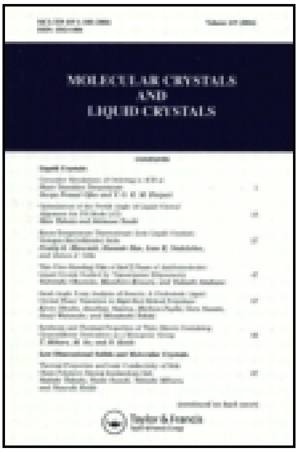

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Currently, substrate thin film solar cells with Cu(In,Ga)Se2(CIS) absorbers yield conversion efficiencies of up 20.4%, the highest published efficiency of CIS superstrate thin film solar cells is 12.8%. It is the maximum efficiency when composition is as follow; Cu, In and Se was 1, 1 and 2.

The maximum efficiency of CIS superstrate thin film solar cell is smaller than that of CIS substrate thin film solar cell, but manufacturing cost of CIS superstrate is lower than that of CIS substrate since the reduce of the manufacturing process. In addition, CIS absorber layer is fabricated through binary phases to reduce the process temperature and processing price.

In this study, CIS superstrate thin film solar cell was fabricated to reduce the device manufacturing cost and CIS absorber layer was deposited by the binary phases. By using substrate (Sodalime Glass,SLG), window layer(i-ZnO, Al:ZnO)were deposited on n-type transparent electrode layer in the upper part. CIS absorber was respectively deposited by In_2Se_3 and CuSe in a binary phases by using MBE(Molecular Beam Epitaxy). The deposited sample went through heat process, and then electrode was created to fabricate the device. In order to identify the structural and electrical characteristics depending on CuSe deposition time, CIS absorber and CIS solar cell device, analysis was conducted by using XRD (X-ray Diffractometer, Bulk, PANalytical), FE-SEM (Field Emission Scanning Electron Microscope, S-4800, HITACHI), ICP(Inductively Coupled Plasma, ICPS-8100, Shimadzu),SIMS (Secondary Ion Mass Spectrometry, IMS 6F, CAMECA) and solar-simulator(AM1.5g, 100 mW/cm_2).

Keywords Cu(In; Ga)Se_2; superstrate; thin film solar cell; binary; co-evaporation

Introduction

From the field test where the CIGS module was long-term exposed to solar light with high thermal energy, its efficiency was found to be maintained, which proves its good thermal stability and moisture tolerance [1].

The commonly CIGS thin film solar cell is the substrate type and it is generally composed of substrate (sodalime glass,SLG)/back contact(Mo)/absorption layer(CIS)/

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buffer layer(CdS)/window layer(i-ZnO, Al:ZnO)/antireflection film(MgF_2)/grid electrode(Al,Ni) [2,3]. In case of CIS substrate thin film solar cell, irradiation through SLG substrate is not available but it is entered through the transparent electrode in the upper part, which requires a window layer with high transmittance transparent electrode. On the contrary, irradiation can be entered through SLG substrate in case of CIS Superstrate thin film solar cell, because CIS Superstrate thin film solar cell is composed of substerate(Sodalime Glass,SLG)/window layer(Al:ZnO, i-ZnO)/absorber layer(CIS)/electrode(Ag) [4–6].

Recently, it has been reported that photovoltaic conversion efficiency of CIS thin film solar cell has reached 20.4% from the substrate type and 12.8% from the superstrate type, showing that the efficiency is comparatively lower than that of substrate-type solar cells. However, the device fabrication cost can be reduced because the number of processes to go through is fewer [7–9].

In addition to the cost reduction caused by the diminish of processes, it is also possible to minimize multi-layered thin film process, which has been the obstacle to the industrialization of CIS thin film solar cell. If this happens, then it can be applied to mass production of CIS thin film solar cell. However, an issue still remains even after the number of processes to fabricate Superstrate CIS thin film solar cell is diminished. It is that the process time and difficulty of process in the production of CIS absorber layer.

CIS absorber layer can be fabricated through binary phases, 3-stage process and 1-stage process with thermal co-evaporator. It can also be fabricated through 2-step process which is sputtering Cu,In,Ga to make a precursor and proceeding with Se heat treatment [10–13].

