Development of New Oxygen Sensor by Microfabrication of Single-Crystal CuFeTe$_2$ Thin Films

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A new oxygen sensor based on resistance change caused by oxygen intercalation for the layered compound CuFeTe$_2$ (CFT) was developed. A microfabrication process for forming many fine pores on the surface of single-crystal CFT thin films by performing wet etching using photolithography was developed with the aim of reducing the response time of the oxygen sensor. A reproducible response of the fabricated samples to oxygen gas was confirmed when 20% oxygen gas and nitrogen gas were alternately introduced into the sample chamber. The microfabricated sample of the single-crystal CFT thin films showed a response time of 2.5 min to 20% oxygen gas, approximately 34% of that of the single-crystal CFT thin films without fine pores.

1. Introduction

The layered compound CuFeTe$_2$ (CFT) is a semiconductor with a layered structure (tetragonal; lattice parameters, $a = 3.934$ Å, $c = 6.078$ Å),[1,2] as shown in Fig. 1. In the crystalline structure of CFT, unit layers consisting of three atomic planes, i.e., Te, M (= Cu or Fe), and Te in this order, are stacked in the c-direction while sandwiching van der Waals (vdW) gaps.[3] Because of these gaps, a strong cleavage in the direction perpendicular to the c-plane is generated.

For certain types of layered material, the insertion of atoms or molecules into a vdW gap is referred to as intercalation, and reversibly, the removal of atoms or molecules is referred to as deintercalation.[4] Lithium-ion batteries of cell phones are typical applications of intercalation/deintercalation.[5] Here, charge/discharge takes place

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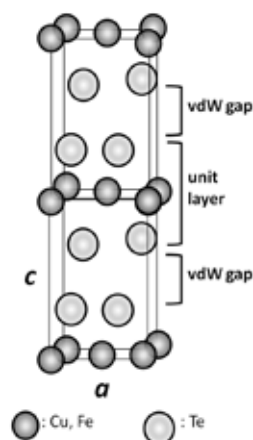[*]Corresponding author: e-mail: m.kouzaki@nbelab.ed.kyushu-u.ac.jp

Fig. 1.   Structure of CFT crystal.

using the reversible intercalation/deintercalation of lithium ions between a graphite electrode and a layered-oxide electrode. An odor sensor such as an aldehyde gas sensor using intercalation has also been reported, and hence the development of new odor sensors using intercalation can be expected.[6] A photo-rechargeable battery using the photointercalation of CFT has been manufactured.[7]

New types of oxygen sensor that can operate at room temperature using the intercalation of oxygen molecules for the layered compounds TiS_2 and CFT have been developed.[8–10] We have found that the resistance in the *c*-direction of these compounds reversibly changes in accordance with partial oxygen pressure under a total pressure of 1 atm. Figure 2 shows a schematic of the intercalation of oxygen molecules for CFT. The above finding is considered to be due to the increase in the resistance in the *c*-direction owing to the expansion of the vdW gaps of CFT layers as a result of the intercalation of oxygen molecules. The response time of oxygen sensors based on intercalation must be reduced for their practical application. Commercially available oxygen sensors exhibit a response time of 0.5 min or shorter. Oxygen molecules are intercalated from the fracture surface of single-crystal CFT and diffuse toward the center of the crystal. Therefore, reducing the oxygen diffusion length L_d can shorten the response time. To this end, the formation of many fine pores on the surface of single-crystal thin films is considered to be effective for creating a number of fracture surfaces as entry points for oxygen molecules as well as for reducing L_d (Fig. 3). Here, L_0 is defined as the distance of fine pores.

In this study, a microfabrication process for forming many fine pores on the surface of single-crystal thin films by wet etching using photolithography for the layered compound CFT was developed. Moreover, we comparatively examined the difference in the time of response to oxygen gas between the microfabricated and non-microfabricated single-crystal thin-film samples.
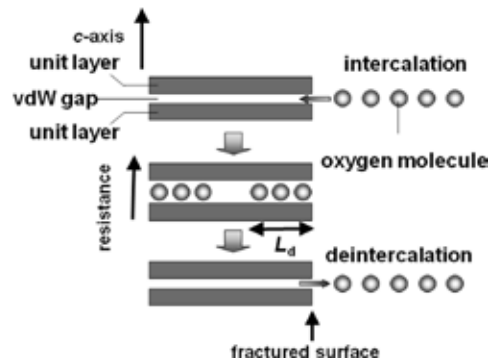
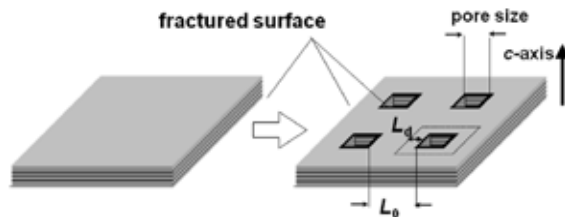Fig. 2.　Schematic of intercalation and deintercalation of oxygen for CFT.

