PS-11-14
Extended Abstracts of the 2019 International Conference on Solid State Devices and Materials, Nagoya, 2019, pp1025-1026

Optical and Humidity Sensors Fabricated by SnS_2 film and SnS_2 bulk Materials

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Abstract

In this study, we reported on fabrications of optical and humidity sensors by using SnS_2 film and bulk materials, which are prepared by thermal evaporation method and chemical vapor transport method, respectively. We compare the optical response of SnS_2 film and bulk and oxidize them by hydrogen peroxide (H_2O_2) to fabricate the SnO_2 humidity sensors. The crystal structure was analyzed by using X-ray diffraction (XRD), Raman scattering spectrum and scanning electron microscope (SEM). The atomic proportion was also determined by energy dispersive x-ray spectrum. In the photoconductivity spectrum, the indirect band gap of SnS_2 was found at 2.22 eV. Alternative experimental measurements were carried out, such as current-voltage (I-V), photoconductivity spectrum (PC), PC mapping and persistent photoconductivity (PPC) for comparison. In addition, we have demonstrated how to make humidity sensors successfully from SnS_2 film and bulk.

1. Introduction

Transition metal dichalcogenides (TMDC) materials are attracting intense research interest due to their appreciable band-gap in optical and electrical properties. TMDCs including MoS_2, WS_2, WSe_2 are MX_2 stoichiometric compounds consisting of a transition metal and chalcogen, among these TMDC semiconductors, although SnS_2 is less explored compared with MoS_2 or WS_2, However, tin (Sn) and sulfur (S) are cheap and rich in the earth, and its potential applications have increased fast. Tin disulfide (SnS_2) is an intrinsic n-type layered semiconductor with a bandgap of 2.18-2.44 eV, and they have a layered hexagonal CdI_2 structure with stacked layers, which interact via weak van der Waals force between adjacent layers[1]. Many characteristics which make SnS_2 a promising candidate for a variety of applications have been demonstrated including high on-off ratios, fast photoresponse rate and good stability.

Humidity sensors in many fields are very important, including environmental monitoring, agricultural production, industrial production, biological monitoring, and medical and chemical monitoring. Humidity sensors based on semiconducting oxides have advantages, such as low cost, small size and ease of placing the sensor in the operating environment. In metal oxide semiconductors (SnO_2, ZnO, WO_3), tin dioxide is a typical n-type wide semiconductor with a bandgap of Eg ≈ 3.7 eV at 300 K[2] and it has been widely used in various applications such as gas sensor and photodetectors.

In the present work, we grew the bulk SnS_2 crystals using chemical vapor transport (CVT), and used E-gun system to evaporate 5/50 nm Ti/Au metallic electrodes on glass substrates in horizontal furnace. Thereafter, we synthesized large area SnS_2 films on metallic electrodes by thermal evaporation method. After samples were grown, we conducted a series of experiments to compare SnS_2 film with SnS_2 bulk, such as X-ray diffraction (XRD), Raman scattering spectroscopy, photoconductivity measurement, and photocurrent mapping spectroscopy. Furthermore, the SnO_2 humidity sensors were fabricated by oxidation of SnS_2 film and bulk materials with hydrogen peroxide (H_2O_2). We find that the SnS_2 film has better performance than the bulk SnS_2 for optical and humidity sensors.

2. Results and discussions

Figure 1(a) shows the scanning electron microscope (SEM) image of the SnS_2 bulk crystals, which clearly indicates a layered structure. It has isostructural with the hexagonal close packed CdI_2 type crystal structure exhibiting unique S-Sn-S stacked layers. Figure 1(b) shows the SEM image of SnS_2 film grown on glass substrates with Ti/Au metallic electrodes. We observe that a continuous film with flower-like surface, which has an advantage for photoresponsivity, has been grown on the glass substrate.

Figure 2(a) shows the XRD patterns for SnS_2 film and bulk. The top of figure 2(a) shows that our SnS_2 bulk has single crystalline nature and can be indexed with hexagonal unit cells of the CdI_2-type (JCPDS no. 23-0677). Therefore, the corresponding XRD pattern of SnS_2 film has many peaks, which represents it has polycrystalline nature. The Raman spectrum of SnS_2 excited by 532 nm laser is presented in Figure 2(b). The Raman spectra of SnS_2 film show a Raman peak at ≈ 312 cm^{-1}, corresponding to the A_{1g} phonon mode of SnS_2, but the SnS_2 bulk has an extra peak at ≈ 202 cm^{-1}. The SnS_2 film without E_g mode that is presumably due to the undetectably weak rejection of the Rayleigh scattered radiation. However, after oxidization with H_2O_2, the SnS_2 film and bulk show Raman peaks at 472.2 and 617.1 cm^{-1}. We anticipated the SnS_2 has been changed to SnO_2 which has good humidity sensing characteristics.

Figure 3(a) presents the results of PC spectra of SnS_2 film and bulk. The photoconductivity spectra illustrate both of the SnS_2 film and bulk materials have band gap energy at around 2.2 eV. Figure 3(b) shows the results of photoresponsivity measured by a 405 nm laser tuned at different laser powers. We find that the photoresponsivities of SnS_2 film and bulk are 20.94 mA/W and 5.31 mA/W, respectively, at laser light intensity of 0.2 uW. Furthermore, we studied the effect of the bias voltage on the photoresponsivity. The results are shown in Figure 3(c), which indicated that responsivity values of SnS_2 film improves very fast as the bias voltage increases up to 20 V. We also observe that SnS_2 film has higher photoresponsivity than SnS_2 bulk at low operating voltage. Figure 3(d) shows the relative balance $[(I_{max}-I_{min})/I_{max}]$ versus switching frequency up to 10 kHz. The relative balance remains 29.51 % for SnS_2 film and drops to 8.45 % for SnS_2 bulk, respectively, at 10 kHz. This result implies that the SnS_2 film is capable of monitoring fast optical signals.

