Proton Degradation-free Flexible Chalcopyrite Solar Cells without Cover Glass and Adhesive

Hiroki Sugimoto[1], Tetsuya Nakamura[2], Mitsuru Imaizumi[2], Shin-ichiro Sato[3], and Takeshi Ohshima[3]

1 PXP Corporation, Sagamihara, Kanagawa 252-0131, Japan
2 Japan Aerospace Exploration Agency, Tsukuba, Ibaraki 305-8505, Japan
3 National Institutes for Quantum Science and Technology, Takasaki, Gunma 370-1292, Japan

***Abstract*— Strong radiation hardness against low-energy and high-energy proton irradiation on newly developed flexible chalcopyrite Cu(In, Ga)(Se, S)$_2$ solar cells without cover glass and adhesive was confirmed. Degradation of efficiency after 300 keV and 3 MeV proton irradiation (fluence varied from 10^{11} to 10^{13} cm^{-2}) was fully recovered by heat light soaking. Capacitance-voltage measurement indicated recovery of the net carrier concentration after the heat light soaking. Compositional depth profile measurement suggested the full-recovery characteristics should be delivered from Ga-less and Cu-poor composition in the depletion layer in Cu(In, Ga)(Se, S)$_2$ absorber layer. We believe these results are one of big steps for achieving light-weight and low-cost space solar cells with long lifetime.**

***Keywords*— flexible, chalcopyrite, Cu(In, Ga)(Se, S)$_2$ solar cell, radiation hardness, proton irradiation**

I. Introduction

In order to endure space missions for more than 10 years in comparably severe irradiation environments, such as the geostationary orbit, the space solar cells need to survive until the fluence of 10^{16} cm^{-2} for the electron irradiation and that of 10^{13} cm^{-2} for the proton irradiation [1,2]. Chalcopyrite Cu(In, Ga)(Se, S)$_2$ (CIGSS) solar cells have been known to have strong radiation hardness. For the electron irradiation, they show almost no degradation until the fluence of 10^{16} cm^{-2} [3,5,8,9][14]-[17], however, there is no reports for proton degradation-free solar cells due to the severe defect introduction by the proton irradiation [2,4,6,7,10,11]. For the low-energy proton irradiation less than 200 keV, the penetration depth of proton corresponds to the depth of the transparent conductive oxide (TCO) and electron transport layer (ETL), fortunately they hardly show any degradation thanks to their strong crystalline structures [4]. However, the low-energy proton irradiation ranging from 200 to 400 keV introduces a large number of defects in the CIGSS absorber layer because the penetration depth of proton just corresponds to the inside of the CIGSS absorber layer, which results in the large degradation of electrical performances of the CIGSS solar cells [2,4,6,7]. Therefore, all space solar cells need cover glass and adhesive to prevent the damages of the low-energy proton irradiation. Regarding the high-energy proton irradiation, the cover glass and adhesive no longer prevent the proton damage, all space solar cells are damaged more or less.

So far, self-recovery characteristics for the radiation damages of the CIGSS solar cells by light soaking (LS) [18,19], heat treatment [25,26] and heat light soaking (HLS) [19,27] have been reported. Among them, the HLS shows drastic recovery for the degradation of the short circuit current (J_{sc}) and the fill factor (FF). Regarding the degradation of open circuit voltage (V_{oc}), complete recovery has been difficult because the Ga-related antisite (Ga_{Cu}) defects are considered to be hardly passivated, while the In-related antisite (In_{Cu}) defects and metastable donor-