From the point of efficiency, 3-stage process which uses thermal co-evaporator is the most desirable method, but it takes a long time to process and the cost of processing is high since it requires high consumption of materials and high processing temperature. In this regard, it is less likely that 3-stage process can be used for mass production.

From the point of efficiency, 3-stage process which uses thermal evaporator is the most desirable method, but it takes a long time to process and the cost of processing is high since it requires high consumption of materials and high processing temperature. In this regard, it is less likely that 3-stage process can be used for mass production. If both photovoltaic conversion efficiency and mass production are considered, binary process with thermal co-evaporation is the most proper method to use. Instead of depositing quaternary CIS, simple compounds of binary selenide such as CuSe and In_2Se_3 are deposited and then Se heat treatment is done in order to fabricate CIS absorber layer. In this way, it can not only reduce the processing time but also lower the processing temperature to under 400°C. In this regard, this research employs CIS binary phases to fabricate CIS superstrate thin film solar cell. SLG is deposited with both Al:ZnO(AZO) as transparent electrode and CIS, the absorber layer, is deposited with In_2Se_3 and CuSe as binary type by using thermal co-evaporator device. The deposition time of CuSe was controlled for the thickness of CuSe to change it.

Then, heat process is done under Se environment to induce the reaction of CuSe + $In_2Se_3 = CuInSe_2$ [13].

After CIS thin layer process is finished, electrode is created by using Ag paste. In order to identify the structural and electrical characteristics of various transparent electrodes, CIS absorber layer and CIS solar cell device, XRD, FE-SEM, ICP, SIMS and solar-simulator were used in this study.

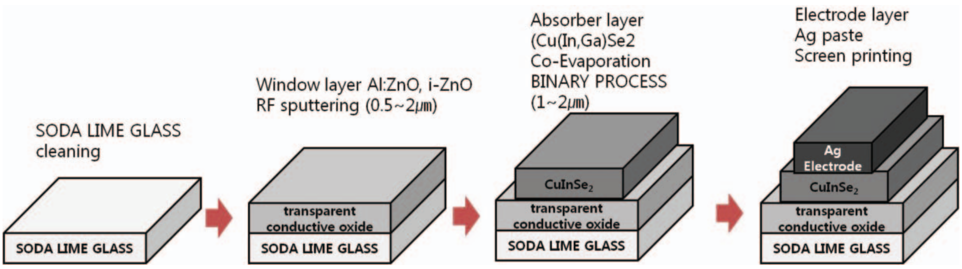

Figure 1. The fabrication processes of CIS superstrate solar cell.

Experimental

The fabrication process and the structure of CIS Superstrate thin film solar cell is explained in Figure 1. AZO (∼800 nm,∼30 nm) is deposited on after sodalime Glass (SLG) cleaning and window layer and then CIS(In_2Se_3 + CuSe + Se treatment) absorber layer (∼1.5 um) and Ag Electrode layer(∼5 um) were proceeded in order. The size of the substrate that is used is 25 cm^2 and the substrate thickness is 1.2mm.

Particularly, thermal co-evaporator (YAS, substrate size: 100 mm × 100 mm) is used to fabricate CIS absorber layer since binary phases is applied in this study.

The materials used in the fabrication of absorber layer are Cu, In and Se which is granular type with 99.999% of purity from Cerac. A halogen heater which can heat up to 800°C is used to heat the plate and effusion cell is used to heat the source.

The binary phases used explained in Figure 2. In this study, 3 step process is used as follow; In/Se deposition, Cu/Se deposition and Se heat treatment. The substrate temperatures of each step process are 400°C, 150°C, and 400°C respectively. The processing time

