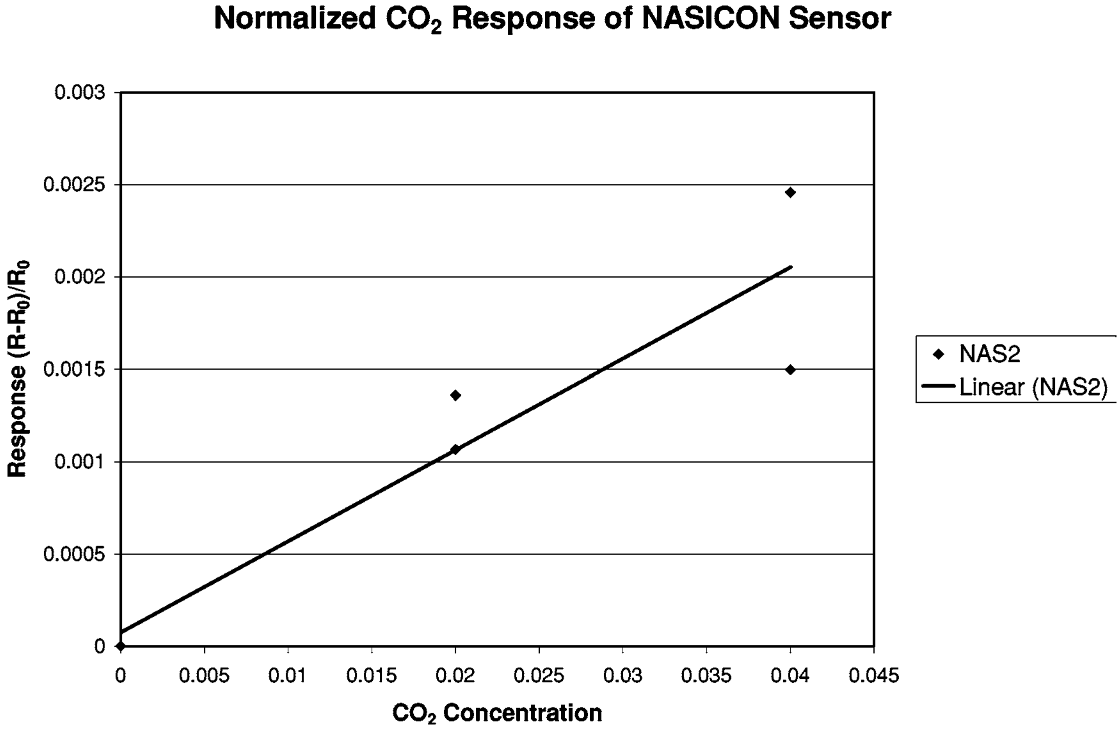

Figure 3 Normalized response of CO_2 sensor to 0–4% CO_2.

The magnetic field in the magnetron sputter gun was designed to accelerate Ar^+ ions in the plasma toward the sputter target (i.e. away from the substrate), so the effect of the magnetic field on a Na^+ ion ejected from the target might be similar. The undesirable qualities and difficulty in processing with this technique led to the use of the thick film printed carbonate for device testing.

3.3. Gas sensitivity

Testing of the sensor fabricated with e-beam deposited NASICON and thick-film printed sodium/barium carbonate showed it to be sensitive to CO_2. Drift in baseline was noted, so the normalized response is shown in Fig. 3. Sensitivity of the device on average was approximately 0.1% increase in current for increase in CO_2 concentration of 2%. Testing only occurred in the range of 0–4% CO_2 in air, so a wider range of test conditions is planned. Response times on the order of 12–18 s were noted, however sampling only occurred every 5–6 s and the chamber volume was relatively large. Response times of significantly less than 10 s are expected under optimum test conditions.

4. Conclusions

A novel amperometric, limiting current CO_2 sensor has been developed using microfabrication and micromachining techniques. The active sensing films, NASICON and sodium/barium carbonate, have been successfully deposited using electron beam evaporation and thick film printing, respectively. These microsensors show definitive response to CO_2 in air. These devices likely can be further refined to improve ionic conductivity for larger output signals.

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