Fig. 3.　Conceptual schematic of fine pores on surface of single-crystal CFT thin film.

2.　Materials and Methods

2.1　*Single-crystal thin films*

　　Single-crystal CFT was grown by the vertical Bridgmann method. The raw materials, i.e., Cu (5N), Fe (4N), and Te (6N), were placed in a 8-mm-diameter carbon-coated quartz ampoule at a mole ratio of Cu:Fe:Te = 1:1:2, and then sealed under vacuum of less than 10^{-6} Torr. The ampoule was slowly heated to 900 °C and left to stand for approximately 10 h for homogenization. The ampoule was then slowly lowered in an electric furnace at a rate of 10 mm/h (temperature gradient near melting point, −20 °C/h).

　　As shown in Fig. 4, the obtained single crystals exhibited a metallic luster and a strong cleavage in the direction perpendicular to the *c*-axis. Energy dispersive X-ray analysis revealed that the molar ratio of the synthesized single-crystal CFT ingot was Cu:Fe:Te = 1.15:1.08:2.00. The extra Cu and Fe atoms out of stoichiometry were considered to have self-intercalated into the vdW gaps during the growth of the single crystals.[11–13] Using the strong cleavage, the single-crystal ingot was cleaved to obtain single-crystal thin-film samples with a thickness of 100 μm. Therefore, the surface plane of the samples was perpendicular to the *c*-plane.
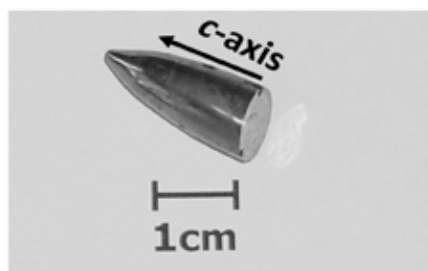
Fig. 4. Cleaved single-crystal CFT.

2.2   *Microfabrication of single-crystal thin films*

Wet etching was carried out using photolithography to microfabricate single-crystal thin films. Single-sided polished Si substrates with a thickness of 600 μm were used. Gold was evaporated onto one side of the Si substrates and onto both sides of the single-crystal CFT thin films. The CFT thin films were bonded to the gold-layer side of the Si substrate using gold paste. The following processing steps were then carried out (Fig. 5): (a) The surface of the CFT thin films was spin-coated with a positive photoresist (OFPR800, Tokyo Ohka Kogyo Co., Ltd.) and prebaked at 80 °C for 20 min. (b) The photoresist was exposed to UV light through the photomask shown in Fig. 6. Here, the pores were 20×20 μm^2 and the distance between pores was $L_0 = 50$ μm. The terminals of the electrodes were installed onto the center of the photomask, where there are no pores. (c) The photoresist was developed using TMA-508 (Kanto Chemical Co., Inc.) and postbaked at 120 °C for 30 min. (d) The gold layer was removed by etching in $KI+I_2$ solution (1:1 mixture of 0.05 mol/L I_2 and 0.1 mol/L KI) for approximately 2 min. (e) The CFT thin films were etched using 20 wt% ammonium peroxodisulfate. (f) Finally, the photoresist was removed with acetone and the obtained films were annealed at 60 °C for 3 h. Figure 7 shows a schematic of the microfabricated CFT sample.

2.3   *Measurement method*

Nitrogen and 20% oxygen gas (a gas mixture of 20% oxygen + 80% nitrogen) were alternately introduced into a sample chamber with a diameter of 15 mm and a length of 150 mm. Mass flow meters were used to control the gas flow at a constant rate of 200 mL/min. Changes in the resistance of the CFT samples in the *c*-direction were measured by the four-point probe method using 50-μm-diameter Cu wire and Ag paste.

