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Original article

CIGS 태양전지용 Cd-Free 버퍼층 제조

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Preparation of Cadmium-free Buffer Layers for CIGS Solar Cells

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초 록

CIGS 태양 전지용 cadmium (Cd)-free $In(OH)_xS_y$ 버퍼층을 화학적 용액성장법을 이용해서 형성시켰고 최적 반응시간을 파악하였다. 투과율 측정과 함께 이온집적빔 시스템으로 직접 박막을 관찰해서 박막성장 조건을 최적화 하였으며 X선 회절분석법과 X선 광전자 분광법, 주사현미경을 이용해서 박막의 특성을 파악하였다. 그 결과 $In(OH)_xS_y$ 버퍼층의 증착을 위한 최적 반응 시간은 온도 섭씨 70°의 조건에서 20 min임을 확인하였으며, 이때의 버퍼층의 두께는 57 nm 가량이었고 밴드갭 에너지는 2.7 eV를 나타내었다. 아울러 molybdenum (Mo)층과 CIGS층 위에서 $In(OH)_xS_y$ 버퍼층을 형성시키는 경우에 XPS 피크의 차이는 볼 수 없었다.

Abstract

Indium hydroxy sulfide ($In(OH)_xS_y$) as a cadmium (Cd)-free buffer layer for $CuInGaSe_2$ (CIGS) solar cells was prepared by the chemical bath deposition (CBD) and the reaction time was optimized. The band gap energy and transmittance data alongside the thickness results from the direct observation with focused ion beam system (FIB) could be a powerful tool for optimizing the conditions. In addition, X-ray diffractometer (XRD), X-ray photoelectron microscopy (XPS), and scanning electron microscope (SEM) were also employed for the layer characterization. The results indicated that the optimum reaction time for $In(OH)_xS_y$ buffer layer deposition by CBD was 20 min at 70 ℃ under the conditions employed. At the optimum conditions, the buffer layer thickness was near 57 nm and the band gap energy was 2.7 eV. In addition, it was found that there was no XPS peak shift in between the buffer layers deposited on molybdenum (Mo)/glass and that on CIGS layer.

***Keywords**: chemical bath deposition, Cd-free buffer layer, CIGS solar cells, $In(OH)_xS_y$, layer thickness*

1. Introduction

In a typical CIGS-based solar cell, a buffer layer is usually deposited between the window layer and the CIGS absorber layer in order to achieve high conversion efficiency[1]. However, although cadmium sulfide (CdS) is a stable compound and commonly used, it is desirable to replace it with a Cd-free material due to commercial and environmental reasons. Accordingly, many studies have been performed for an alternative buffer layer material which is less toxic than Cd. Moreover, it is desirable when the new material provides a wider band gap energy (> 2.4 eV) than CdS to achieve higher spectral response in the blue region. Up to now, the reported alternative buffer materials include ZnO[2], $In(OH)_xS_y$[3,4], In_2S_3[5,6], ZnS[7], and MnS. In particular, cadmium free buffer such as $In(OH)_xS_y$ (Eg ≈ 2.54 eV [8]) thin films can be promising candidate for the buffer layers for CIGS cells. Moreover, it has been shown that the interface window/buffer has a critical influence on the performance of CIGS solar cells when using indium hydroxy sulphide ($In(OH)_xS_y$) as a buffer material[9]. In this work, we obtained Cd-free indium (In)-based buffer layers for the CIGS solar cells for achieving high active area conversion efficiencies and investigated the optical and electrical properties of the layers on glass substrates. The buffer layer was coated onto molybdenum (Mo) and CIGS/Mo layer on soda-lime glass substrates by CBD and the layers were characterized by SEM, FIB, XPS, XRD, and UV-Vis.

