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Overview of CZTS-Based Thin Film Solar Cells

Hironori Katagiri[1,2], Tsukasa Washio[1,2] and Kazuo Jimbo[1]

[1] Nagaoka National College of Tech.
888 Nishikatakai, Nagaoka, 940-8532, Japan
Phone: +81-258-34-9240 E-mail: hiro@nagaoka-ct.ac.jp
[2] Japan Science and Technology Agency, CREST
888 Nishikatakai, Nagaoka, 940-8532, Japan

Abstract

In 1996, we reported a new type of thin film solar cells having the structure of SLG/Mo/CZTS/CdS/AZO and achieved the conversion efficiency of 0.66 % for the first time. The conversion efficiency has increased to almost 7% in our laboratory by the end of 2008. Our empirical results revealed that in order to increase the photovoltaic properties, the off-stoichiometric composition; namely Cu-poor and Zn-rich, is desirable. In this presentation, we will survey the development of CZTS-based thin film solar cells achieved in our laboratory and show the latest related topics.

1. Introduction

In 1988, K. Ito and T. Nakazawa of Shinshu University succeeded in fabricating the CZTS thin film by an atomic beam sputtering technique, and clarified that the optical band gap energy was near the optimum value of 1.45 eV as a solar cell absorber layer. In addition, they reported the photovoltaic effect of 165 mV by making hetero diode with transparent conduction film of Cadmium Tin Oxide (CTO) [1]. In 1996, the authors fabricated successfully a CZTS thin film on a soda-lime glass (SLG) substrate by an electron beam (EB) evaporation followed by a sulfurization technique. As a result, the open-circuit voltage of 400 mV and the conversion efficiency of 0.66% were obtained for the first time by making a thin film solar cell structure of SLG/Mo/CZTS/CdS/AZO [2].

Fig. 1 shows the chronology of the conversion efficiency of CZTS-based thin film solar cells. The conversion efficiency of less than 1% in 1996 has increased to almost 7% in our laboratory. After 2007, we can see that several institutes had started to develop this new material. And in 2010, IBM group achieved 9.6% with CZTSSe by the wet process [3]. By the end of 2012, they reported 11.1 % efficiency with CZTSSe. These data definitely showed a remarkable possibility of rare metal–free thin film solar cells.

In our laboratory, to improve the conversion efficiency, many experiments have been conducted. In the late 1900's, the authors focused on the stoichiometric CZTS films to characterize their properties. As for now, this might be one of the reasons limiting the conversion efficiency. Table I shows the fabrication process used and the obtained photovoltaic properties in our early works. In fact, our study

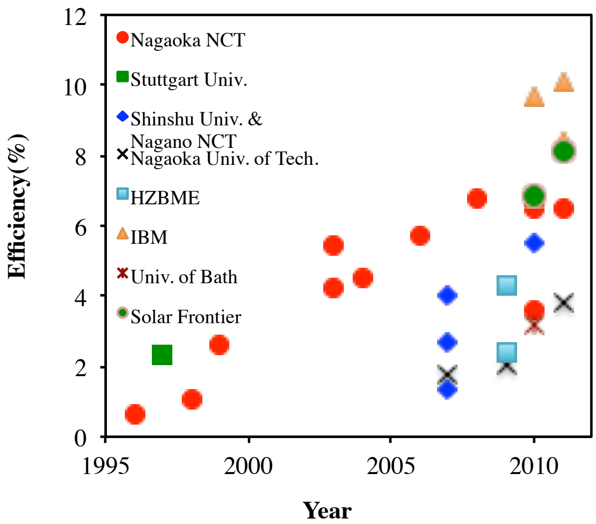

Fig. 1 Chronology of the conversion efficiency of CZTS-based thin film solar cells.

after process (4) revealed that in order to obtain the high conversion efficiency cells, CZTS of the off-stoichiometric composition; namely Cu-poor and Zn-rich composition, was preferable to the stoichiometry. To clarify such active composition, a co-sputtering system was utilized in our laboratory. In this presentation, a sulfurization of physical vapor deposited precursor layers will be the subject.

2. Survey of our early work

Our fabrication method is a two-stage process and it consists of a precursor fabrication and a sulfurization. In process (1) to (5), an electron beam (EB) evaporation system was used to make the precursors. In process (1), these precursors consisted of SLG/(Mo)/Zn/Sn/Cu and the stacking order was fixed. Then CZTS was obtained through a heat treatment in a N_2+H_2S atmosphere. From the optical measurements, we confirmed that CZTS films had the band gap energy of about 1.45 eV and the large absorption coefficients in the order of 10^4 cm^{-1}. These optical properties showed that CZTS films were very suitable for absorbers of thin film solar cells. The film composition was determined by the electron probe microanalysis (EPMA). The composition ratios of CZTS film showing desirable properties in both XRD and optical measurements were as follows:

Table I The fabrication processes used and the obtained photovoltaic properties in our laboratory