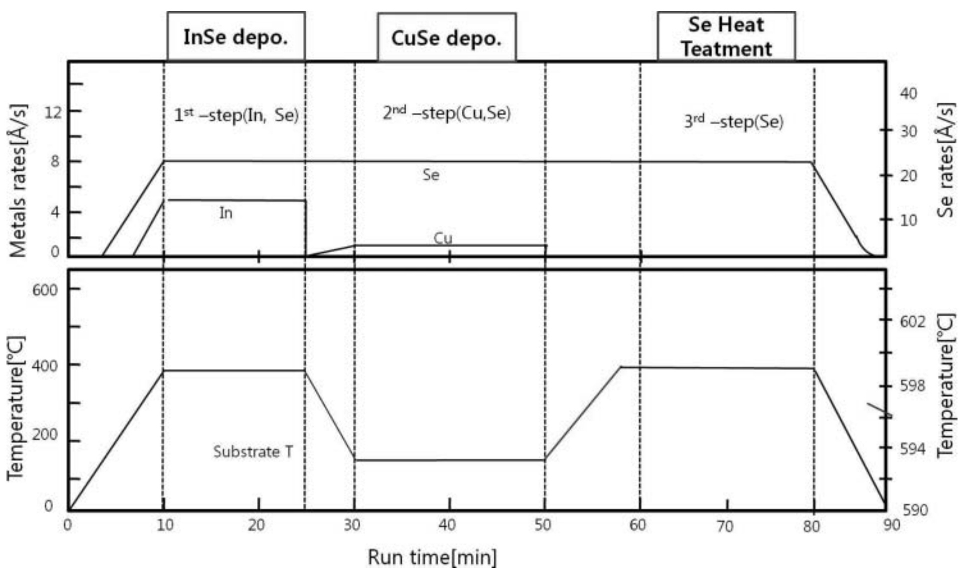

Figure 2. The variation of elemental fluxes and the substrate temperature during the binary CIS deposition process.

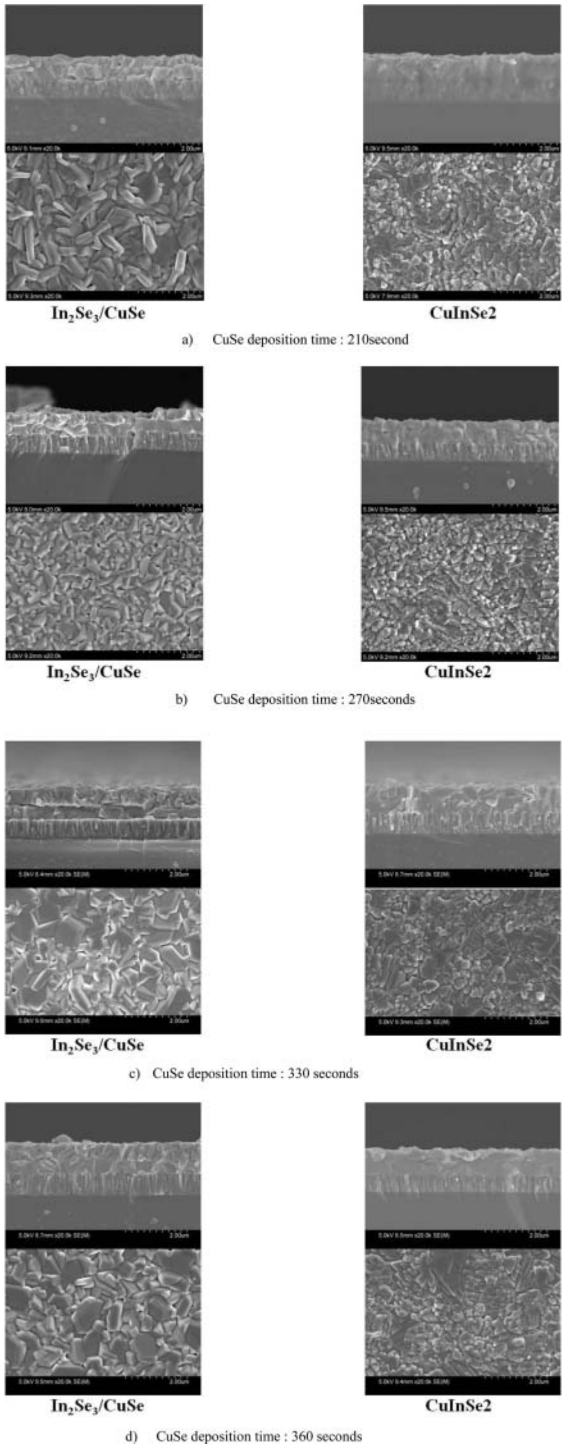

Figure 3. The XRD patterns of the CIS binary samples.