3.   Results and Discussion

Figure 8 shows the resistance of the non-microfabricated single-crystal CFT thin film in response to oxygen gas. When 20% oxygen gas was introduced into the sample chamber, oxygen molecules were intercalated to increase the resistance, which then
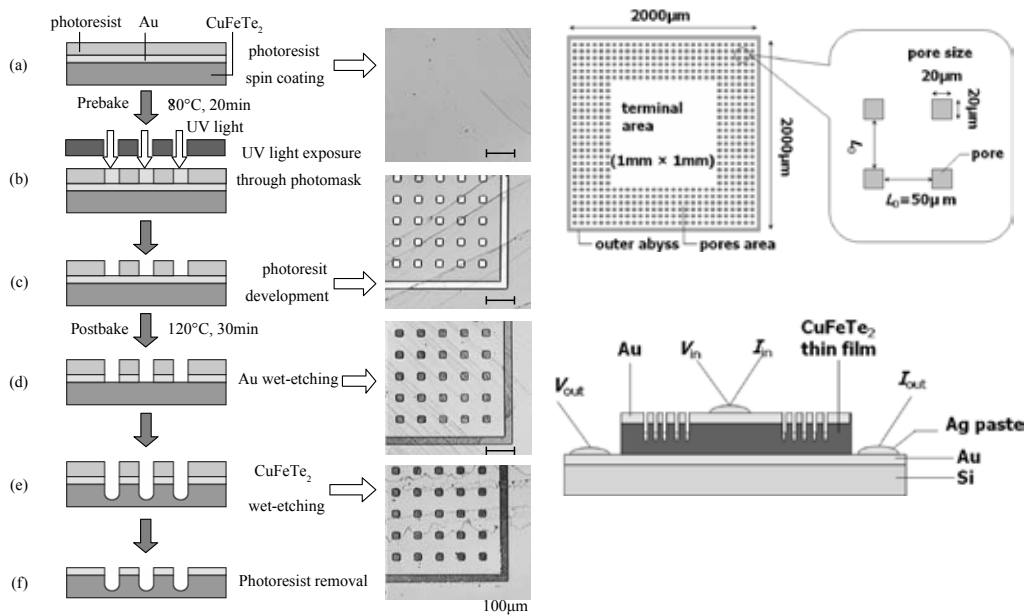
Fig. 5 (left).   Microfabrication of single-crystal CFT thin film.
Fig. 6 (upper right).   Design of photomask used for CFT microfabrication.   The right-side figure shows the enlargement of a pore region.
Fig. 7 (lower right).   Cross-sectional image of microfabricated single-crystal CFT thin-film sample.
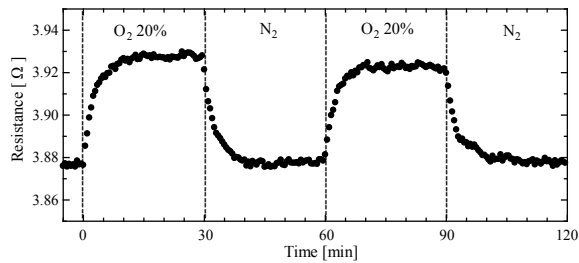

Fig. 8.   Resistance of non-microfabricated single-crystal CFT thin-film sample in response to oxygen gas.

saturated at a certain value.   A reproducible response to oxygen gas was obtained when 20% oxygen gas and nitrogen gas were alternately introduced into the sample chamber. The rise response time for 20% oxygen gas was 7.4 min.   Here, rise response time refers to the time taken for the resistance to reach 90% of the saturation resistance. When nitrogen gas was introduced after the introduction of oxygen gas, the resistance decreased to its initial value owing to the deintercalation of oxygen molecules.   The fall
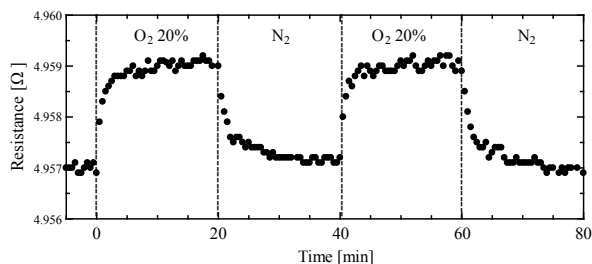
Fig. 9.   Resistance of microfabricated single-crystal CFT thin-film sample in response to oxygen gas.

response time in this case was 8.0 min. Here, fall response time refers to the time taken for the resistance to fall to 10% of the saturation resistance.

Figure 9 shows the resistance of the microfabricated CFT sample in response to oxygen gas. The rise response time was 2.5 min, which was approximately 34% of that for the non-microfabricated CFT sample. In contrast, the fall response time was 7.0 min, which was approximately 88% of that for the non-microfabricated CFT sample.

The fall response time was longer than the rise response time for both microfabricated and non-microfabricated CFT samples. This may be because oxygen molecules, which are generally reducible, are trapped by ionized Cu and Fe atoms, which self-intercalate into vdW gaps. As a result, deintercalation requires a longer time than intercalation.

As discussed above, we confirmed that response time can be reduced with the formation of many fine pores on the surface of the single-crystal CFT thin films. It is considered that the diffusion length of oxygen molecules can be reduced by microfabricating CFT thin films using a photomask with a smaller L_0 and hence the response time can be reduced to below 0.5 min.

4.   Conclusions

A microfabrication process for forming many fine pores on the surface of single-crystal thin films by wet etching using photolithography for the layered compound CFT was developed. A reproducible response of the CFT samples to oxygen gas was confirmed by measuring their resistance when nitrogen and 20% oxygen gas were alternately introduced. The response time of the single-crystal CFT thin film to 20% oxygen gas was reduced from 7.4 to 2.5 min (approximately 34%) with the formation of many fine pores through microfabrication. Thus, it was demonstrated that the microfabrication of a surface of single crystals is effective for reducing the response time.

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