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04/02/94 LaRC
Surface acoustic wave (SAW) pressure measuring devices of the prior art are based on the change in resonant frequency caused by the mechanical force of pressure on the piezoelectric material of the SAW device. If the piezoelectric material is fabricated as a thin membrane and arranged in such a way that the force of pressure causes the membrane to distort or flex, the sensitivity of the device can be enhanced somewhat. However, SAW pressure sensors of this type lack sensitivity for the measurement of pressures below 100 Pa.

By the present invention, a transducer is provided which is useful in measuring absolute gas-state oxygen pressure from low pressures (pressures less than 100 Pa) to atmospheric pressure (1.01 x 10^6 Pa). This was accomplished by providing a SAW device having a piezoelectric material which is coated with a chemical that will selectively and reversibly bind oxygen.

The novelty of the invention resides in the coating which is used on the piezoelectric material of the SAW device. This coating is a chemical which will selectively and reversibly bind oxygen. When oxygen is bound by the coating on the SAW device, the mass of the coating increases by an amount equal to the mass of the bound oxygen. An increase in the mass of the coating caused by the bound oxygen causes a corresponding decrease in the resonant frequency of the SAW device.

Inventors: Donald M. Oglesby Billy T. Upchurch
Address: 3213 Little Island Road 1213 Bluebird Drive
Virginia Beach, VA 23456 Virginia Beach, VA 23451
Employer: Old Dominion University NASA LaRC

Inventors: Bradley D. Leighty
Address: 943 Lowry Place
Newport News, VA 23602
Employer: NASA LaRC

Initial Evaluator: George Wood
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Origin of the Invention

The invention described herein was jointly made by employees of the United States Government and a NASA Contractor employee in the performance of work under NASA Contract NAS1-19858 with Old Dominion University and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the contractor has elected not to retain title.

Background of the Invention

1. Field of the Invention

This invention relates generally to oxygen pressure sensors. It relates particularly to an oxygen pressure sensor prepared by coating a surface acoustic wave (SAW) piezoelectric device with an oxygen binding agent tailored to provide variable sensitivity.

2. Description of the Related Art

SAW pressure measuring devices of the prior art are based on the change in resonant frequency caused by the mechanical force of pressure on the piezoelectric material of the SAW device. If the piezoelectric material is fabricated as a thin membrane and arranged in such a way that the force of pressure causes the membrane to distort or flex, the sensitivity of the device can be enhanced somewhat. U.S. patent 4,100,811. However, SAW pressure sensors of this type lack sensitivity for the measurement of pressures below 100 Pa.

Summary of the Invention

It is accordingly a primary object of the present invention to overcome difficulties presented by prior art devices and provide a transducer which is useful in measuring absolute gas-state oxygen pressure from low pressures (pressures less than 100 Pa) to atmospheric pressure (1.01 x 10^5 Pa).

It is also a primary object of the present invention to provide a highly sensitive air pressure sensor.

These and other objects and their attending benefits are achieved by providing a surface acoustic wave (SAW) device, the piezoelectric material of which is coated with a chemical that will selectively and reversibly bind oxygen. Since air is 20.9% oxygen, this device will serve as an air pressure sensor with high sensitivity.

Brief Description of the Drawings

For a more complete understanding of the present invention, including its objects and attending benefits, reference should be made to the Description of the Preferred Embodiments, which is set forth in detail.
below. This Description should be read together with the accompanying drawings, wherein:

FIG. 1 is a schematic diagram of a surface acoustic wave (SAW) oxygen pressure sensor according to the present invention;

FIG. 2 is a structural formula showing the oxygen binding Co(II)C₁/₂ picnic-basket porphyrin with poly(octylmethacrylate-co-vinylpyridine providing the axial ligand;

FIG. 3 is a typical frequency oxygen pressure response curve for an SAW oxygen pressure sensor according to the present invention; and

FIG. 4 is the actual frequency/oxygen pressure response curve for the SAW oxygen pressure sensor described in the Example, infra.

Description of the Preferred Embodiments

This invention relates to a new transducer for the measurement of absolute gas-state oxygen pressure from low pressures (less than 100 Pa) to atmospheric pressure (1.01 x 10⁵ Pa), and is based on a surface acoustic wave (SAW) device with a coating that will selectively and reversibly bind oxygen. This invention may also be used as a sensitive gaseous oxygen detector.

The piezoelectric material of an SAW device (see, e.g., U.S. 4,100,811 is coated with a chemical which will selectively and reversibly bind oxygen. When oxygen is bound by the coating on the SAW device the mass of the coating increases by an amount equal to the mass of the bound oxygen. The resonant frequency of the SAW device is given by the equation:

\[ \Delta f = (k_1 + k_2) f^2 \left( \frac{m}{A} \right) \]
An increase in the mass of the coating caused by the bound oxygen causes a corresponding decrease in the resonant frequency of the SAW device. A diagram of the device is shown in FIG. 1. The fundamental resonant frequency of the uncoated SAW device is determined by the piezoelectric material and fabrication of the electrodes, but greater sensitivity is achievable if it has a resonant frequency greater than 100 megahertz (MHz). The upper frequency is limited by electrode fabrication constraints. Devices having resonant frequencies of 158 MHz or 200 MHz were used for the embodiment given herein.