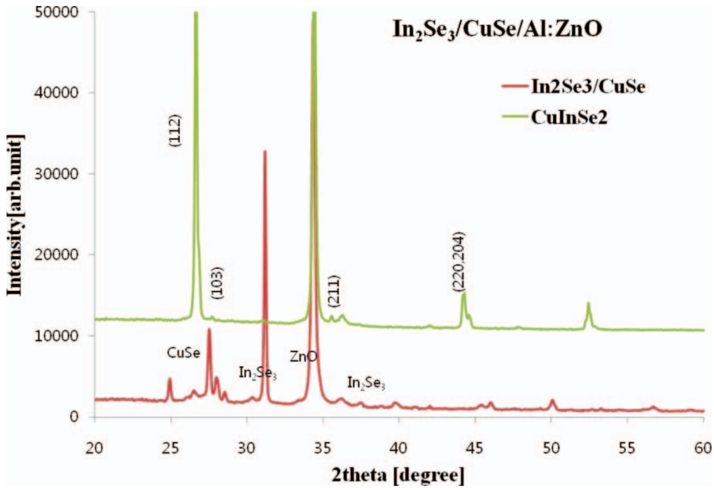

Figure 4. The XRD patterns of the Cu deposition times.

for Cu/Se deposition times is 210, 270, 330, 360 seconds and Se heat treatment times is 60 seconds.

In this way, a sample was fabricated and then Ag electrode was formed through screen printing method.

Measurements

The characteristics of absorber layer and device was analyzed by using devices such as XRD (X-ray Diffractometer, PANalytical), FE-SEM (Field Emission Scanning Electron Microscope, S-4800, HITACHI), ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy, ICPS-8100, Shimatzu) and solar-simulator (AM1.5G, 100 mW/cm_2).

Results and Discussion

The binary structures which are fabricated by sputtering are identified in binary phases. The SEM pictures explained in Figure 3. As can be seen from the SEM results, these structures are confirmed to converse the formation of a single layer after heat treatment. This layer is expected to $CuInSe_2$, but the exact composition could not be analyzed.

In order to know the exact composition, XRD analysis is subjected. This result showed in Figure 4. After annealing in Se atmosphere, the step-by-step analysis of binary phases and the crystallization of CIS were analyzed in order to confirm $CuInSe_2$.

Since the substrate temperature was remained at 400°C during In and Se deposition processing, it has the characteristics of In_2Se_3 material. And since the substrate temperature was remained at 150°C during Cu and Se deposition processing, it has the characteristics of CuSe material.

In this regard, the phase can be identified with XRD. Since the substrate temperature was remained at 400°C during heat treatment processing, it has the characteristics of CIS material.

The result of analysis on XRD is explained in Figure 5, and it was analyzed for each process according to CuSe deposition time.

