

## Diffusion coefficients of Cu, Zn, Sn, S atoms in argon gas アルゴン雰囲気におけるCu, Zn, Sn, およびS原子の拡散係数

Nayan Nafarizal<sup>1,2</sup> and Koichi Sasaki<sup>1</sup>  
ナファリザル ナヤン<sup>1,2</sup>, 佐々木浩一<sup>1</sup>

<sup>1</sup>*Division of Quantum Science and Engineering, Hokkaido University,  
Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan*

北海道大学大学院工学院量子理工学部門 〒060-8628 札幌市北区北13条西8丁目

<sup>2</sup>*Microelectronics and Nanotechnology Research Centre, Faculty of Electrical and Electronic Engineering,  
Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor 86400, Malaysia*

The diffusion coefficients of magnetron-sputtered Cu, Zn, Sn and S atoms in argon gas environment were evaluated experimentally. Magnetron sputtering plasma employing a stoichiometric Cu<sub>2</sub>ZnSnS<sub>4</sub> compound target was produced using a pulse-modulated rf power supply, and the temporal variations of the atom densities in the afterglow were measured using laser-induced fluorescence spectroscopy (for Cu, Zn and Sn atoms) and vacuum ultraviolet absorption spectroscopy (for S atom) techniques. The time constants of the temporal decays of the atom densities were plotted as a function of the argon gas pressure. Then, the diffusion coefficients were evaluated from the slopes of linear fittings for the relationships between the decay time constants and the argon pressure.

### 1. Introduction

Recently, Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) has been proposed as a replacement of CdTe and CIGS in thin film solar cells. It is a multi-compound semiconductor consisting of abundant and non-toxic elements. CZTS is a p-type semiconductor that has a band gap energy of 1.4-1.5 eV and an absorption coefficient greater than 10<sup>4</sup> cm<sup>-1</sup>, which are useful as an absorber layer in solar cells [1]. Magnetron sputtering is the most promising technique to deposit a large-scale CZTS thin film with high uniformity, which is essential for the mass production of commercial CZTS solar cells. Since the single-step synthesis of CZTS thin films is preferable from industrial point of view, in the present study, we employed magnetron sputtering of a stoichiometric CZTS target in pure argon.

In order to understand the growth mechanism of the CZTS thin film on a substrate, it is essential to know the diffusion coefficients of Cu, Zn, Sn and S atoms in argon. To our best knowledge, two papers have reported the diffusion coefficient of Cu [2,3], and only one paper has reported the diffusion coefficient of Zn [4]. We have found no papers which report the diffusion coefficients of Sn and S. In this study, we experimentally investigated the diffusion coefficients of Cu, Zn, Sn and S atoms sputtered from a stoichiometric CZTS compound target in argon. The diffusion coefficients were estimated from the decay time constants of the atom densities in the afterglow of pulse-modulated magnetron sputtering plasmas. The atom densities

were measured by laser-induced fluorescence (LIF) for Cu, Sn and Zn and by vacuum ultraviolet absorption spectroscopy (VUVAS) for S.

### 2. Experimental setup

A magnetron sputtering source was inserted from the top of a cylindrical chamber. The stoichiometric CZTS target had a diameter of 50 mm, and was bonded on the copper surface of the magnetron source. The target or the discharge cathode was surrounded by an electrically grounded shield (the anode) with a diameter of 80 mm. A substrate holder was placed at a distance of 50 mm from the target. The diameter of the substrate holder was 100 mm. The base pressure of the vacuum chamber was approximately 10<sup>-7</sup> Torr.

Magnetron sputtering plasmas were produced using a pulse-modulated radio frequency (rf) power supply at 13.56 MHz. The repetition frequency of the discharge was 10 Hz, and the on- and off-periods of the rf power were 80 or 90 ms and 10 or 20 ms, respectively. The rf power was fixed at 80 W at all experimental conditions. The discharge gas was argon (Ar) and its pressure was controlled using a gate valve near the pumping unit. The gas pressure was monitored using a capacitance gauge.

Tunable laser pulses yield from an optical parametric oscillator (OPO) were introduced into the discharge space between the CZTS target and the substrate holder. The OPO wavelengths were tuned to excite Cu, Zn and Sn at their ground states. We detected fluorescence from the laser-excited

states using a charge coupled device camera with an image intensifier (for Cu and Sn) and a photomultiplier tube via a monochromator (for Zn). By changing the delay time between the laser pulse and the termination of the rf power, we obtained the temporal variations of the Cu, Sn and Zn atom densities in the afterglow. The decay time constants of the atom densities were evaluated by the exponential fittings of the temporal variations.

