

Development of Fabrication process for tin sulfide (SnS_x) thin films by solution-based atmospheric-pressure mist CVD

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Abstract

Recently, transitional metal dichalcogenide (TMD) layered materials represented by molybdenum disulfide (MoS_2) are attracting attention as one of the next generation electronic and semiconductor materials. In this paper, we focused on the research of the way for SnS_x thin film fabrication and the evaluation of those properties using solution-based atmospheric-pressure mist CVD. As the result, single crystal-like SnS_2 thin films can be obtained by the 3rd G mist CVD system. It is found that the 3rd G mist CVD system is more powerful technique for preparing metal sulfide thin films. Additionally, optical constants of the SnS_x thin films was analyzed by spectroscopic ellipsometry.

1. Introduction

Mist CVD is a solution-based atmospheric-pressure functional film fabrication technique, and has been developed for preparing metal oxide thin films, generally [1]. Recently, mist CVD can be used for a fabrication of metal sulfide thin films such as ZnS [2] and MoS_2 [3,4]. Among of them, tin sulfide (SnS_x) are attracting attention to the electronics and mechanical applications, such as light absorption layer of solar cells and solid lubricant with excellent friction characteristics using mist CVD [5,6]. We focused on the research of the way for SnS_x fabrication and the evaluation of those properties using mist CVD in this research.

2. Experiment

Two types of mist CVD system, second generation (2nd G) and third generation (3rd G) mist CVD system were used, in this study. The 2nd G mist CVD system consists of a solution chamber and a fine-channel reactor [1]. The 3rd G mist CVD system consists of two (or more) solution chambers, a

mist mixing chamber, and a fine-channel reactor [7]. In the 3rd G mist CVD system, each precursor material is dissolved in each solvent and those solutions are set into multiple solution chambers individually, whereas, in the 2nd G system, the all precursors are directly dissolved in the solvents in one solution chamber. Thus, complex reaction and the formation of precipitates which are occurred before the materials arrived in the reactor can be avoided, in the 3rd G mist CVD system. First, SnS_x thin films were prepared by the 2nd G mist CVD under the condition A, then SnS_x thin films were prepared by the 3rd G mist CVD under the condition B. Tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and thiourea ($\text{CH}_4\text{N}_2\text{S}$) were used as precursors. Both precursors were dissolved in methanol and thin films were fabricated at the temperature from 200 to 400 °C in condition A. On the other hand, in condition B, each precursor was dissolved in methanol individually and set into two solution chambers separately. Carrier and dilution gas flow rate were changed under the fixed total gas flow rate of 5.0, 10.0, 15.0 L/min, for control the material supply rate in the reactor. The SnS_x thin films were fabricated on the 30 mm square quartz substrates. After fabrication of SnS_x thin films, bonding state and crystal structure were evaluated by Raman spectroscopy (HORIBA, LabRAM HR-800; excitation laser wavelength $\lambda = 532$ nm), and X-ray diffraction and grazing incident X-ray diffraction (GIXD) (Rigaku, SmartLab, X-ray source; $\text{Cu K}\alpha$). Additionally, optical constants of the SnS_x was analyzed by spectroscopic ellipsometry (JA Woollam, M-2000D).

3. Results

Prior to fabrication of SnS_x thin films, we evaluated thermal decomposition temperature of each precursor by thermogravimetric-differential thermal analysis (TG-DTA) (Hitachi, STA7200). Figure 1 shows TG-DTA results of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$

Table Experimental Conditions

	Cond. A	Cond. B
Solute A	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O} + \text{CH}_4\text{N}_2\text{S}$	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
Solvent A	-	Methanol
Solute B	Methanol	$\text{CH}_4\text{N}_2\text{S}$
Solvent B	-	Methanol
Concentration [mol/L]	$\text{Sn} : \text{S} = 0.02 : 0.02$	$\text{A} : \text{B} = 0.02 : 0.02$
Growth time	10 min	
Substrate Temp.	200-400 °C (intervals 50 °C)	
Substrate	Quartz	
Growth system	Fine Channel type mist CVD	Fine Channel Dual mist CVD
Gas	N_2	
Total gas flow rate [L/min]	7.0	5.0 10.0 15.0
Ultrasonic transducer	2.4 MHz, 24 V · 0.625 A, 3	

and $\text{CH}_4\text{N}_2\text{S}$. In the case of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, an exothermic reaction and an abrupt loss of weight were observed at the temperature reached $\sim 240^\circ\text{C}$ (see fig. 1(a)), and in the case of $\text{CH}_4\text{N}_2\text{S}$, an endothermic reaction and an abrupt loss of weight were observed at the temperature reached $\sim 163^\circ\text{C}$ (see fig. 1(b)). The behaviors indicate the decomposition of those materials. From these results, it is estimated that SnS_x thin films can be prepared at the temperature above 240°C .

