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Low-Temperature Direct Conversion of Cu−In Films to $CuInSe_2$ via Selenization Reaction in Supercritical Fluid

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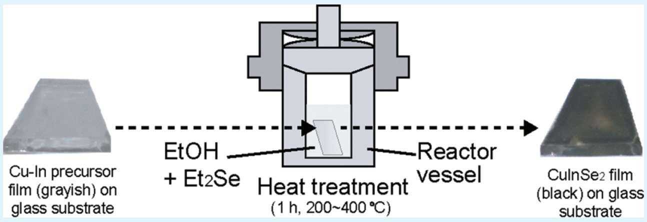
ABSTRACT: In this study, we achieve the direct conversion of metallic Cu−In films to compound semiconductor $CuInSe_2$ films, at quite low temperature around 300 °C using less hazardous metalorganic selenium source in supercritical fluid (SCF). We investigated the effects of temperature and fluid (ethanol) density, and found that supercritical ethanol plays a crucial role in this low-temperature selenization reaction. Such SCF-assisted direct conversion reactions can facilitate large-scale, low-temperature, and rapid synthesis of $CuInSe_2$ films, which can potentially lead to the low-cost production of solar cells.



KEYWORDS: CIS/CIGS solar cells, compound semiconductor, conversion reaction, and supercritical fluid

INTRODUCTION

Recently, as an alternative to Si-based solar cells, CIS/CIGS solar cells have emerged in the solar-energy market. $CuInSe_2$ and $CuIn_xGa_{1-x}Se_2$ chalcopyrite semiconductor alloys are well-known as promising materials for low-material-cost, high-efficiency, lightweight, and radiation-resistant solar cells. Low-cost fabrication of $CuInSe_2$ is a topical issue for the large-scale application of high-efficiency solar cells because the current vapor-phase fabrication process limits their industrial production.

One of the most used preparative techniques in industrial applications is the deposition of Cu and In precursor films followed by high-temperature (400−550 °C) vapor-phase selenization using the very toxic and hazardous gas, H_2Se. To achieve the goal of low-cost $CuInSe_2$ film fabrication, reduction of the selenization temperature and the usage of less hazardous selenium sources are required. Recently, as less hazardous alternative candidates, metal−organic selenides such as diethylselenide [$(C_2H_5)_2Se$: Et_2Se] have been proposed.[1−3] Et_2Se is less dangerous to the health and environment compared to H_2Se. However, the use of Et_2Se requires the selenization temperature greater than 490 °C; this high temperature is problematic for the low-cost fabrication of solar cells with low-cost and flexible substrates, which have poor heat tolerances.

Here, we employed an SCF as a reaction medium to reduce the selenization temperature for the preparation of $CuInSe_2$ compound semiconductor films. SCFs are environmentally benign solvents with adjustable physical properties (density, viscosity, and dielectric constant) that vary with temperature and pressure. SCFs are advantageous reaction media because liquid-like high densities and high solubilities are maintained with high diffusion coefficients. Moreover, it is well-known that the reaction equilibrium shifts under high pressure conditions compared to ambient pressure conditions; in some cases, the reaction temperature can be reduced by employing SCFs as the reaction medium.[4,5] Owing to these properties, SCFs are used in chemical syntheses,[6] extractions/separations,[7] and material processing.[8] Recently, utilization in compound semiconductor fabrication has led to significant advances. Although the majority of products are limited to nanoparticles, there are many reports for the direct fabrication of compound semiconductors using SCFs.[9−11] However, semiconductor film preparation in SCFs has been limited,[12] and there are no reports on the direct conversion reaction of precursor films in SCF.

In this study, we developed a novel fabrication process for $CuInSe_2$ films in SCF and achieved the direct conversion of Cu−In precursor films to $CuInSe_2$ films at quite low temperature of 300 °C using the less hazardous metal−organic selenium source, Et_2Se.