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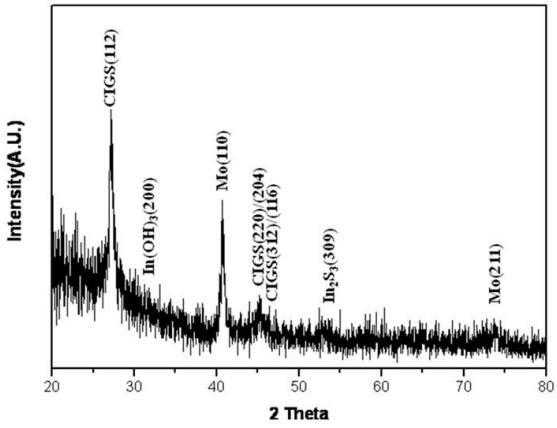

Figure 1. XRD patterns of glass/Mo/CIGS/In(OH)$_x$S$_y$.

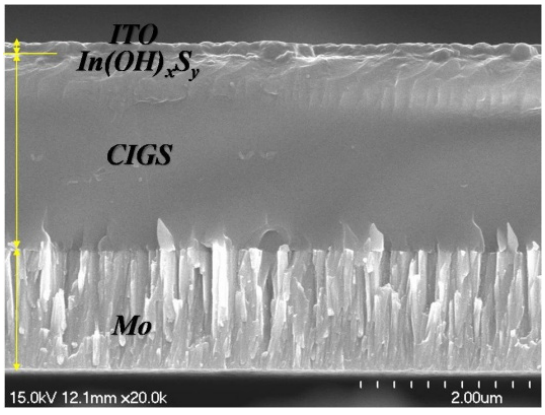

Figure 2. Cross-sectional SEM micrograph of glass/Mo/CIGS/In-based buffer/ITO layers.

2. Experimental

2.1. Preparation of Mo back contact layer

Before the deposition, the substrate was ultrasonically cleaned with deionized water (D.I. Water) for 15 min and with isopropyl alcohol (IPA) for 15 min and then dried with N_2 gas. The deposition chamber was evacuated to pressure of 2.2×10^{-6} Torr. The Mo thin film was prepared with 1 mTorr of working pressure and with 0.08 A of input current. The substrate was located 90 mm away from the common axis of the targets and at a distance of 50 mm (target to target).

2.2. Preparation of CIGS electrode layer

The deposition chamber was evacuated to a pressure of 2.4×10^{-6} Torr. The CIGS thin film was prepared with 10 mTorr working pressure and with 0.08 A of input current. The substrate was located 90 mm away from the common axis of the targets and at a distance of 70 mm (target to substrate).

2.3. CBD for In(OH)$_x$S$_y$ buffer Layers

In-based buffer layers were grown by the CBD technique. The CBD process involved the reaction of indium chloride ($InCl_3$) with thioacetamide (CH_3CSNH_2) in an acidic aqueous solution under thermostatic conditions. The In(OH)$_x$S$_y$ layers were prepared as follows: aqueous solutions of indium chloride ($InCl_3$; 0.025 M) and thioacetamide (CH_3CSNH_2; 0.1 to 0.3 M) were mixed with a magnetic bar and the pH value of the solution was adjusted to 1.8 to 2.2 by acetic acid. Acetic acid as a complexing agent was added into the bath during the deposition of In(OH)$_x$S$_y$ to improve the film quality. By addition of the complexing agent, more adherent, reproducible, and homogeneous films of In(OH)$_x$S$_y$ could be obtained. The bath temperature was 70 ℃ and the reaction time did not exceed 30 min. Buffer layer films deposited onto Mo/Soda-lime glass or GIGS/Mo/Soda-lime glass substrates were dipped into the solution and the In-based buffer layers were fabricated.

2.4. Characterization

The structures of the layers were observed by SEM (Hitachi S-4700). The thickness of the buffer layers were measured by direct observation from the images of FIB (FEI, Nova 200 STEM). The optical property was measured by UV-VIS spectrophotometer (Agilent 8453 Diode Array Spectrophotometer) and the layer structure was analyzed by XRD (D/MAX-2000/PC). XPS (K-Alpha/Thermo Electron)) was employed for measuring the elemental composition.