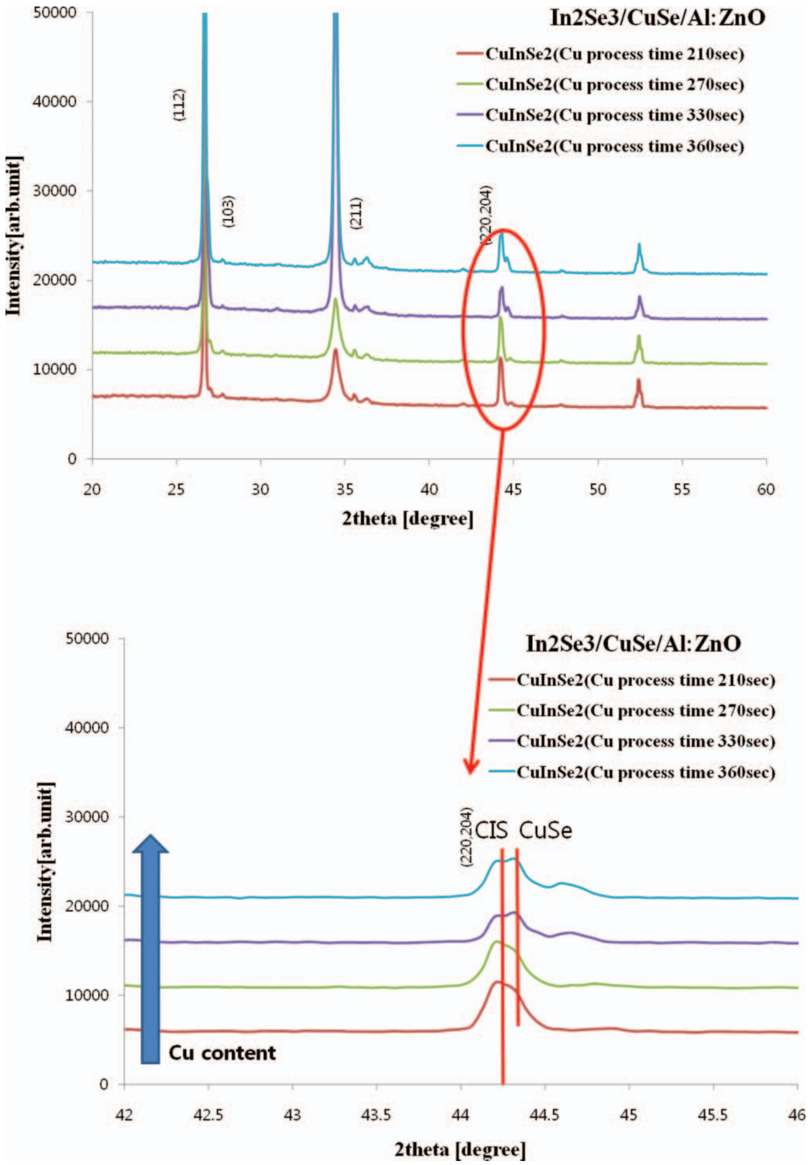

Figure 5. Cross-sectional and plan-view SEM images depending on Cu deposition times.

As CuSe deposition time increases, the peak of CuSe phases appeared next to the peak of CIS (220,224) phases.

However, because fabricated CIS exited various binary phases, exact composition analysis is difficult. In order to analyze it accurately, we used ICP analysis. ICP analysis result of CuSe deposition time is shown in Table 1. The CuSe deposition time increases, the composition of Cu increased. When CuSe deposition time is 210 seconds, the composition of Cu, In and Se was 0.20, 0.20 and 0.6 respectively. After Se heating treatment, the composition of Cu, In and Se was 0.23, 0.23 and 0.54 respectively. When CuSe deposition time is 270 seconds, the composition of Cu, In and Se was 0.20, 0.20 and 0.6. After Se

Table 1. ICP measurement resultsd of CuSe deposition time

CuSe Deposition time[sec]	Binary phases	Mol Fraction Cu	Mol Fraction In	Mol Fraction Se	Composition ratio Cu/In	Composition ratio Cu/Se
210	In_2Se_3/CuSe	0.2	0.2	0.6	1.01	0.33
270	In_2Se_3/CuSe	0.2	0.2	0.6	0.98	0.33
330	In_2Se_3/CuSe	0.25	0.17	0.58	1.43	0.43
360	In_2Se_3/CuSe	0.26	0.16	0.58	1.65	0.45
210	$CuInSe_2$	0.23	0.23	0.54	0.98	0.42
270	$CuInSe_2$	0.24	0.22	0.54	1.10	0.45
330	$CuInSe_2$	0.3	0.19	0.51	1.52	0.58
360	$CuInSe_2$	0.3	0.2	0.5	1.54	0.59

heating treatment is the composition of Cu, In and Se was 0.24, 0.22 and 0.54 respectively. When CuSe deposition time is 330 seconds and 360 seconds, the composition of Cu, In and Se was 0.25, 0.17, 0.58 and 0.26, 0.16, 0.58 respectively. After Se heating treatment is the composition of Cu, In and Se was 0.3, 0.19, 0.55 and 0.3, 0.2, 0.55 respectively.

As CuSe deposition time increasing, while the ratio of Cu is increased, the ratio of In was conversely decreased.