The coating may be prepared from, but is not limited to, any one of numerous oxygen binding compounds, including the oxygen-binding porphryins, Salen Schiff-bases, and lacunar cyclidines. The requirements of the oxygen-binding compound in the coating on the SAW device are:

- The coating should have the appropriate equilibrium constant (binding constant) for the reaction: \( \text{Binding Agent} + \text{O}_2 = \text{Binding Agent} \cdot \text{O}_2 \).
- Oxygen-binding must be rapid and reversible.
- The coating must be stable and not undergo oxidation.
- The compound must be amenable to coating or bonding onto the surface of the SAW device.
- It is convenient to define the binding constant as the partial pressure of oxygen when one-half the available oxygen sites in the
coating are filled with oxygen. The following designations are used:

\[
\begin{align*}
P_{o_2} &= \text{partial pressure of oxygen (torr)} \\
P_{1/2o_2} &= \text{the partial pressure of oxygen when one-half of} \\
& \quad \text{the binding sites are occupied.}
\end{align*}
\]

The relationship between \( P_{1/2o_2} \) and the standard equilibrium constant of \( P_{1/2o_2} = 1/K_{eq} \).

The preferred embodiment of the invention uses coatings containing the oxygen-binding porphyrins. The picket-fence porphyrins and the picnic-basket porphyrins (PBP) (as understood by those of skill in the art) are preferred because they are stable, bind oxygen reversibly, and may be synthetically modified to control the binding constant. The formula and structure of a typical picnic-basket porphyrin is shown in FIG. 2. In addition to the possibility of changing the central metal ion (Co in FIG. 2), the length of the bridge or "handle" can be changed to change the oxygen binding constant. The bridging group of the PBP used for this invention consists of a -OCH\(_2\)- unit between the isophthalate rings which are joined to the porphyrin ring by the amide linkages. This PBP is designated as \( C_{1/2}\text{PBP} \). The ability to modify the binding constant of the active ingredient of the coating is important because the binding constant determines the optimum pressure-measurement range for the invention.

The central metal ion such as Co(II) or Fe(II) of an oxygen-binding porphyrin has six bond sites. Four are occupied by nitrogens from the porphyrin molecule. The fifth must be occupied by an electron pair donor molecule called the axial ligand, and the sixth site can bind oxygen reversibly. SAW device coatings based on oxygen-binding porphyrins must contain a substance that will serve as the axial ligand. This substance may be but is not limited to, pyridine, methyl imidazole, 1,5-dicycloimidazole or a substance which will furnish these types of chemical groups. An example of a substance which will furnish an axial ligand to the oxygen-binding porphyrin is a copolymer containing an axial
ligand along the polymer chain, such as poly(octylmethacrylate-co-vinylpyridine).

A typical frequency/oxygen-pressure response curve is illustrated by FIG. 3. The optimum pressure-measurement range for the coating depicted in FIG. 3 is between 1.0 kPa and 100 kPa. For a given pressure range there is an optimum binding constant for the activity ingredient of the coating. Table I gives the optimum values of $P_{1/2}$ for different oxygen (and air) pressure ranges. The minimum pressure of each range is based on the pressure required to produce a signal change of 500 Hz and the maximum pressure for each range is that required to saturate 70% of the binding sites. Since air has a constant concentration of oxygen this invention may be used to measure air pressure.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>OPTIMUM BINDING CONSTANTS FOR SAW DEVICE COATINGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Pressure Range (kPa)</td>
<td>Air Pressure Range (kPa)</td>
</tr>
<tr>
<td>0.002 - 0.3</td>
<td>0.013 - 1.3</td>
</tr>
<tr>
<td>0.010 - 1.3</td>
<td>0.070 - 6.7</td>
</tr>
<tr>
<td>0.130 - 13.0</td>
<td>0.070 - 67.0</td>
</tr>
<tr>
<td>0.700 - 53.0</td>
<td>3.300 - 267.0</td>
</tr>
<tr>
<td>1.300 - 133.0</td>
<td>6.700 - 667.0</td>
</tr>
<tr>
<td>2.700 - 267.0</td>
<td>13.000 - 1333.0</td>
</tr>
</tbody>
</table>

**Example**

A 158 MHz SAW device (Microsensor Systems, Incorporated, 62 Corporate Court, Bowling Green, Kentucky 42103) was spray-coated in a nitrogen atmosphere. The coating solution was 99.24% toluene, 0.35% 1,5-dicyclohexylimidazole, and 0.41% cobalt(II)C$_{1/2}$ picket-fence porphyrin. The SAW device was then cured at 60°C under nitrogen for
30 minutes. The frequency response to oxygen (or Air) pressure was measured with a CEM-158-B dual delay line oscillator system (Microsensor Systems, Incorporated). The device was suitable for measuring oxygen pressure in the range of 0.25 KPa-26 KPa with a sensitivity ranging from 436 HZ/kPa to 6 Hz/kPa. The response of the device is illustrated by FIG. 4.

What is claimed is:
Abstract of the Disclosure

A transducer for the measurement of absolute gas-state oxygen pressure from pressures of less than 100 Pa to atmospheric pressure (1.01 x 10^5 Pa) is based on a standard surface acoustic wave (SAW) device. The piezoelectric material of the SAW device is coated with a compound which will selectively and reversibly bind oxygen. When oxygen is bound by the coating, the mass of the coating increases by an amount equal to the mass of the bound oxygen. Such an increase in the mass of the coating causes a corresponding decrease in the resonant frequency of the SAW device.
FIG. 2