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New Type Oxygen Sensor Using Micro-fabricated Layered Semiconductor Compound

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1. Introduction

Nowadays, oxygen sensor has been an important device in our daily live. The most popular type of oxygen sensor is zirconia (zirconium dioxide) oxygen sensor. This type of oxygen sensor has to be in elevated temperature (about 400ºC) to operate. Hence, power consumption comes high. To reduce power consumption room temperature oxygen sensor is developed. The only one of this type is galvanic cell oxygen sensor. We are developing new type with a new mechanism room temperature oxygen sensor using intercalation phenomenon [1], [2]. Application of intercalation is limited so far, e.g. lithium-ion battery that mostly used by mobile peripherals.

Our new type room temperature oxygen sensor is developed by using layered semiconductor material. $CuFeTe_2$ is a layered semiconductor material that intercalate oxygen gas molecule selectively [3], [4], [5]. When intercalation occurs, oxygen molecules penetrate into $CuFeTe_2$ interlayer, van der Waals gap stretch and increase *c*-axis resistance. Change of *c*-axis resistance is reversible towards oxygen partial pressure [6]. At some point of time, intercalated area and non-intercalated area are yielded. Total resistance of $CuFeTe_2$ thin film will be sum of parallel resistance of both areas.

In previous experiment, response time towards oxygen partial pressure improvement was succeeded by using ceramic sample of $CuFeTe_2$ [5]. In this study, we are going to demonstrate the using of photolithography technology to apply micro-fabrication onto $CuFeTe_2$ single crystal in order to obtain improvement of response time.

2. Experimental

Single crystal manufacturing

$CuFeTe_2$ single crystal was prepared by growing crystal using vertical Bridgman method. Raw material used here, copper (5N), iron (4N) and tellurium (6N) are inserted into silica tube with diameter of 10mm and 2mm thick, with mole ratio Cu : Fe : Te = 1 : 1 : 2, then vacuumed and sealed. Ampoule was slowly heated to 950ºC and kept at this temperature for about 10 hours to homogenize the materials. The ampoule was then drawn out of furnace at a rate of 10 mm/h [1].

Simulation

Simulation based on designed pattern is performed before micro-fabrication process implemented. The design used on this experiment shown in Fig. 1. Here, fabrication size is defined as distance between pores. Applying numerous fine pores on $CuFeTe_2$ single crystal thin film will increase number of gates for oxygen molecules penetration. By increasing the number of gates, it is expected to accelerate intercalation speed and finally improve the response time. Response time is defined as demanded time to reach 90% of saturated resistance value.

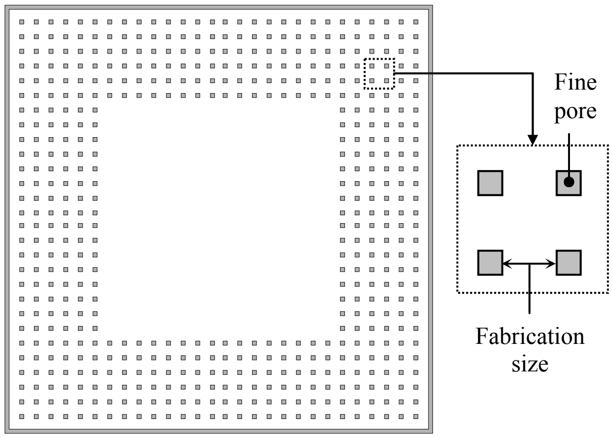

Fig. 1 Photo-mask design

Simulation result is shown in Fig. 2. Smaller fabrication size shows shorter response time.

In this experiment, as first trial we implemented micro-fabrication process by using fabrication size of 50µm.

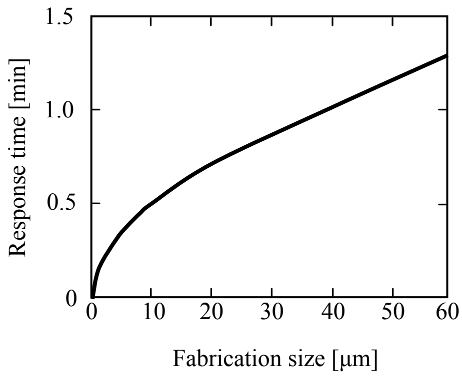

Fig. 2 Simulation result of relation between fabrication size and response time.

Micro-fabrication Process

This semiconductor process application on $CuFeTe_2$ using photolithography was the first with no case of success before. Therefore, to find the most suitable etching solution to be applied in wet etching process, we tried many different kinds of etching solution. And we found that Ammonium Peroxodisulfate ($(NH_4)_2S_2O_8$) is the most suitable etching solution to be applied to $CuFeTe_2$ wet etching.