3. Results and Discussion

3.1. XRD measurements

The XRD patterns of the Mo and In-based film deposited on soda-lime glass substrates are shown in Figure 1. The XRD patterns demonstrate that the films on soda-lime glass substrates exhibited good polycrystalline structures. The diffraction pattern of the film exhibits two peaks. The Mo film peak at 40.4, 73.6° correspond to (110) and (211) of Mo, respectively (JCPDS# 65-7442). The CIGS peak at 26.9° correspond to (112) of CIGS (JCPDS# 35-1102). The In based film peaks at 31.6° correspond to (200) of In $(OH)_3$ (JCPDS# 16-0161) and the peak at 43.5°correspond to (309) of Indium Sulfide (JCPDS# 51-1160). The result indicated that the In-based films deposited on soda-lime glass substrates exhibited polycrystalline structure and contained $In(OH)_3$ and In_2S_3 phases. However, since the $In(OH)_3$ and In_2S_3 peaks were not clear enough, XPS measurements were also performed for confirming the existence of $In(OH)_3$ and In_2S_3 in the buffer layers and the results were discussed in the elemental compositional analysis section.

3.2. Surface morphology and film thickness

Cross-sectional SEM micrograph of glass/Mo/In-based buffer/ITO layers is shown in Figure 2. The image showed that the thicknesses of Mo, CIGS, In(OH)$_x$S$_y$ and the ITO were near 1, 2, 0.05, and 0.2 μm respectively. Thickness of the buffer layer seemed to be increased with reaction time although the image did not provide accurate thickness value. However, thickness of the buffer layer is an important parameter for buffer layer deposition since the transmittance and the band gap energy are strong function of the thickness. Accordingly, the buffer layer thickness was measured by observing the FIB image. As

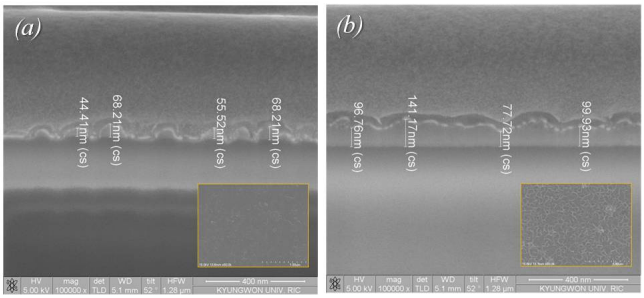

Figure 3. FIB photographs of In-based buffer layers on glass substrate at different reaction time: (a) 20 min; (b) 30 min.

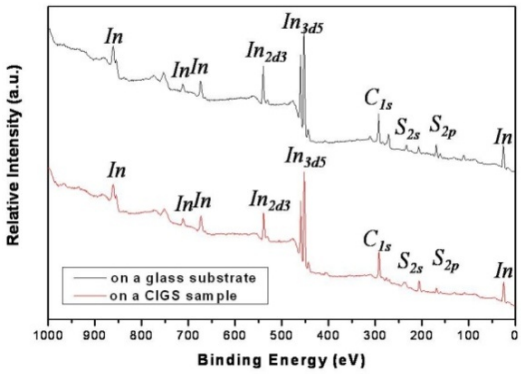

Figure 4. XPS patterns of Mo/CIGS/In-based film on soda-lime glass.