Fig. 4(a) shows the current-time (I-T) plot of the bulk SnS_2 humidity sensor at bias voltage of 20 V. Each peak represents a human exhalation. The sensor shows a good response and quick recovery time to water molecules generated by human exhalation at room temperature. Fig. 4(b) shows the resistance of the humility sensors against the relative humidity values. From this result we observed that the resistance decreased with increasing humidity. Here we also find the humidity sensor made from SnS_2 film has better response than that of SnS_2 bulk.

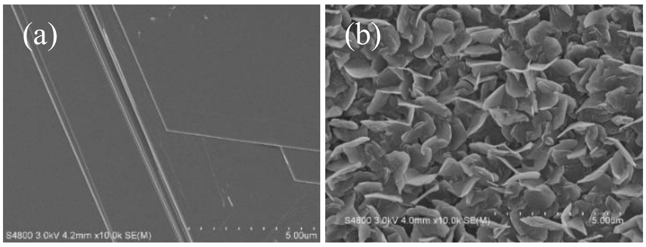

Fig. 1 (a) SEM image of SnS_2 bulk, and (b) SEM image of SnS_2 film.

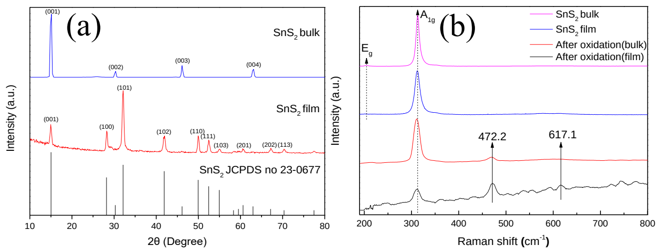

Fig. 2 SnS_2 film and bulk (a) X-ray diffraction, and (b) Raman scattering spectrum excited by 532 nm laser.

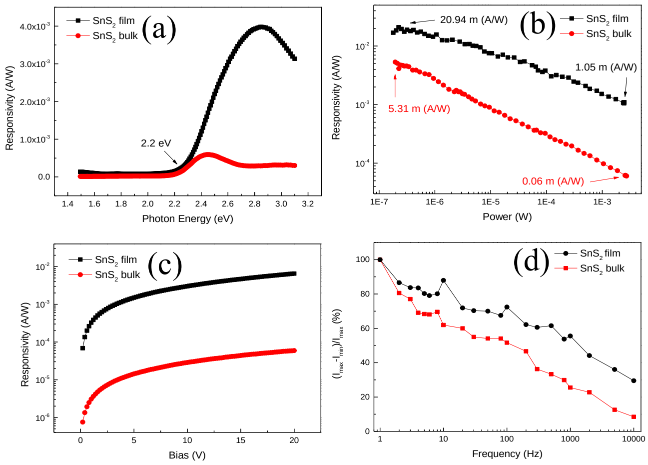

Fig. 3 (a) Photoconductivity spectrum modulated at 10 Hz and V_{sd} = 3 and 20 V (film and bulk,respectively), (b) photoresponsivity profiles for 405 nm laser power, (c) bias voltage-dependent of SnS_2 film and bulk, (d) the relative balance $[(I_{max}-I_{min})/I_{max}]$ versus switching frequency.

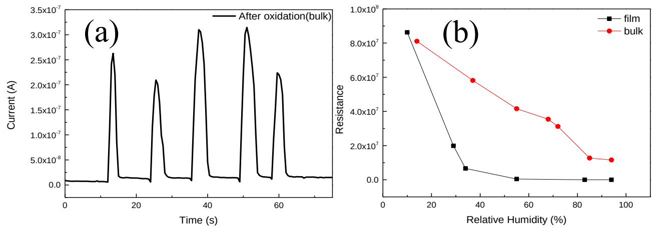

Fig. 4 (a) Repeatability measurement of the sensor device with 20 V voltage upon exposure to human exhalation, and (b) resistance measurement at relative humidity.

3. Conclusions

In conclusion, we have successfully synthesized the SnS_2 film by low pressure thermal sulfurization process and grow the SnS_2 bulk crystals by CVT method. The results from XRD and SEM show the good quality of the SnS_2 film and bulk materials. Furthermore, Raman scattering spectroscopy with atomic vibration modes at 472.2 cm^{-1} and 617.1 cm^{-1} revealed that SnS_2 were transformed to SnO_2 by using H_2O_2 oxidation process. We performed a series of optical studies and find that the photoresponsivity up to 20.94 mA/W and 5.31 mA/W and the relative balance remains at 29.51 % and 8.45 % for SnS_2 film and SnS_2 bulk, respectively. The humidity sensing analysis showed the SnO_2 film made from SnS_2 film has better sensitivity and shorter response time than that of the SnS_2 bulk. Our results demonstrated that SnS_2 film and bulk materials are suitable for photodetector and humidity sensor applications.

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