Extended Abstracts of the 2009 International Conference on Solid State Devices and Materials, Sendai, 2009, pp607-608

New Type Oxygen Sensing Device Using Oxygen Intercalation of Layered Semiconductor TiS_2

Takeshi Imamura, Tri Nugroho, Yukimasa Ikawa, Koichi Kishiro and Hisao Kuriyaki

Department of Electronics, Graduate School of Information Science and Electrical Engineering, Kyushu University
744, Motooka, Nishi-ku, Fukuoka 819-0395, Japan
Phone: +81-92-608-3735 E-mail: t.imamura@fmate.ed.kyushu-u.ac.jp

1. Introduction

Oxygen sensor is widely used in industries as well as in medical, environmental and sanitation fields, so they have been an important device in our daily life. Most of popular type of oxygen sensor in actual use is zirconia (zirconium dioxide) oxygen sensor[1-2] or oxide semiconductor oxygen sensor[3-4]. 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. However, there are some problems: low durability of the sensor and the complexity of the structure. Therefore, we are developing new type with a new mechanism low temperature oxygen sensor using intercalation phenomenon[5-7]. Lithium-ion battery mostly used by mobile peripherals is well known for applications of intercalation phenomenon [8].

We are developing a new type low temperature oxygen sensing device using intercalation phenomenon. TiS_2 is a layered semiconductor that intercalate oxygen gas molecule selectively. When intercalation occurs, oxygen molecules penetrate into TiS_2 interlayer. The resistivity showed reversible response to partial oxygen pressure[7]. In previous experiment, we used TiS_2 ceramics when we measured the response. In this study, we succeed in developing a new method of polycrystalline TiS_2 film growth. Owing to the method, we can manufacture the film easily. Then, we confirmed the response of the resistivity towards oxygen partial pressure and compared the response of the resistivity with that of TiS_2 ceramics.

2. Experimental

TiS_2 film manufacturing

We tried to develop the easier method of TiS_2 film preparation. We used titanium plate (2 x 4 x 0.5mm^3, 4N), sulfur (5N) as raw materials. They are inserted into silica tube. Then, the tube was vacuumed and sealed. While ampoule is heated, it is kept for 1 hour at 500ºC and 600ºC respectively. The reason is avoiding damage for silica tube. Then, ampoule is slowly heated to 700ºC and kept at this temperature for about 20 hours to grow polycrystalline TiS_2 film on the titanium plate. After keeping at 700ºC, the ampoule is slowly cooled. Then, it is kept for 1 hour at the temperature of 600ºC to avoid silica tube rupturing caused by high temperature sulfur gas and the formation of TiS_3. After that, the ampoule is kept at 500ºC for 2 hours in order to avoid silica tube damage.

The phases of the film are identified using powder X-ray diffraction (XRD). Figure 1 shows the result of XRD patterns of TiS_2 film (as-grown-film). We confirmed the film is consisted of single phase (hexagonal; a = 0.341nm, c = 0.570nm) because the patterns have diffraction peaks of TiS_2.

However, the film is nonstoichiometry. There are several weak diffraction peaks which are not original peaks of TiS_2. To obtain more stoichiometrical film, previously prepared TiS_2 film (as-grown-film) and sulfur were inserted into another silica tube which is divided into two zones at the center. When the materials inserted into the tube, we put as-grown-film in the zone (zone A) and put sulfur on the other zone (zone B). While zone A was heated to 450ºC, zone B was heated to 550ºC for 10days. Thus, weobtained the more stoichiometrical TiS_2 film (reheated -film).

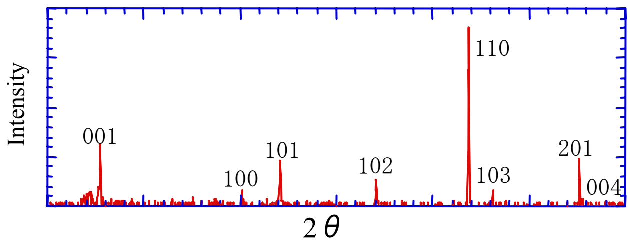


Fig. 1 The result of XRD patterns of as-grown TiS_2 film.

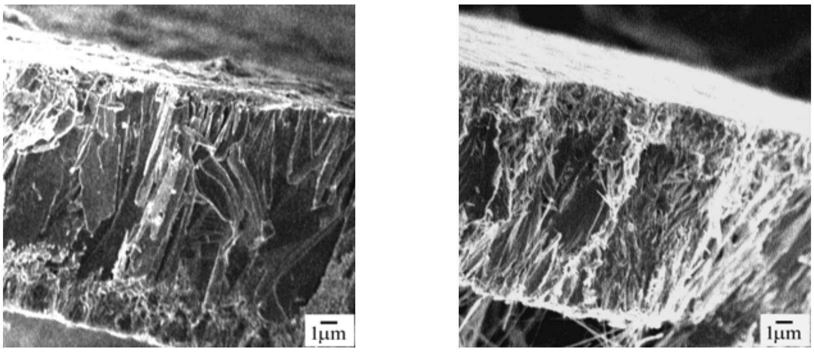
Measurement Method

We prepared rectangular 5 x 2mm samples with thickness of approximately 200μm for gas sensing test.