An electron cyclotron resonance (ECR) plasma employing SF<sub>6</sub>/Ar mixture was produced as the light source for measuring the absolute S atom density by VUVAS. The light from the ECR plasma passed through the center of the magnetron sputtering plasma, and the transmitted light intensity was measured using a secondary electron multiplier tube via a VUV monochromator. The temporal variation of the S atom density (and its decay time constant) was obtained from the temporal variation of the transmitted light intensity. For the sake of comparison, we employed three wavelengths for evaluating the S atom density.

### 3. Results and discussion

Figure 1 shows the relationship between the decay time constants (lifetimes) of Cu, Sn, Zn and S and the argon pressure. According to Chantry [5], the lifetime of a particle in a chamber is given by the following equation, if the diffusion is the dominant loss process (namely the gas-phase loss due to chemical reactions is negligible),

$$\tau_d = \frac{\Lambda_0^2}{Dp} p + \frac{2l_0(2-\alpha)}{\bar{v}\alpha} \quad (1)$$

where  $p$  and  $D$  denote the pressure and the diffusion coefficient, respectively,  $\Lambda_0$  is the geometric diffusion length,  $l_0$  is the ratio between the volume and the surface area of the chamber,  $\bar{v}$  is the mean velocity of the particle, and  $\alpha$  is the sticking probability. Therefore, the linear relationships shown in Fig. 1 indicate negligible gas-phase losses of Cu, Sn, Zn and S, and in this case, we can evaluate the diffusion coefficients from the slopes of the linear relationships, provided that we have the knowledge on the geometrical diffusion length  $\Lambda_0$ .

Unfortunately, the evaluation of  $\Lambda_0$  in the chamber with the substrate holder and the magnetron source was not an easy task. Instead of the direct evaluation, we compared the slope of the linear relationship of Cu with the diffusion coefficients reported in literature. The diffusion coefficient of Cu in argon has been reported by two authors, and they have reported the same value of

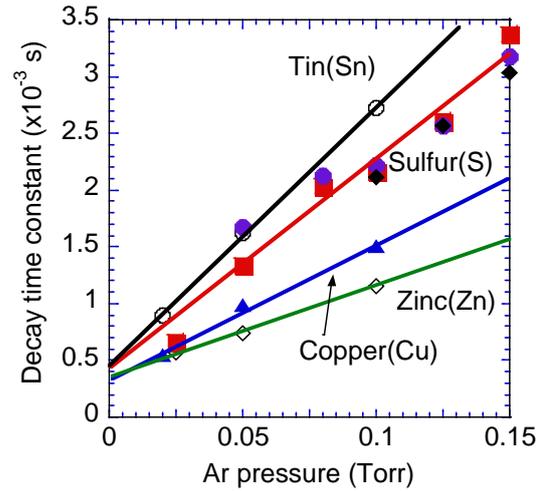


Fig.1. Decay time constants of Cu, Zn, Sn and S atom densities as a function of the argon pressure. Solid squares, solid circles, and solid diamonds were obtained by VUVAS at 142.5 nm, 147.4 nm and 129.5 nm, respectively.

$Dp=140$  cm<sup>2</sup>Torr/s [2,3]. This diffusion coefficient gives us an estimation of  $\Lambda_0^2=1.65$  cm<sup>2</sup>.

If we believe the above estimation on  $\Lambda_0$ , we can evaluate the diffusion coefficients of Sn, Zn, and S as shown in Table I. According to a theoretical work by Gardner *et al* [4], the diffusion coefficient of Zn in argon is estimated to be 240 cm<sup>2</sup>Torr/s in the present experimental condition, which is roughly consistent with the value listed in Table I. This work gives us the experimental estimations on the diffusion coefficients of Sn and S in argon for the first time.

Table I. Diffusion coefficients of Cu, Zn, Sn and S in argon.

	Slope (x10 <sup>-3</sup> s/Torr)	$Dp$ (cm <sup>2</sup> Torr/s)
Cu	11.81	(140)
Zn	7.94	208
Sn	22.75	73
S	17.64	94

### References

- [1] M. P. Suryawanshi, G. L. Agawane, S. M. Bhosale, S. W. Shin, P. S. Patil, and J. H. Kim, *Mater. Technol. Adv. Perform. Mater.* **28**, 98 (2013).
- [2] H. Sekido, T. Kondo, A. Kono, and T. Goto, *J. Phys. D: Appl. Phys.* **26**, 1414 (1993).
- [3] A. Bogaerts, R. Gijbels, and R. J. Carman, *Spectrochim. Acta Part B At. Spectrosc.* **53**, 1679 (1998).
- [4] P. J. Gardner, P. Pang, and S. R. Preston, *J. Chem. Eng. Data.* **36**, 265 (1991).
- [5] P. J. Chantry, *J. Appl. Phys.* **62**, 1141 (1987).