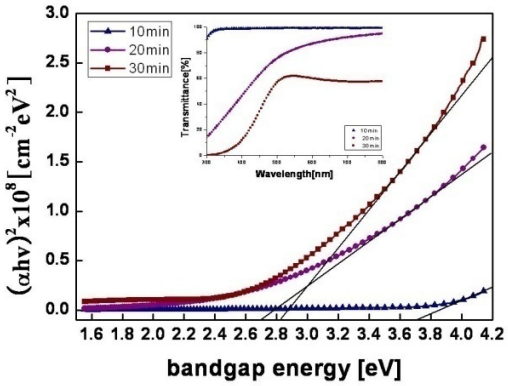

Figure 5. Optical transmittance and $(\alpha h\nu)^2$ vs $h\nu$ plot for the $In(OH)_xS_y$ thin films deposited with varying reaction time on the glass substrate by CBD process.

shown in Figure 3, average thicknesses of the buffer layers were about 57 nm and 95 nm corresponding to the reaction time of 20 min and 30 min, respectively. At 10 min of reaction, the thickness was near 17 nm (the image was not presented). In general, the buffer layer thickness should be more than 50 nm and not exceed 100 nm. Indeed, when we utilize FIB for direct observation of buffer layer with a few nm resolution, it could be a time saving tool for optimizing the conditions of buffer layer formation.

3.3. Elemental compositional analysis

The surface composition of $In(OH)_xS_y$ layer deposited on glass and GIGS were characterized by XPS, and the resulting binding energy spectra are shown in Figure 4. Indium, oxygen, sulfur, and carbon were detected in the $In(OH)_xS_y$ layer. Accordingly, the results indicated that the In-based buffer layer was successfully formed on Mo/glass and CIGS/Mo/glass surfaces. Moreover, since there is no binding energy peak shift between the layer deposited on a Mo/glass and that on CIGS samples, it can be inferred that the CBD process for buffer layers in CIGS solar cells could be optimized on Mo/glass substrate before applying the new buffer material on CIGS surface.

3.4. Optical properties

The transmittance for the $In(OH)_xS_y$ films grown on soda-lime glass substrates was measured using a UV-Vis spectrophotometer, and the results are shown in Figure 5. The $In(OH)_xS_y$ films with shorter deposition time have higher transmittance at shorter wavelength. The buffer layers grown with longer deposition time, however, could provide a better shield effect against sputtering damage during the window layer deposition step and thereby reduce the interface recombination[3]. Thus, the buffer layer thickness needs to be optimized for solar cell performance. The band-gap energy of $In(OH)_xS_y$ was determined from the direct transition, $(\alpha h\nu)^2$ was plotted against $h\nu$ for the $In(OH)_xS_y$ films as illustrated in Figure 5. In order to determine absorption coefficients and band gap energy values, transmittance measurements were performed using the following equation[10].

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

Where α is the absorption coefficient, A is a constant and Eg is the energy gap. From the straight line of $(\alpha h\nu)^2$ vs $h\nu$ with a photon-energy axis intercept, the band gap energy can be evaluated. The band gap energy of $In(OH)_xS_y$ were 2.7 eV and 2.9 eV for the reaction time of 20 min and 30 min, respectively. In reality, E_g depends on the films stoichiometry and should lie between the energy for CIGS absorber (1.1 eV) and those for window layers (3.2 to 3.6 eV)[11]. When the CBD was terminated after 10 min of reaction, the transmittance was very high but the band gap energy was not acceptable as buffer layer for CIGS solar cells. On the other hand, at 30 min of reaction, the transmittance of the film was too low to be a buffer layer (less than 60%). In summary, the band gap energy and transmittance data along with the thickness results indicated that the optimum reaction time for $In(OH)_xS_y$ buffer layer deposition by CBD was 20 min under the conditions employed (indium chloride ($InCl_3$; 0.025 M)-thioacetamide ($CH_3CS\ NH_2$; 0.1 to 0.3 M), 70℃ and pH 1.8-2.2).

4. Conclusion

The In-based Cd-free buffer layers for CIGS solar cells were prepared by CBD and the reaction time was optimized by employing various experimental techniques. In particular, the direct observation by FIB could be a powerful tool for optimizing the conditions. In fact, the optimum conditions provided buffer layer with thickness of near 57 nm and the band gap energy of 2.7 eV.

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