The sample is placed in a chamber and exposed to mixture of oxygen and nitrogen gas under atmospheric pressure. The mixture gas was introduced through mass flow meters which control oxygen-nitrogen gas ratio. The mixture gas is constantly flowed at 100 cm^3/min. The concentration is monitored by commercial oxygen sensor (Fujikura, FCX-SW).

Resistivity is measured by four-point method using 50μm diameter copper wire attached to terminals by gold paste.

Figure 2 shows scanning electron microscopy images of (a) as-grown-film and (b) reheated-film. Column TiS_2 crystals are grown vertically on the titanium substrate.



(a) (b)

Fig. 2 Scanning electron microscopy images of (a) as-grown-film and (b) reheated-film.

3. Result and Discussion

We defined the sensitivity S as $S=(\rho_{Po2}-\rho_0)/\rho_0$, where ρ_0 is defined as initial resistivity. ρ_{Po2} is defined as measured resistivity. Figure 3 shows the oxygen gas responses of the sensitivity of TiS_2: (a) as-grown-film and (b) reheated-film. Sensitivity of reheated-film is over six times higher compared with that of as-grown-film.

Sensitivity, response time, and recover time of (a) as-grown-film, (b) reheated-film, and (c) ceramics[7] is shown in Table I. Sensitivity became higher by reheating in the sulfur atmosphere, however, sensitivity of the film was lower than that of TiS_2 ceramics. Concerning response time, both of film is improved from ceramics. Response time of films became three to four times shorter than that of ceramics.

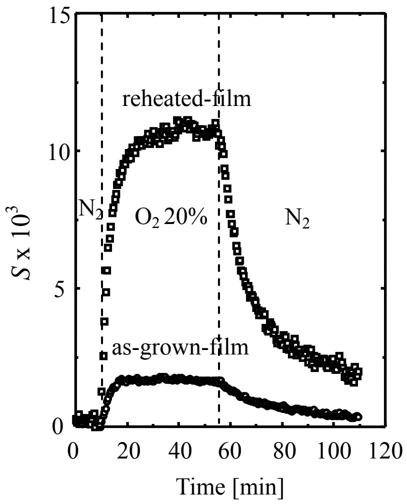


Fig. 3 The oxygen gas responses of the sensitivity of TiS_2 (a) as-grown- film and (b) reheated-film.

Table I Sensitivity and response time comparison between (a) as-grown-film, (b) reheated-film, and (c) ceramics[7].

	Sensitivity	Response time [min]
(a) As-grown-film	1.5×10^{-3}	2.9
(b) reheated-film	9.4×10^{-3}	3.7
(c) Ceramics	2.0×10^{-2}	12.0

4. Conclusions

We developed a new type oxygen sensing device using intercalation phenomenon. By heating titanium plate in the sulfur atmosphere, we succeed to obtain TiS_2 film easily and confirmed the manufactured film is consisted of single phase. The response time of these films is three to four times faster than that of ceramics. Though the sensitivity of reheated-film is about six times higher than that of as-grown-film, the reheated-film sensitivity is half of ceramics.

In order to improve oxygen response of TiS_2 film, it is needed to search better thermal treatment condition for the higher sensitivity or the faster response time on next study.

References

1) T. Usui, Y. Kurumiya, K. Nuri and M. Nakazawa, Sens. & Actuat. **16** (1989) 345.
2) A. M. Azad, S. A. Akbar, S. G. Mhaisalkar, L. D. Biekefeld and K. S. Goto, J.Electrochem. Soc. **139** (1992) 3690.
3) A. Takami, Ceram. Bull. **67** (1988) 1956
4) L. Ketron, Ceram. Bull. **68** (1989) 860.
5) H. Kuriyaki, Y. Higuchi, T. Nakamura, A. Ikeda, Y Kuroki, *The 7th Int. Joint Sympo. between Chungnam National Univ. & Kyushu Univ.* (2005) 150.
6) G. V. Subba Rao and M. W. Shafer, *Intercalated Layered Materials*, F. Levy, ED. Dordrecht: D. Reidel Pub. (1979) 99.
7) K. Kishiro, S. Takemoto, H. Kuriyaki and K. Hirakawa, Jpn. J. Appl. Phys. **33** (1994) 1069.
8) T. Nugroho, A. Ikeda, Y. Kakihara, H. Kuriyaki ,Y.Kuroki, *2007 Int. Conf. on Solid State Dev. & Mater.* (2007) 1142