		Process (1)	Process (2)	Process (3)	Process (4)	Process (5-1)	Process (5-2)	Process (6)
Precursor Fabrication	Method	EB Evaporation	EB Evaporation	EB Evaporation	EB Evaporation	EB Evaporation	EB Evaporation	Co-Sputtering
	Precursor	Zn/Sn/Cu	ZnS/Sn/Cu	ZnS/Sn(SnS_2)/Cu	ZnS/Sn/Cu	ZnS/Cu/Sn	5x(ZnS/SnS_2/Cu)	Cu+ZnS+SnS
	Substrate Temp.	150 °C	150 °C	200→400 °C	150 °C	150 °C	200→400 °C	Non-Heating
Sulfurization Procedure	Sulfurization System	Pyrex glass tube Hot Wall Type Resistive Heater	Quartz glass tube Hot Wall Type Resistive Heater	Quartz glass tube Hot Wall Type Resistive Heater	SUS Chamber Cold Wall Type Lamp Heater	SUS Chamber Cold Wall Type Lamp Heater	SUS Chamber Cold Wall Type Lamp Heater	SUS Chamber Cold Wall Type SiC Heater
	Atmosphere	H_2S(5 vol%) N_2-balanced	H_2S(5 vol%) N_2-balanced	H_2S(5 vol%) N_2-balanced	H_2S(5 vol%) N_2-balanced	H_2S(5 vol%) N_2-balanced	H_2S(5 vol%) N_2-balanced	H_2S(20 vol%) N_2-balanced
	Tsub/Time	500°C/1, 3h	530°C/1+6h	550°C/1, 3h	550°C/3h	520°C/3h	540°C/1h	580°C/3h
	Rate of Temp.	20°C/min (to 300°C) 10, 2°C/min (to 500°C) 2°C/min (to 300°C)	10°C/min (to 200°C) 2°C/min (to 530°C) 2°C/min (to 300°C)	10°C/min (to 200°C) 2°C/min (to 550°C) 2°C/min (to 300°C)	10°C/min (to 200°C) 2°C/min (to 550°C) 2°C/min (to 300°C)	5°C/min (to 520°C) - Natural Cooling	10°C/min (to 540°C) - Natural Cooling	5°C/min (to 580°C) - 5°C/min (to 200°C)
Cell Structure	Cd-Source in CBD-CdS	$CdSO_4$	$CdSO_4$	$CdSO_4$	$CdSO_4$, CdI_2	CdI_2	CdI_2	CdI_2
	Window Layer	AZO(Al_2O_3:1wt%)	AZO(Al_2O_3:1wt%)	AZO(Al_2O_3:2wt%)	AZO(Al_2O_3:2wt%)	AZO(Al_2O_3:2wt%)	AZO(Al_2O_3:2wt%)	AZO(Al_2O_3:2wt%)
Composition Ratio	Method	EPMA	EPMA	EPMA	EPMA	EDS	EDS	ICP
	Cu/(Zn+Sn)	0.96	0.99	0.936	0.96	0.85	0.73	0.87
	Zn/Sn	0.916	1.01	1.02	1.08	1.03	1.7	1.15
Photovoltaic Properties	Voc (mV)	400	372	522	530, 659, 582	629	644	662
	Jsc (mA/cm^2)	6	8.36	14.1	14.8, 10.3, 15.5	12.5	9.23	15.7
	Fill Factor	0.277	0.347	0.355	0.46, 0.63, 0.60	0.58	0.66	0.55
	Area (cm^2)	0.187	0.105	0.128	0.16, 0.11, 0.11	0.113	0.113	0.155
	Efficiency (%)	0.66	1.08	2.62	3.46, 4.25, 5.45	4.53	3.93	5.74

Cu/(Zn+Sn)=0.960, Zn/Sn=0.916 and S/Metal=1.03. For the stoichiometry film, all these ratios mentioned above have to become one.

To fabricate a CZTS cell, a CdS buffer layer of 20 nm in thickness was deposited on the CZTS absorber. This was conducted by a chemical bath deposition (CBD) process with Cd sulfate, thiourea, ammonia solution and de-ionized water in a CBD solution at a temperature of 60 ºC. Then an Al-doped ZnO window layer was deposited by an RF sputtering technique using an AZO (ZnO+Al_2O_3 : 1wt%) target. As a result, the first CZTS solar cell, with an open circuit voltage (Voc) of 400 mV, a short circuit current density (Jsc) of 6.0 mA/cm^2, a fill factor (FF) of 0.277 and a conversion efficiency of 0.66%, was reported for the first time.

In process (2), ZnS was used as first layer of precursor instead of Zn to enhance the adhesion of CZTS films to the substrates. In process (3), an influence of the CZTS absorber thickness on photovoltaic properties was examined. In process (4), a new sulfurization system constructed with a stainless steel chamber and a turbo molecular pump (TMP) was introduced to eliminate the influence of the residual gas. In process (5-1), to improve the morphology of CZTS thin films, the stacking order was changed to SLG/Mo/ZnS/Cu/Sn. Sn was deposited as the final layer instead of the middle layer. By this trial, it was confirmed that the morphology of CZTS absorber was much improved by the SEM observation. In process (5-2), to improve the morphology of CZTS precursors and to enhance the inter-diffusion of elements in them, a multi-period type precursor was examined. Each period consisted of ZnS/SnS_2/Cu. From these examinations, it was confirmed that both the enhancement of an inter-diffusion of elements in a precursor and the improvement of film morphology are quite important to achieve high conversion efficiency.

In order to enhance the inter-diffusion of elements in a precursor, a co-sputtering method was one of the most useful candidates. In process (6), a fabrication of a mixed-precursor using a co-sputtering system with annealing chamber was started. To clarify the region of composition ratio in achieving the high conversion efficiency, we fabricated solar cells with CZTS absorber layers having the wide range of composition ratio (Cu/(Zn+Sn); 0.75-1.25, Zn/Sn; 0.80-1.35). As a result, it was confirmed that the high efficient cells existed in a relatively narrow region in the map even in the range of Cu-poor and Zn-rich composition. The regions were as follows: around 0.85 for Cu/(Zn+Sn), 1.1 to 1.3 for Zn/Sn and 1.8 to 2.0 for Cu/Sn. We named this region an active composition.

3. Conclusions

CZTS film has suitable optical properties for single junction solar cells. In order to clarify the precise physical properties of CZTS film and to increase the conversion efficiency, the establishment of the fabrication process of CZTS film with high reproducibility will be most essential. We think that the experimental results obtained by CZTS compound target with an active composition would be useful for this objective. Those examinations are under progress now.

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