EXPERIMENTAL METHOD

Cu−In precursor films were deposited on low-alkali glass substrates using a spin−coating method.[3] The spin coating solutions for In_2O_3 and CuO films (Kojundo Chemical Laboratory) were mixed together and spin coated at 1000 rpm for 5 s and then at 3000 rpm for 10s on substrates. After 5 min of drying in vacuum, the film was oxidized at 520 °C in a furnace under air condition to remove carbon contents; then, the film was deoxidized in a N_2 + 10% H_2 environment at 450 °C. This procedure was repeated 10 times to obtain approximately 2-μm-thick films. The composition of the Cu−In precursor film, analyzed by energy-dispersive X-ray spectroscopy (EDX), was C/O/Cu/In = 0/20/40/40, indicating that all carbon components were successfully removed although some metal oxides still remained.

In this study, we employed supercritical ethanol as the reaction medium. Among SCFs, nonassociating fluids (such as carbon dioxide, fluoroform, and ethane) have moderate critical temperatures, but they display limited solubility for compounds of no or little volatility without the addition of a cosolvent. On the

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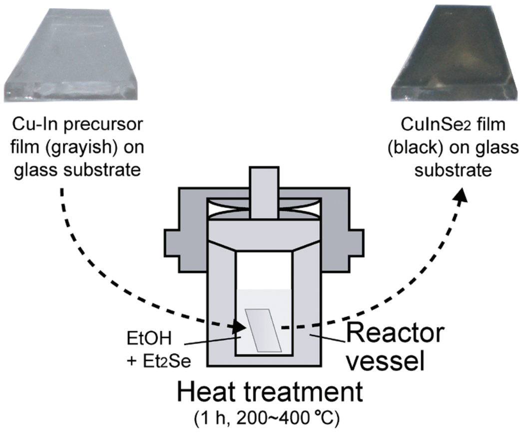

Figure 1. Scheme illustrating the experimental procedure (top-left picture, Cu−In precursor film; top-right picture, $CuInSe_2$ film).

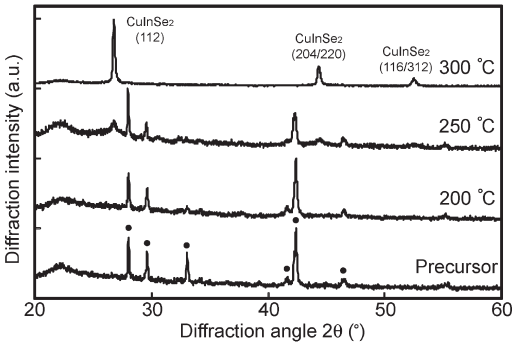

Figure 2. XRD patterns of the Cu−In precursor film and the $CuInSe_2$ films as a function of treated temperature in supercritical ethanol with fluid density of 0.55 g/cm^3 (●, precursor).

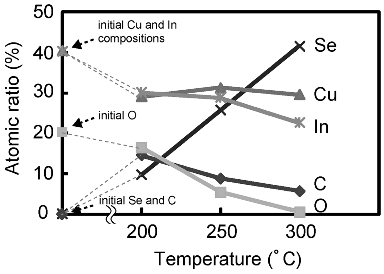

Figure 3. Composition of the $CuInSe_2$ films as a function of treated temperature from 200 to 300 °C in supercritical ethanol with fluid density of 0.55 g/cm^3.

other hand, in spite of high solubility, supercritical water eliminates most chemical syntheses other than oxidation reaction owing to the decomposition of water at high temperatures. In comparison, ethanol [$T_c = 241$ °C, $Pc = 6.14$ MPa, $\rho_c = 0.276$ g/cm^3 (6.0 mol/L)] is less corrosive than supercritical water and more reactive than supercritical CO_2.