TABLE I. Summary of Proton Irradiation Effects on Chalcopyrite Solar Cells

Irradiation			Introduced defects (as irrad.)					LS recovery				HLS recovery			
Dose [1,2]	Energy [2,4]	Damage [2,4,6,7]	Defects [10,11]	Type [12]-[13]	Impact on cells [6,7,10,11,16,17]			Modification [12]-[13]	Impact on cells [19]			Modification [12]-[13] [20]-[24]	Impact on cells [19], [25]-[27]		
					V_{oc}	J_{sc}	FF		V_{oc}	J_{sc}	FF		V_{oc}	J_{sc}	FF
Proton ~10^{13} cm^{-2}	Low 200~400 keV	Extra large	so many $V_{Se,S}$-V_{Cu}	Donor (meta-stable)	much down		much down	Acceptor (meta-stable)	recover		recover	Acceptor (meta-stable)	recover		recover
			so many In_{Cu}	Deep level	much down	down	much down	Weak deep level	down	slightly down	down	Donor (passivated)	recover	recover	recover
			so many Ga_{Cu}	Deep level	much down	down	much down	Weak deep level	down	slightly down	down	Weak deep level (passivated)	recover (this work) / down	recover	recover
	High >1 MeV	Large	many $V_{Se,S}$-V_{Cu}	Donor (meta-stable)	down		down	Acceptor (meta-stable)	recover		recover	Acceptor (meta-stable)	recover		recover
			many In_{Cu}	Deep level	down	slightly down	down	Weak deep level	down	recover	recover	Donor (passivated)	recover	recover	recover
			many Ga_{Cu}	Deep level	down	slightly down	down	Weak deep level	down	recover	recover	Weak deep level (passivated)	recover (this work) / down	recover	recover

like defects related to the defect pairs of Se,S-vacancy ($V_{Se,S}$) and Cu-vacancy (V_{Cu}) could be easily passivated [12,13]. These proton irradiation effects on the chalcopyrite solar cells are summarized in Table I. The purpose of this paper is to realize the proton degradation-free CIGSS solar cells by restricting the effect of the antisite defects.

II. Experimental Detail

In order to investigate the proton irradiation hardness, newly developed flexible CIGSS solar cells with initial air-mass (AM) 1.5 efficiency (Eff) of about 15.8% (17.0% with anti-reflective coating) were prepared. The CIGSS solar cells used for this study were specially developed for severe space environments. Not only the radiation hardness but also high temperature tolerance, thermal cycle tolerance and mechanical vibration tolerance were much improved than conventional CIGSS solar cells. The CIGSS solar cells were fabricated by highly productive sputtering-based process. The basic structure was Ag grid electrode/In-based TCO/Zn-based ETL/CIGSS absorber layer/Mo back electrode on Ti film without cover glass and adhesive. The thickness of the CIGSS device layer and the Ti substrate was about 3 um and 50 um, respectively. The weight of the CIGSS solar cells were about 250 g/m^2.

After the cell fabrication, all samples were stabilized by the HLS (30 min at 200C in N_2 box) and initial electrical parameters were measured before the proton irradiation in order to eliminate over estimation of recovery effects after the proton irradiation. We performed 300 keV and 3 MeV proton irradiation tests on the CIGSS solar cells at the National Institutes for Quantum Science and Technology, Takasaki. Then, the electrical parameters were checked after 1 day stock in the dry-air box. Then, the all samples were put on the temperature-controlled plate and the LS (3 hours at 25C in air) were applied. After the electrical parameter measurements, the HLS (1 hour at 150C in N_2 box) were conducted. Finally, we checked the electrical parameters again.

The current–voltage characteristics were measured by a class A solar simulator (XI-05A1V2-L, SERIC Ltd., Japan) with AM 1.5 and 100 mW/cm^2 illumination at 25C. Capacitance–voltage (C–V) profiles were recorded at the frequency of 10 kHz using a 4294A Precision Impedance Analyzer (Hewlett-Packard Company, USA) in the dark at room temperature. Compositional depth profiles in the CIGSS absorber layer were measured by Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (JSM-7001F, JEOL Ltd., Japan) on the cross section polished by the ion milling.