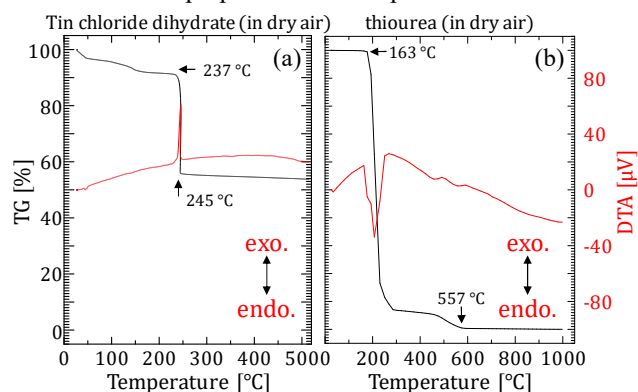


Fig. 1 TG-DTA results of (a) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in dry air and (b) $\text{CH}_4\text{N}_2\text{S}$ in dry air.

Figure 2 shows photo images of substrate surface before and after fabrication of SnS_x under the condition A. The color of the substrates clearly changed after the deposition. The results of Raman spectroscopy are shown in figure 3(a). Two Raman peaks around 223 cm^{-1} (SnS , A_g) and 303 cm^{-1} (SnS_2 , A_{1g}) were observed from the sample prepared at 300°C and 350°C . In the XRD spectra, any peaks corresponding to the SnS_x cannot be observed. However, in the GIXD spectra, a broad and weak peak corresponding to the SnS_2 (001) plane is observed around 15° in the sample fabricated at 350°C (Fig.4). From these results, it is considered that the fabrication of SnS_x thin films are difficult by the 2nd G mist CVD system or higher temperature is required for fabrication of it. In other word, it is considered that unexpected reaction is occurring before the thin films fabricate on the substrates by dissolving the two precursors in one solvent. Thus, we have fabricated SnS_x thin films by the 3rd G mist CVD system. In the case of condition B, the Raman peak corresponding to SnS_2 was observed around 303 cm^{-1} in the samples fabricated at the temperature from 200 to 400°C . In addition, a peak can also be confirmed around 223 cm^{-1} in the sample fabricated at the temperature of 350°C (Fig.3(b)). XRD and GIXD spectra of the sample fabricated under the condition B show in figure 4. The sharp peak corresponding to the SnS_2 (001) plane is observed around 15° in the samples fabricated at 250 to 400°C . Furthermore, the results suggest that a single crystal-like SnS_2 thin films with uniform orientation is formed in the samples fabricated at 300 to 400°C .

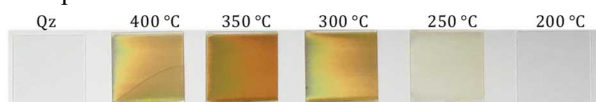


Fig. 2 Photo images of substrate surface before and after fabrication of tin sulfide under the condition A.

4. Conclusions

We have developed the fabrication technique for metal sulfide thin films by mist CVD, and SnS_x thin films were fabricated and evaluated using the 2nd and the 3rd generation mist CVD systems. As the results, both processes could prepare SnS_x thin films. In particular, single crystal-like SnS_2 thin films could be fabricated by the 3rd G mist CVD system. However, high temperature was necessary for fabrication the SnS_x thin films by the 2nd G mist CVD system because one of the precursors stabilized in the solution. From these results, the 3rd G mist CVD system is more powerful technique for preparing metal sulfide thin films. The details of experiments and other results will be discussed in the conference.

References

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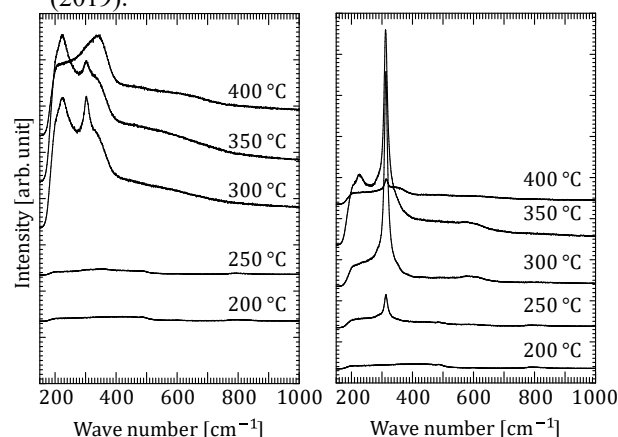


Fig. 3 Raman spectra of (a) samples fabricated under the condition A and (b) condition B.

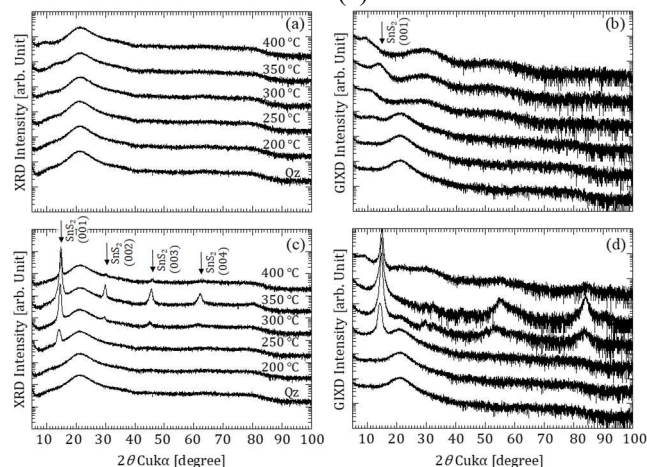


Fig. 4 (a)XRD and (b) GIXD spectra of the samples fabricated under condition. A. (c) XRD and (d) GIXD spectra of the samples fabricated under condition B.