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Measurement of spatial distributions of metal atom densities in magnetron sputtering plasmas employing a CZTS target
CZTS ターゲットマグネトロンスパッタリングプラズマにおける金属密度分布計測

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We investigated spatial distributions of metal atom densities in magnetron sputtering plasmas employing Cu and Cu_2ZnSnS_4 (CZTS) targets by laser-induced fluorescence (LIF) imaging spectroscopy. LIF pictures which represented distributions of Cu atom densities had different shapes at different Ar gas pressures. The comparison between the density distributions observed using Cu and Cu_2ZnSnS_4 targets suggests that sulfuration of Cu atoms in the gas phase is not significant.

1. Introduction

Cu_2ZnSnS_4 (CZTS) thin film is an attractive material as a light absorption media of a solar cell. It has a band gap energy of 1.4-1.5 eV and an absorption coefficient greater than 10^4 cm^{-1}. The most attractive point of CZTS in comparison with $Cu(In,Ga)Se_2$ is its element composition. CZTS includes no toxic elements, and is composed of abundant elements on the earth. Recently, a conversion efficiency of 9.6 % has achieved in CZTS-based solar cells [1]. For these reasons, many researchers has been investigating fabrication technologies of CZTS thin films for many years. There are several deposition methods for CZTS thin films, for example, co-evaporation, sol-gel methods, pulsed laser deposition and RF magnetron sputtering.

RF magnetron sputtering is the most suitable method for the mass-production of CZTS-based solar cells, since it has advantages of the large-area deposition and the uniformity of film thickness. However, magnetron sputtering has difficulty in depositing CZTS thin films with fine stoichiometry. The principal problem is the less abundant composition of sulfur and zinc atoms in the film.

A method to understand the deposition mechanism of CZTS thin films and to understand the reason for the less abundant composition of S and Zn is observing density distributions of various atom densities in the gas phase of magnetron sputtering plasmas. In this study, we measured two-dimensional distributions of Cu densities by laser-induced fluorescence (LIF) imaging spectroscopy. We employed Cu and CZTS targets in this experiment. We discuss the significance of gas-phase reactions of Cu on the basis of the comparison between the density distributions observed in Cu and CZTS magnetron sputtering plasmas.

2. Experiment

Figure 1 shows the experimental apparatus. We used a magnetron sputtering source which was connected to an RF power supply via a circuit for impedance matching. The magnetron sputtering source consisted of cylindrical permanent magnets and an indirect water-cooling system. The RF power and the frequency were 80 W and 13.56 MHz, respectively. A sintered CZTS or Cu target (50 mm in diameter) was placed on the permanent magnets. The chemical composition of the CZTS target was perfectly stoichiometric, i.e., Cu:Zn:Sn:S = 2:1:1:4. Ar gas was used for discharges, and the pressure was varied between 3 and 30 mTorr.

We used an optical parametric oscillator (OPO) pumped by a Nd:YAG laser for exciting Cu atoms in plasmas. The laser beam from the OPO laser was arranged to have a planer shape with a width of 80 mm and a thickness of 2 mm using two cylindrical lenses. Excitation wavelength for Cu atoms at the ground state was 324.754 nm (the $4s^2S_{1/2}$ - $4p^2P^o_{3/2}$ transition). On the other hand, the wavelength of the LIF emission was 510.554 nm which corresponded to the $4p^2P^o_{3/2}$ - $4s^2D_{5/2}$]transition. The image of LIF formed on the planar laser beam was captured using a charge coupled device camera with a gated image intensifier (ICCD camera) [2]. An interference filter was placed in front of the camera to separate the LIF emission from self-emissions of the plasma. The tone of the LIF image represented the two-dimensional density distribution