III. Results and Discussion

Figure 1 shows the remaining factors of electrical parameters of the CIGSS solar cells after the 300 keV and 3 MeV proton irradiation as a function of different fluences. The results of as irradiated samples showed the 300 keV proton irradiation introduced larger degradation than the 3 MeV proton irradiation. Large degradation of both V_{oc} and FF should be delivered from the decrease in the acceptor concentration in the CIGSS absorber layer, as reported in the other papers [11,19]. Increase in recombination centers could cause additional V_{oc} and J_{sc} degradation. After the LS, the FF showed big recovery while the degradation of V_{oc} still remained, which suggested the acceptor concentration should be recovered while the recombination centers were not passivated yet. After the HLS, surprisingly all parameters were much recovered. Actually, the 3 MeV proton irradiated samples showed rather improvement than the initial performance. Judging from the improvement of FF, the acceptor concentration seemed to be increased. One possibility for the increasement of acceptor concentration was considered to be due to the irradiation-induced acceptor-like V_{Cu} defects, the other reason could be due to the irradiation-induced metastable $V_{Se,S}$-V_{Cu} defect pairs. Even in the severe 300 keV proton irradiation, all parameters were fully recovered, which indicated the recombination centers should be almost passivated as well as the acceptor concentration seemed to be recovered.

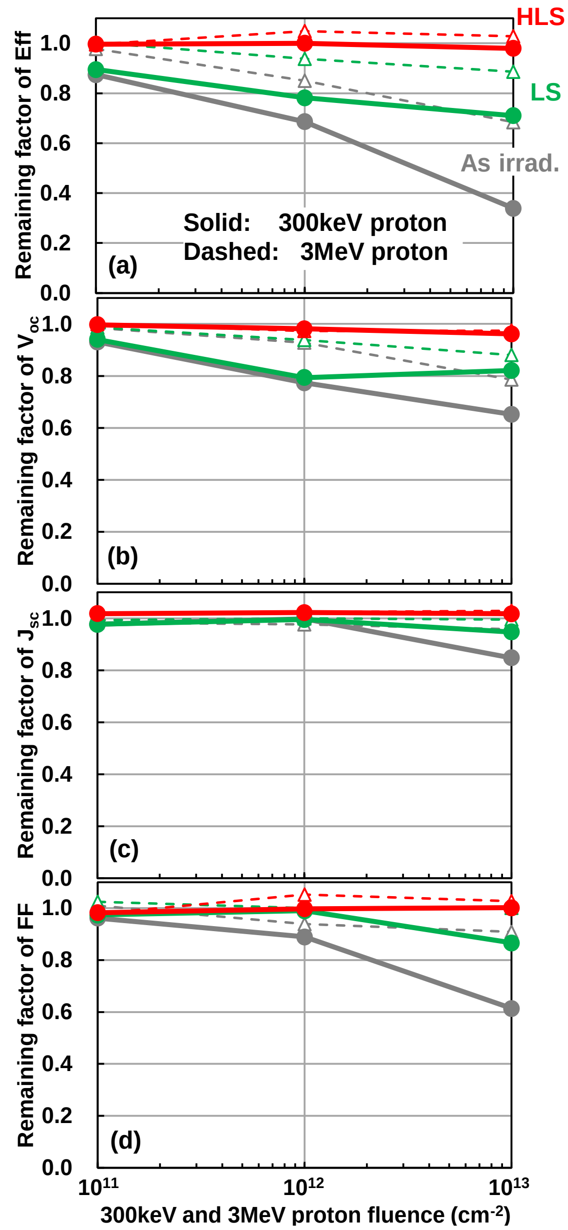

Fig. 1. Remaining factors of (a) Eff, (b) V_{oc}, (c) J_{sc} and (d) FF of CIGSS solar cells after 300 keV (solid line) and 3 MeV (dashed line) proton irradiation as a function of different fluences. Gray, green and red lines represent as irradiated, after LS and HLS, respectively.

Net carrier concentration (N_{CV}) profiles investigated by the C-V measurement on the CIGSS solar cells before and after 300 keV proton irradiation with fluences of $1x10^{11}$ and $1x10^{13}$ cm^{-2} are shown in Fig. 2. So far, the decrease in the N_{CV} of the CIGSS solar cells by the proton irradiation and the recovery of N_{CV} by the HLS have been reported [11,19]. As shown in Fig 2, we confirmed the N_{CV} of the proton-irradiated CIGSS solar cells were also recovered to almost comparable level of their initial value by the HLS. These results indicated the metastable donor-like defects and deep-donor antisite defects should be passivated by the HLS.

