## $\begin{array}{c} Characteristics \ of \ SnS_x \ by \ Atomic \ Layer \ Deposition \ for \\ CIGS \ solar \ cells \end{array}$

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Recently, solar cells based on crystalline silicon show very high conversion efficiencies, but many researchers are studying thin film solar cells since they have lower production costs than crystalline silicon. In particular, copper indium gallium selenide (CIGS) solar cells have been researched the most intensively in field of thin film solar cell. Because CIGS solar cells have many advantages such as high absorption coefficient, direct bandgap and a competitive cost compared to crystalline Si based solar cells. Also, they can be produced on glass or flexible substrates. But, gallium and indium used as absorber layer materials are rare earth resources [1]. Therefore, the production cost of CIGS solar cells are gradually increasing. Furthermore, cadmium sulfide (CdS), which is one of toxic material, is used as a buffer layer to buffer energy difference between CIGS absorber layer and zinc oxide (ZnO) windows layer. For these reason, Cd-free buffer layers have been studied to reduce the environmental impact in vacuum process. Typically, Zn(S,O,OH), In<sub>2</sub>S<sub>3</sub> and ZnSe were noted as alternative materials due to the less toxicity [2,3,4] and lower production cost than CdS [5]. In order to solve these problems, many researchers have studied. As an alternative material of absorber layer, a SnS is one of candidate materials due to the p-type property and optical bandgap of 1.0-1.5 eV [6]. And  $SnS_2$  is known to have a n-type property and optical bandgap of 2.2-2.4 eV which can be used as a buffer layer [7].

In this study, we deposited tin sulfides  $(SnS_{x=1,2})$  films using Tetrakis(dimethylamino)tin (TDMASn) as a Sn source and hydrogen sulfide (H<sub>2</sub>S) as a sulfur reactant gas by ALD. During the ALD process, a mass flow controller (MFC) controlled the rate of dosing for the Sn precursor and argon (Ar) gas. Ar was used as a bubbler gas at 30 sccm for the TDMASn delivery and as a purging gas at 200 sccm. SnS<sub>x</sub> thin films were deposited at the various process temperatures using this optimized sequence, and were analyzed by SEM, XRD, TEM, XPS, UPS and UVvis.

Figure 1 show The XRD spectra of 50 nm-thick SnS<sub>x</sub> films deposited from 100 to 180 °C. In the XRD results, the diffraction peaks corresponding to SnS<sub>x</sub> films at 100 and 120 °C were not observed. Thus, it was proposed that the crystal structures of the SnS<sub>x</sub> films were amorphous below deposition temperatures of 120 °C. On the other hand, the XRD spectra of the SnS<sub>x</sub> thin film deposited at 140 °C showed peaks associated with the (001) SnS<sub>2</sub> hexagonal structure, which were located at 15.02° (JCPDS No. 23-0677). The multiple diffraction peaks of the SnS<sub>x</sub> films deposited at 160 and 180 °C corresponded to the SnS orthorhombic structure, which were located at  $25.7^\circ$  and  $31.6^\circ\!,$  corresponding to the (120) and (111) plane, respectively (JCPDS No. 39-0354). These results clearly indicate that the deposition temperature plays an important role in the crystal structure of SnS<sub>x</sub> films.

Figure 2(a) shows the measured optical transmittance spectra of the 50 nm-thick  $SnS_x$  films deposited from 60 to 180 °C upon the incident monochromatic light with from 1 to 6 eV of photon energy. As shown in Fig. 2(a),

the average transmittances of films in the visible range of the spectra (from 1.6 to 3.1 eV) gradually decreased from approximately 79.23 to 56.86 % by increasing the deposition temperature from 60 to 140 °C. The absorbance spectrum is shown in Fig. 2(b). Consistent to the transmittance results, absorbance increased with the deposition temperature and increased sharply above 160 °C (Fig. 2(b)). The inset plot in Fig. 2(b) shows curves of  $(\alpha hv)^2$  versus hv on 50 nm-thick SnS<sub>x</sub> films for each temperature. The optical band (E<sub>dir</sub>) was estimated by determining the intercept of the linear extrapolation with the photon energy for the absorption onset of the  $(\alpha hv)^2$  curve.

More results will be presented in Meeting.

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Figure 1. XRD spectra of 50 nm-thick  $SnS_x$  films deposited with various temperature.



Figure 2. (a) Optical transmission and (b) absorbance curves of  $\text{SnS}_x$  films with various temperature. The inset figure is the direct optical bandgap plot estimated from the absorption spectra caculated by  $(\alpha hv)^2 = A(hv - E_g)$ .