Novel Oxygen Sensor
Using Oxygen Intercalation of Layered Semiconductor CuFeTe$_2$

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Abstract
A novel oxygen sensor based on resistance change caused by oxygen intercalation into a layered semiconductor CuFeTe$_2$ has been developed. We fabricated highly c-axis oriented CuFeTe$_2$ ceramics. The impedance plots in the direction of perpendicular to the surface of the ceramics showed single semicircles. In addition, the radius increased with increasing the oxygen concentration. The sintering temperature was also found to affect considerably the sensitivity for the oxygen response.

1. Introduction
Oxygen sensors are used in many fields. The most popular type of oxygen sensor is zirconia oxygen sensor, but its power consumption is high due to high operating temperature (above 500K) [1]. Hence, we are developing a new type oxygen sensor that can operate at room temperature using the intercalation oxygen molecules into CuFeTe$_2$ [2].

The CuFeTe$_2$ crystallizes in a tetragonal structure with unit cell parameters of $a = 0.3934$ nm and $c = 0.6078$ nm, formed by conductive planes of Cu and Fe cations and planes of Te anions, perpendicular to the c-axis. Two adjacent planes of Te atoms are separated by van der Waals gaps that allow the cleavage in directions perpendicular to the c-axis [3]. We have found that the resistance in the c-direction of CuFeTe$_2$ reversely changes in accordance with partial oxygen pressure at 1atm total pressure (Fig.1) [4].

In this study, we investigated the oxygen gas sensing property of the CuFeTe$_2$ ceramics by impedance plot, and the relationship between the sensitivity and the sintering temperature.

2. Experimental
Sample manufacturing
CuFeTe$_2$ single crystals were prepared by the vertical Bridgman method [2]. The ingot was pulverized and uniaxially pressed (3 ton /cm$^2$) into a pellet with a thickness of 0.2 mm. The pellet was cut into rectangular form (2 mm × 7 mm), and then sintered at 450°C for 10h under a vacuum of less than 10$^{-4}$ Pa. It was confirmed from X-ray diffraction measurements that the highly c-axis ceramics was able to be prepared by uniaxially pressing the fine powder with a large shape anisotropy as shown in Fig.2.

Measurement method
The sample is placed in a chamber with a diameter of 15 mm and exposed to a mixture of oxygen and nitrogen gas. Mass flow meters were used to control gas flow (200 ml/min) and oxygen-nitrogen gas ratio. The resistance is measured by four-probe method using 50 μm diameter copper wires attached to terminals by silver paste.

The impedance in both directions parallel ($Z_{\parallel}$) and perpendicular ($Z_{\perp}$) to the surface of the sample was measured with LCR meter (HP-4284A).

3. Result and Discussion
Impedance plots
The impedance plots of $Z_{\parallel}$ versus some oxygen concentrations are shown in Fig.3 (a). The plot of all concentrations exhibits a single point on Re-axis. It indicates the AC equivalent circuit represents a single resistor ($R = 2.1$ kΩ). On the other hand, the impedance plots of $Z_{\parallel}$ versus some oxygen concentrations are shown in Fig.3 (b). The plot of all concentrations exhibits single semicircles. It indicates the AC equivalent circuit can be decomposed as a parallel RC-circuit. In addition, the radius increased with increasing the oxygen concentration.

Fig.1 Operating principle of CuFeTe$_2$ oxygen gas sensor

Fig.2 The schematic illustration of the highly c-axis oriented ceramics

Fig.3 Impedance plots of $Z_{\parallel}$ versus some oxygen concentrations
Fig. 3 Impedance variation with oxygen concentration in the (a) parallel and (b) perpendicular directions to the surface of the ceramics in the range of 0 - 20% O₂.

Sintering temperature

In order to evaluate the relationship between the sintering temperature and the sensitivity, four samples were prepared with variable sintering temperatures from 300 to 450°C. The resistance of the samples was measured by a DC measurement.

Fig. 4 shows the sensitivity of the sintered sample in the response to 20% oxygen gas. We defined the sensitivity S as \( S = \frac{R_{O2} - R_0}{R_0} \), where \( R_{O2} \) and \( R_0 \) is the resistances \( R_1 \) in 20% oxygen gas with nitrogen carrier, and pure nitrogen gas just before oxygen gases flowed to the chamber, respectively. The sintering temperature was found to affect considerably the sensitivity for the oxygen response.

Fig.4 (a) Sensing response of the CuFeTe₂ ceramics fabricated by sintering at 300°C, 350°C, 400°C, 450°C to 20% O₂ (b) Relationship between the sensitivity and the sintering temperature

4. Conclusions

We fabricated the highly c-axis oriented ceramics. It was found that the AC equivalent circuit perpendicular to the surface of the sample represents a resistance \( R_1 \) and a capacitance \( C_1 \), respectively. The radius of impedance plots increased with increasing the oxygen concentration. The sintering temperature was found to affect considerably the sensitivity for the oxygen response.

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