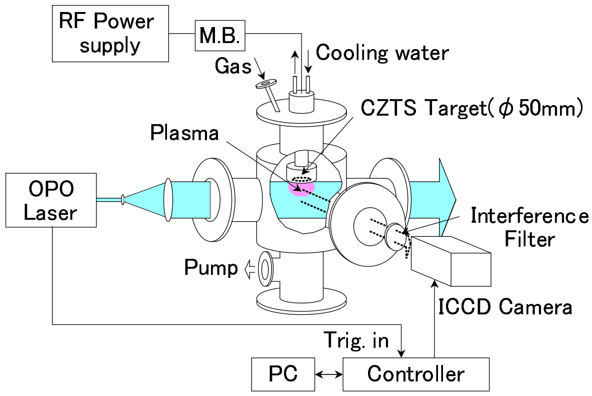
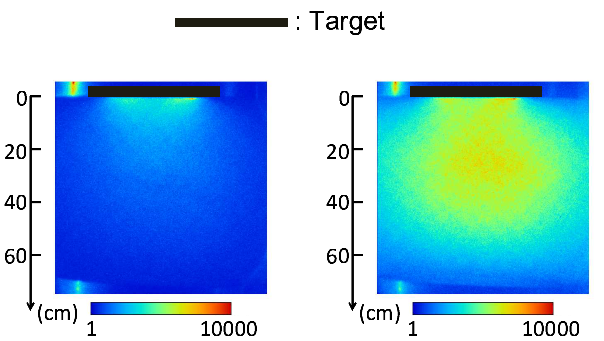


Figure 1: Experimental apparatus.

of ground-state Cu atoms.

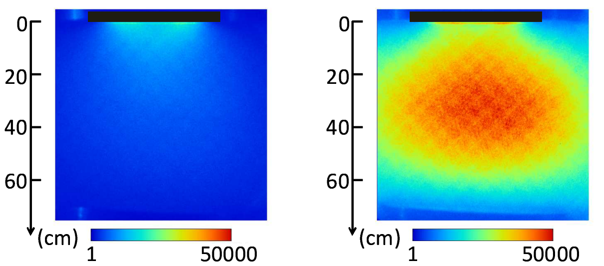
3. Results

Figure. 2 shows two-dimensional distributions of Cu atom densities in CZTS and Cu magnetron sputtering plasmas at pressures of 5 and 20 mTorr. The vertical and horizontal lengths of the pictures correspond to 80 mm × 80 mm. The target is placed at the top of the images.



(a) CZTS target, 5 mTorr

(b) CZTS target, 20 mTorr



(c) Cu target, 5 mTorr

(d) Cu target, 20 mTorr

Figure 2: Spatial distributions of Cu atom densities in Cu and CZTS sputtering plasmas. The gas pressure were 5 and 20 mTorr, and the RF power was 80 W.

Figures 2(a) and 2(b) were observed with a CZTS target, while we observed Figs. 2(c) and 2(d) with a Cu target. It was found that the Cu atom density with a CZTS target is approximately 1/6 of that with a Cu target. The spatial distribution of the Cu density was dependent on the discharge pressure, but the normalized distributions were roughly the same when we employed Cu and CZTS targets.

4. Discussion

As reported previously [3], the variation of the axial distribution of the Cu density with the discharge pressure is a long-time mystery. The distribution observed at 20 mTorr, which has the peak at a separated distance from the target, cannot be explained by the spatial distribution of the speed of sputtered Cu atoms [4]. Although the fundamental understanding on the spatial distribution is still insufficient, the comparison between the Cu atom densities in the Cu and CZTS sputtering plasmas gives us valuable insight into the transport and chemical reactions of Cu atoms.

A point is the ratio of Cu densities in the Cu and CZTS sputtering plasmas. The density ratio of approximately 1/6 is not deviated significantly from the ratio of the number of Cu atoms contained in the Cu and CZTS targets. The gas-phase loss of Cu atoms in the Cu sputtering plasma is basically negligible. Therefore, the unremarkable deviation of the ratio of the Cu densities from the ratio of the numbers of Cu atoms contained in the targets suggests negligible gas-phase loss of Cu atoms in the CZTS sputtering plasma. The insignificant gas-phase loss of Cu atoms in the CZTS sputtering plasma is supported by the similar spatial distributions of the Cu densities in the Cu and CZTS sputtering plasmas. The similar distributions indicates negligible loss of Cu atoms during the transport from the target to the downstream region.

The most likely gas-phase reaction in the CZTS plasma is sulfuration of metal atoms. The production of sulfides in the gas phase means the transport of S atoms to the film with tight chemical bonding with other elements, which would result in efficient sulfuration of the film. The present experiment suggests negligible sulfuration of Cu in the gas phase, and we will examine sulfurations of Zn and Sn in future work.

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