All selenization processes were carried out in a 10 mL batch-type reactor. In a typical experiment, Cu−In films were treated in the reactor vessel containing Et_2Se and ethanol (see Figure 1). In the liquid phase under ambient condition, Et_2Se forms a homogeneous phase with ethanol, and it is highly probable that Et_2Se, which has a boiling temperature of 108 °C at ambient pressure, and ethanol also form a homogeneous mixed state under supercritical conditions. The concentration of Et_2Se in the reactor was 50 mmol/L. After the sealed reactor vessel reached the selected temperature (which took 10 min) in a specially designed tube furnace, the reaction proceeded for 60 min. The reaction was terminated by submerging the hot reactor in a water bath. The treated films were repeatedly washed with ethanol and dried at 70 °C. The crystalline structures of the films were analyzed by $\theta-2\theta$ X-ray diffraction (XRD) using Cu−Kα radiation. The chemical compositions of the films were determined by EDX with scanning electron microscopy (SEM).

■ RESULTS AND DISCUSSION

The XRD patterns of the film as a function of temperature from 200 to 300 °C are shown in Figure 2. The ethanol fluid density is constant at 0.55 g/cm^3 ($2\rho_c$). In the XRD pattern of the Cu−In precursor film, the diffraction peaks from Cu, In, Cu−In alloy, and its oxide are present. There are no change in the XRD patterns when the precursor films are immersed in ethanol containing Et_2Se (70 mmol/L) at room temperature.

The pattern for the film after thermal treatment at 200 °C, which is below the critical temperature of ethanol, shows only the diffraction peaks derived from the Cu−In precursor. At 250 °C, the diffraction peaks corresponding to the chalcopyrite structure of $CuInSe_2$ emerge. Moreover, at a temperature greater than 300 °C, the Cu−In precursor peaks disappear and only the peaks corresponding to $CuInSe_2$, i.e., (112), (204)/(220), and (116)/(312) at 26.6, 44.2/44.3, and 52.2/52.4°, respectively, are observed.

The results of the EDX analysis of the treated films as a function of temperature are shown in Figure 3; it can be clearly seen that the selenium component in the films increases as the temperature increases up to 300 °C. This result indicates that the conversion reaction from the Cu−In precursor to $CuInSe_2$ progresses as the temperature increases. Moreover, the carbon component which is supposed to be derived from the ethyl group in Et_2Se decreases as the conversion reaction progresses. These temperature trends are consistent with the results of the XRD analysis. Therefore, it is confirmed that by using supercritical ethanol, selenization of the Cu−In precursor at 300 °C occurs, although in previous reported studies,[3] a higher temperature, greater than 490 °C, was required for the selenization using Et_2Se. Although in this study we employed a high-temperature step above 500 °C for preparation of the precursor films, application of well-established low-temperature deposition processes of metal precursor films, such as ink deposition[13] and electrodepositon,[14] should enable us to keep all the CIS fabrication process below 300 °C.

Interestingly, we also observed a decrease in the percentage of the oxygen component, which is contained in the precursor films, as the temperature increased to 300 °C. As the solubility of metal oxide is generally less than that of metal, the dissolution of the metal oxide in precursor film should not reduce the percentage of the oxygen component. Therefore, we infer that the deoxidation reaction progressed simultaneously with the selenization reaction. It is known that alcohol contained in supercritical carbon dioxide assists the reduction of metalorganic compounds in chemical fluid deposition.[15] Moreover, recently, the formation of metallic nanoparticles by reduction of metal nitrate has been reported in supercritical ethanol.[16] From these reported studies, we assume that the additional reducing power of supercritical ethanol removes the oxygen component.