Items	Result	Unit	Remark
V_{oc}	0.081171	V	
I_{sc}	1.552923	mA	
J_{sc}	1.5529	mA/cm2	
Fill Factor	26.066	%	
I_{max}	0.657	mA	
V_{max}	0.05	V	
P_{max}	0.033	mW	
Efficiency	0.033	%	

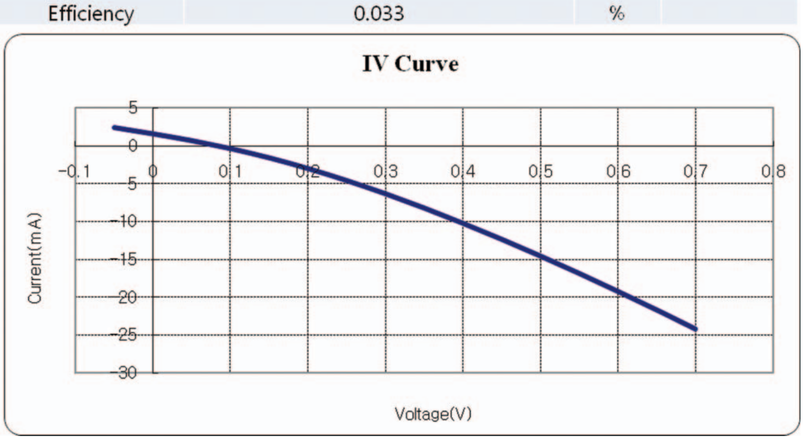

Figure 6. Current–voltage characteristics of CIS Superstrate solar cells measured under AM1.5 standard test condition.

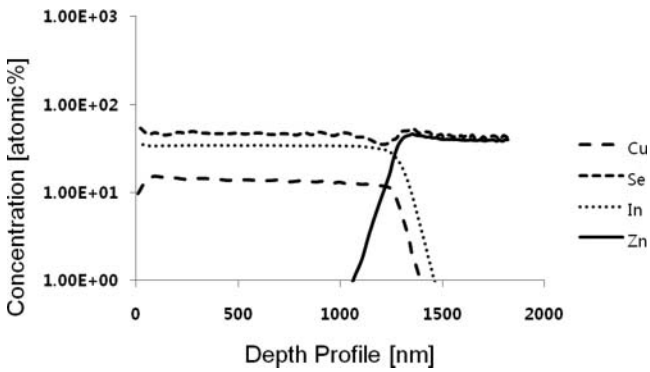

Figure 7. The SIMS measurement results.

Depending on deposition time increased, the ratio of Cu and the ratio of In are increased after Se heating treatment, the proportion of Se are relatively decreased. Because CIS exited in a state of $CuInSe_2$, Se surplus is expected to decrease.

Current-voltage curve showed in Figure 6. The current-voltage curve evaluated the solar cell device which Cu/Se deposition time is 210 second, because this fabrication condition was optimized composition. However, this curve was shown in poor characteristic owing to creation of leaky device with low shunt resistance.

The SIMS profile of CIS with AZO transparent electrode was shown in Figure 7. The result showed that a lot of Se diffused into the using Al:ZnO transparent electrode after 400°C heating process.

Conclusions

In this study, CIS thin film with transparent electrode was deposited to Al:ZnO to fabricate the device in the order of In,Se and Cu,Se and Se heat treatment by using binary phases.

Since the substrate temperature was remained at 400°C during In and Se deposition processing, it has the characteristics of In_2Se_3 material. And since the substrate temperature was remained at 150°C during Cu and Se deposition processing, it has the characteristics of CuSe material.

Since the substrate temperature was remained at 400°C during heat treatment processing, it has the characteristics of CIS material.

Accordingly, the optimal composition showed that the Cu, Se deposition time is 210 seconds. The Cu, Se deposition time was increased, the compositions of Cu was increased. The CuSe deposition time was increased, the surplus CuSe could find in XRD phase. This phenomenon was explained that the ratio of Se was decreased after Se heating treatment.

The result of observation of the diffusion of heat treatment process under CIS binary process to window layer shows that a lot of Se diffuse in Al:ZnO transparent electrode even under 400°C of heat process. Accordingly, it is confirmed that the heat treatment appropriate for transparent electrode is needed and the CIS composition in CIS binary process is important.

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