In this process, single-sided polished silicon wafers with a thickness of approximately 600μm were used as substrates. Gold evaporation was applied onto one side of the silicon substrates and the $CuFeTe_2$ single crystal thin films. Next, the uncovered side of $CuFeTe_2$ single crystal thin film and the covered side of silicon wafer were bonded together using gold paste. The remainder of the process was as follows: (a) The $CuFeTe_2$ surface was spin coated with positive photo-resist （OFPR800, Tokyo Ohka Kogyo Co.） and pre-baked at 60ºC for 30 min; (b) The photo-resist was exposed to UV light through the photo-mask; (c) The photo-resist was developed and post-baked at 120ºC for 30min; (d) The gold was removed by etching in $KI+I_2$ solution (1:1 mixture of I_2:0.05mol/L, KI:0.1mol/L) for about two minutes; (e) The $CuFeTe_2$ thin films were wet etched for 10 minutes in 20wt% ammonium peroxodisulfate. Finally the photo-resist was removed with acetone. The resulting sample and fabricated $CuFeTe_2$ thin film surface are shown in Fig. 3(a) and (b).

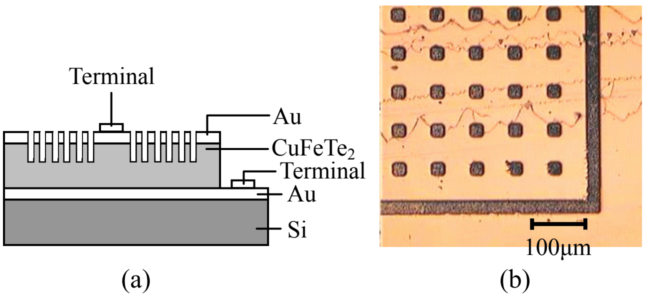

Fig. 3 (a) Cross-section diagram of sensor element using micro-fabricated $CuFeTe_2$ crystal (b) Micro-fabricated $CuFeTe_2$ thin film surface observed by metallurgical microscope

Measurement Method

For $CuFeTe_2$ single crystal thin film sample, we prepared rectangular 2mm x 2mm sample with thickness of approximately 100μm.

Sample is placed in a chamber with a diameter of 15mm and exposed to mixture of oxygen and nitrogen gas. Mass flow meters were used to control gas flow and oxygen-nitrogen gas ratio (20%O_2+80% N_2 and 100%N_2). Here, resistant is measured by four-point method using 50μm diameter copper wire attached to terminals by silver paste.

Result and Discussion

Fig. 4 shows the oxygen gas response of the resistance of $CuFeTe_2$ crystal with micro-fabrication. In this experiment reproducible result has been obtained.

Response time comparison between micro-fabricated sample and single crystal sample is shown in Table I. Application of micro-fabrication process on the $CuFeTe_2$ single crystal thin film resulted response time improvement by about 1/3.

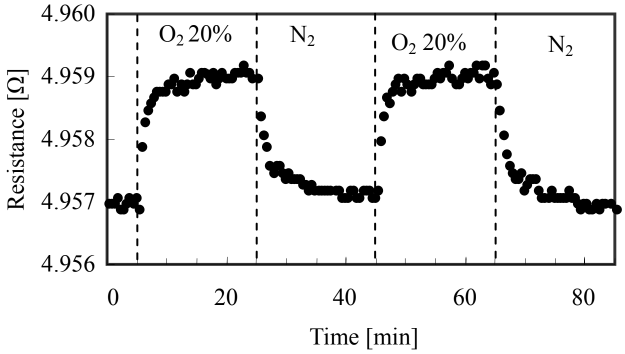

Fig. 3 Oxygen gas response of the resistance of micro-fabricated $CuFeTe_2$ crystal thin film.

Table I Response time comparison

Micro-fabricated Sample		Single Crystal Sample	
Rise	Fall	Rise	Fall
2.1 min	3.8 min	6.7 min	6.6 min

3. Conclusions

Micro-fabrication of $CuFeTe_2$ thin films by applying semiconductor process using photolithography technology is succeeded for the first time. From micro-fabricated $CuFeTe_2$ samples, reproducible result is obtained. Experimental result shows that applying a number of fine pores in the surface of single crystal $CuFeTe_2$ thin films improved response time to oxygen gas by 1/3. Though, compared to the simulation result this result is about 1.8 times larger. Conceivable reasons of this result are possibly inadequacy of fabrication depth and low aspect ratio.

In order to achieve oxygen sensor response time standard based on commercial oxygen sensor i.e. 30sec response time, smaller fabrication size (based on simulation, 10μm) will be apply on next study.

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