Comparison of Cu, Zn, and Sn densities in magnetron sputtering plasmas employing Cu_2ZnSnS_4 and metal targets

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Cu_2ZnSnS_4 (CZTS) thin films are attractive materials as the light absorption media of solar cells, since they include no rare metals and no toxic elements. There are several methods for depositing CZTS thin films. Among them, rf magnetron sputtering is believed to be the most suitable method for the mass production, since it has an advantage in large-scale deposition with high uniformity. However, the magnetron sputtering deposition of CZTS thin films is a problematic process. The principal problem is the deviation from the stoichiometric compositions of the four elements. In this work, we examined the gas phase of a magnetron sputtering plasma employing a CZTS target.

The magnetron source was a conventional one with a small (50 mm) cathode electrode. A stoichiometric CZTS target was placed on the cathode electrode and was connected to an rf power supply at 13.56 MHz via a matching circuit. For the sake of comparison, we also employed metallic Cu, Zn, and Sn targets. Tunable laser beams were launched into the gas phase of the magnetron sputtering plasma, and the densities of Cu, Zn, and Sn atoms were measured by laser-induced fluorescence (LIF) spectroscopy.

We compared the densities of Cu, Zn, and Sn in the CZTS sputtering plasma with those in the sputtering plasmas employing the corresponding metal targets. The sputtering plasmas were produced at the same rf power of 80 W and the same Ar pressure of 5 mTorr. As a result, the ratio in the Cu densities (near the target) was 0.2, the ratio in the Zn densities was 0.1, and the ratio in the Sn densities was 0.05. On the other hand, we could estimate the ratio of the Cu, Zn, and Sn densities in the metal sputtering plasmas by referring their sputtering yields and lifetimes. The lifetimes were examined by the temporal decay of the densities in the afterglow. The estimated ratio in the metal sputtering plasmas was [Cu]:[Zn]:[Sn]=1:3:0.7. This ratio resulted in the estimated density ratio in the CZTS sputtering plasma to be [Cu]:[Zn]:[Sn]=1:1.4:0.2, suggesting a problematic element composition in the gas phase. In addition, this result also suggests a small sputtering yield of Sn from the CZTS target.