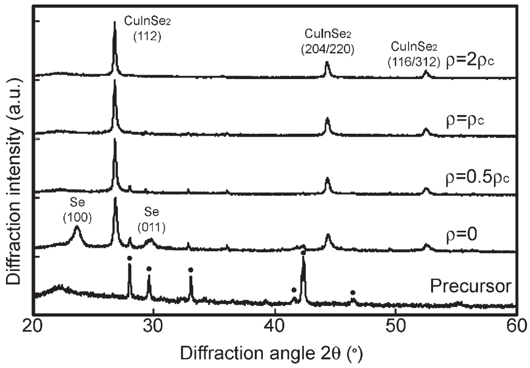

Figure 4. XRD patterns of precursor and treated films as a function of fluid density of supercritical ethanol from 0 to 0.55 g/cm^3 (from 0 to $2\rho_c$) at temperature of 300 °C (●, precursor).

To verify the individual contributions of supercritical ethanol and the thermal decomposition of Et_2Se in the selenization reaction at 300 °C, we varied the fluid density of ethanol (ρ) from 0 to 0.55 g/cm^3 ($2\rho_c$). Figure 4 shows the XRD patterns of the treated films as a function of ethanol density. Without ethanol, in addition to the diffraction patterns from the Cu−In precursor and chalcopyrite structure of $CuInSe_2$, peaks at 22.5−24 and 28.5−30° with broad widths from structureless/amorphous materials appear. The (100) and (011) peaks of Se at 23.4 and 29.6°, respectively, are close to the observed peaks. The SEM images showed that the substrate surface was covered by a smooth film, and the EDX analysis revealed that the dominant material was selenium (∼80%). From these results, we conclude that besides the selenization reaction, an amorphous-like phase of selenium forms without ethanol. Et_2Se thermally decomposes to selenium at 300 °C and some selenium is deposited on the surface without being converting to $CuInSe_2$.

In the presence of ethanol, the XRD patterns do not show any undesired amorphous-like selenium features. Moreover, as the ethanol density increases, the peaks derived from the unselenized Cu−In precursor, which are presented in the XRD patterns at $0.5\rho_c$, diminish. This means that supercritical ethanol plays an essential role in the selenization process. Although Et_2Se is thermally decomposed to selenium at high temperatures without ethanol, supercritical ethanol prevents the deposition of an amorphous selenium layer.

One possible role of ethanol is just as solvent and the ethanol may solve the excess selenium species. However, the concentrations of Et_2Se in the reactor are identical and if the reaction, which Et_2Se reacts directly with the precursor films, is dominant, the selenization should progress identically even at various ethanol densities. Therefore, to explain the progress of selenization at higer ethanol density, we should consider another mechanism.

We infer that the reaction species in the presence of ethanol are different from those formed without ethanol. In SCFs, solvolysis reactions such as hydrolysis and alcoholysis are enhanced.[17,18] Therefore, the ethanolysis reaction may occur in supercritical ethanol, and the intermediate products C_2H_5SeH and H_2Se are stabilized, in contrast to the high-temperature condition without ethanol, enabling the selenization reaction to progress without the deposition of excess selenium.

It is noteworthy that there is no deposition of the $CuInSe_2$ film on the wall of the reactor vessel; therefore, we can assume that surface reaction progressed in supercritical ethanol as follows: The intermidiate selenium species only presented under supercritical condition are supplied to the precursor films. The metallic Cu and In on the film surface react with the selenium species to form $CuInSe_2$. Se atoms diffused from the surface into the film as the conventional selenization reaction, and the Cu−In metallic precursor film is gradually converted to the $CuInSe_2$ compound semiconductor film over time.

CONCLUSION

In this study, Cu−In metallic films were directly converted to $CuInSe_2$ compound semiconductor films via the selenization reaction in supercritical ethanol using the less hazardous metal−organic selenium source Et_2Se at 300 °C. The supercritical ethanol favorably assisted the selenization without the deposition of excess selenium. Such SCF-assisted direct conversion reactions developed in this study can facilitate the large-scale, low-temperature, and rapid synthesis of $CuInSe_2$ films, which allow for the low-cost production of solar cells, and contribute to the development of low-cost fabrication of other compound semiconductor (e.g., CdS, GaAs, and InN) devices in the future.

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