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A first attempt to measure the lifetime of S atom in magnetron sputtering plasma employing a CuZnSnS target

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Introduction

A new compound of Cu_2ZnSnS_4 (CZTS) has drawn wide attention for their usage as a new material of a thin film solar cell. A CZTS solar cell consists of non-toxic and abundant materials compared to a CuInGaSe solar cell. For the mass production of CZTS thin film using the magnetron sputtering deposition technique, it is very important to understand its deposition mechanisms. Especially since it consists of four elements, it is very difficult to control the thin film stoichiometric properties. It is also well known that the high vapor pressures of Zn and S element result in reduction of their composition in CZTS thin film.

In previous works, the lifetimes of Cu, Sn and Zn atoms in the afterglow of magnetron sputtering plasmas have been evaluated using laser induced fluorescence (LIF) spectroscopy techniques, and their surface loss probabilities have been evaluated. However, the detection of S atoms using LIF did not succeed due to the poor measurement sensitivity. In the present work, we report our first attempt on the measurement of the S atom density using vacuum ultraviolet absorption spectroscopy (VUVAS).

Experimental setup

rf magnetron sputtering plasma employing a CZTS stoichiometric target was produced at a pulse-modulated mode at 10 Hz. The rf power and the Ar pressure were 80 W and 25~100 mTorr, respectively. The S density after the termination of the rf power was evaluated by VUVAS. An electron cyclotron resonance (ECR) plasma using SF_6+Ar gases was produced as the light source. In such plasma as light source, the most severe issue arises from the radiation trapping effect in the light source. Therefore, for the sake of comparison, the lifetime of S atoms was measured at two absorption wavelengths.

Results and discussion

The exponential decays of the S atom densities after the termination of the rf power were successfully fitted and their lifetimes were evaluated. The lifetimes of S atoms at various Ar discharge pressures were measured and plotted in figure 1. The absorption measurements were done at 142.5 nm and 147.4 nm, which are optically thick and optically thin lines, respectively. Details of the wavelength selection will not be discussed here. However, figure 1 shows that the lifetime of S atoms measured at two absorption wavelengths are almost the same. The influence of the radiation trapping on the determination of the lifetime was negligible.

In the afterglow plasma, the major loss process of S atoms is due to the diffusion to the chamber wall. Their decay time constant can be expressed by $\tau = \frac{\Lambda^2}{Dp}p + \frac{2l_o(2-\alpha)}{\bar{v}\alpha}$, where D and p denote the diffusion coefficient and the Ar pressure, respectively. Λ is the geometric diffusion length, l_o=V/S with V and S being the volume and surface area of the sputtering chamber, respectively, $\bar{v}$ is the mean velocity of S atom and α is the surface loss probability of S atom. For a circular cylinder Λ is given by $\frac{1}{\Lambda^2} = \left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{r}\right)^2$, where L=18 cm is the length of the cylinder and r=8 cm is the radius. From these equations and our chamber geometry, we calculated the diffusion coefficient of S atom in Ar environment as Dp=165.5 cm^2Torr/s and the surface loss probability of S atom on chamber wall as α=0.14 (the temperature is assumed to be 400 K). Note that in this experiment there was no substrate placed in front of the CZTS target, so thus the sputtered atoms were freely diffused to the chamber walls. Further investigation to compare the surface loss probabilities of Cu, Sn, Zn and S on a substrate surface is essential.

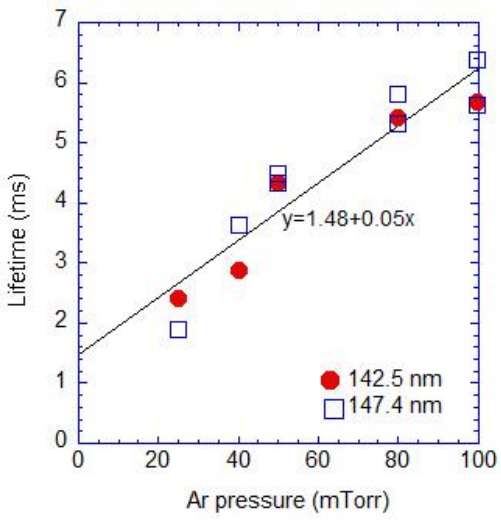

Figure 1. Relationship between the discharge Ar gas pressure and the lifetime of S atoms measured at two absorption wavelengths.