Figure 3 shows compositional depth profiles of Ga/(In+Ga) and Cu/(In+Ga) ratio on the newly developed CIGSS solar cells. Compared with conventional chalcopyrite solar cells [28,29], notable structures of Ga-less and Cu-poor compositions in the depletion layer in the CIGSS absorber layer were observed. The activation energy of self-recovery by the HLS has been reported as low as around 0.8~1.0 eV [18,27], which corresponds to the migration energy of V_{Cu} [23,24]. From these results, these full-recovery characteristics should be delivered from the passivation of the antisite defects, such as In_{Cu} and Ga_{Cu} defects, by the thermally migrated V_{Cu} as well as the restriction of Ga_{Cu} defects by the Ga-less composition. We also found that there was the strong Ga grading at front side of the CIGSS absorber layer, which should also help the full-recovery characteristics by enhancing the generated electron collection.

Calculated from the activation energy of the HLS recovery, the current HLS condition of 1 hour at 150C corresponds to around 16~69 days at operation temperature of 60C, which indicates sufficient self-recovery could be conducted also in actual space environments. Further investigations about the actual activation energy for the newly developed CIGS solar cells are required, however, these findings allow us to eliminate the expensive cover glass and adhesive for space solar cells.

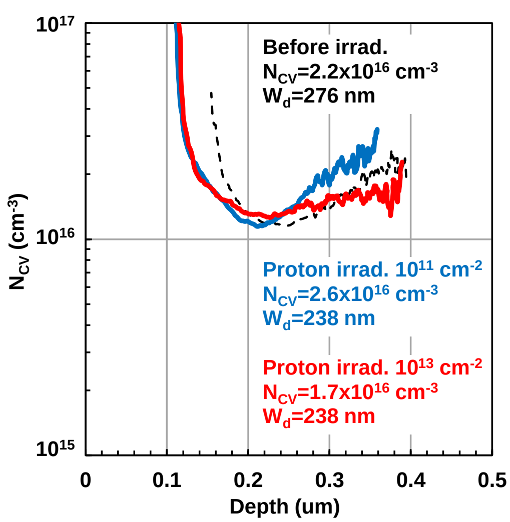

Fig. 2. N_{CV} profiles of CIGSS solar cells before (black dashed line) and after 300 keV proton irradiation with fluences of (blue line) $1x10^{11}$ cm^2 and (red line) $1x10^{13}$ cm^{-2}. W_d denotes width of depletion layer. All samples were treated by HLS before measurements.

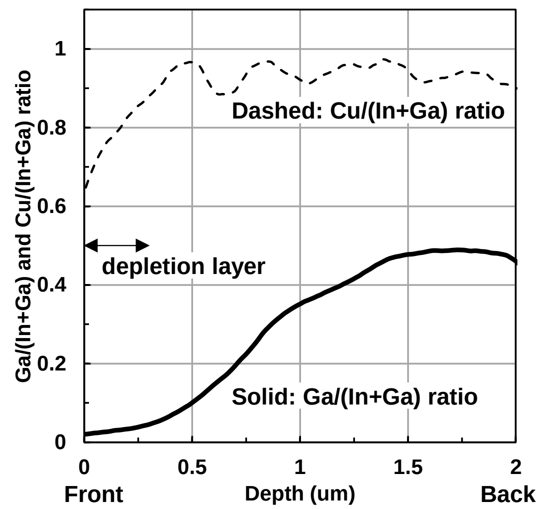

Fig. 3. Compositional depth profiles of Ga/(In+Ga) (solid line) and Cu/(In+Ga) (dashed line) ratio on newly developed CIGSS solar cells.

IV. Summary

Strong radiation hardness against low-energy and high-energy proton irradiation on newly developed flexible chalcopyrite CIGSS solar cells without cover glass and adhesive was confirmed. Degradation of Eff after the proton irradiation was fully recovered by HLS. The full-recovery characteristics should be delivered from Ga-less and Cu-poor composition in the depletion layer in the CIGSS absorber layer. We believe these results are one of big steps for achieving light-weight and low-cost space solar cells with long lifetime.

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