Cu₂ZnSnS₄ (CZTS) and related materials have many advantages of high efficiency thin-film solar cell absorber material, such as high absorption coefficient (over 10⁴ cm⁻¹) and suitable direct bandgap (around 1.4 eV). [1] Many papers have been reported. A theoretical efficiency of around 25 % is predicted for CZTS-based thin-film solar cell, however, it has not reached yet. There are various reasons for low conversion efficiency. One of the reasons is that Zn and Sn are easily replaced. Therefore, Zn must be larger than the stoichiometric composition. In other words, Zn/Sn ratio must be larger than 1. [2] On the other hand, it is well known that the surface properties of the CZTS absorber layer affects device characteristics greatly. Many methods for improving the surface condition have been reported. One of the methods for improving the surface state is solution treatment. This method has several advantages, for example, extremely simple and inexpensive. We also reported the influence of the surface treatment on bromine water, ammonia water and ultrapure water. [3-5] In this work, we report the influence of surface chemical composition, conditions, and morphologies of CZTS surface treated by using sodium hypochlorite (NaClO).

The CZTS thin films deposited on Mo/soda lime glass substrate by sulfurization process. After deposition of CZTS thin films, the CZTS samples were soaked in NaClO solution at various experimental conditions. After soaking in NaClO solution, the CZTS samples were rinsed with ultrapure water at 30 seconds. For the comparison, we studied the soaking only ultrapure water. The samples were observed by SEM, EDX, XPS, XRD and Raman spectroscopy. Raman spectra and XRD patterns before and after NaClO treatment were almost same. These results suggested that the bulk structure did not change with NaClO soaking treatment. Figure 1 shows the SEM image of CZTS sample after NaClO treatment. From the SEM images, it was confirmed that a part of surface was covered. As a result of EDX analysis, it is considered that the coated substance is considered to be some complex such as zinc tetrahydroxyde or salt. However, details of this substance are known. Figure 2 shows the XPS spectra of Cu 2p and Zn 2p of the samples. From the XPS spectra of Cu 2p (Fig. 2), Cu-O peak appeared after dipping in NaClO solution for 100 seconds. Similar results could be confirmed from the XPS spectra of Zn and Sn. These results suggested that oxides may have been formed from the sulfide at the surface. Therefore, it is considered that the removal of the oxide cased by the NaClO treatment leads to improvement of the surface condition and thus the improvement of the conversion efficiency.


*Figure 1:* SEM image of the soaked sample at 100 seconds in 10 at.% NaClO solution.

*Figure 2:* XPS spectra of Cu 2p of the as-prepared (non-treated) sample and soaked sample at 100 seconds in 10 at.% NaClO solution.