

Title	Thin-film polycrystalline silicon solar cells formed by flash lamp annealing of a-Si films
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Citation	Thin Solid Films, 518(17): 5003-5006
Issue Date	2010-06-30
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/9051
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Description	



THIN-FILM POLYCRYSTALLINE SILICON SOLAR CELLS FORMED BY FLASH LAMP ANNEALING OF a-SI FILMS

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ABSTRACT

We have fabricated thin-film solar cells using polycrystalline silicon (poly-Si) films formed by flash lamp annealing (FLA) of 4.5- μm -thick amorphous Si (a-Si) films deposited on Cr-coated glass substrates. High-pressure water-vapor annealing (HPWVA) is effective to improve the minority carrier lifetime of poly-Si films up to 10 μs long. Diode and solar cell characteristics can be seen only in the solar cells formed using poly-Si films after HPWVA, indicating the need for defect termination. The actual solar cell operation demonstrated indicates feasibility of using poly-Si films formed through FLA on glass substrates as a thin-film solar cell material.

KEYWORDS : Flash lamp annealing; Polycrystalline silicon; High-pressure water vapor annealing; Minority carrier lifetime

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1. INTRODUCTION

Polycrystalline silicon (poly-Si), used for bulk crystalline Si (c-Si) solar cells, is generally formed by the casting method. With the recent surging of the solar cell market, the problem of Si material shortage has occurred, and hence, a large number of studies have been conducted on technologies for more effective utilization of the material, such as wafer manufacturing without kerf loss [1,2] and direct wafer formation from Si melt [3], although they are all developing technologies. For a cost-effective fabrication process for poly-Si solar cells, post-crystallization of amorphous silicon (a-Si) films formed on glass substrates has been extensively studied [4-7]. One of the most advanced works is the development of thin-film poly-Si solar cells formed through solid-phase crystallization by furnace annealing at 600 °C for more than 1 hour [6], demonstrating solar cells with conversion efficiencies of over 10%. If the throughput of poly-crystallization is significantly improved, more cost-effective solar cell fabrication will be realized.

Flash lamp annealing (FLA) is a millisecond-order treatment [8-10], and thus, can convert micrometer-thick a-Si films to poly-Si films without thermal damage to entire glass substrates with low thermal resistivity, because the thermal diffusion length of glass is shorter than its thickness. We have actually clarified that 4.5- μm -thick a-Si films deposited by catalytic chemical vapor deposition (Cat-CVD) on Chromium (Cr)-coated glass substrates can be crystallized by FLA with only one shot of irradiation, and without peeling of the Si films [11,12]. Defects in the poly-Si films, formed during the crystallization by FLA, should be terminated to obtain long minority carrier lifetime and high-efficiency solar cells. Of a number of defect termination techniques, high-pressure water-vapor annealing (HPWVA) [13,14] seems to be most suitable for

the defect termination of the poly-Si films, because of the thickness of the poly-Si films, up to 4.5 μm . We have not attempted HPWVA of the poly-Si films formed through FLA on Cr-coated glass substrates, although the effectiveness of HPWVA for poly-Si films formed directly on glass substrates has been clarified [15]. The effective defect termination will be necessary to demonstrate actual solar cell operation using the poly-Si films.

In this paper, we investigate defect termination of the poly-Si films, formed by FLA on Cr-coated glass substrates, through use of HPWVA. We also propose a substrate-type solar cell structure using the bottom Cr adhesion films as back electrodes, and demonstrate actual solar cell operation using well-defect-terminated poly-Si films.

2. EXPERIMENTS

Cr films of 60 to 200 nm in thickness were first deposited on quartz substrates, by sputtering, with a size of $20 \times 20 \times 0.7 \text{ mm}^3$, followed by deposition of a-Si films by Cat-CVD. Samples with only intrinsic (i-) Si films 4.5 μm in thickness were used for investigation of the effect of HPWVA, while p-i-n stacked a-Si films, whose thicknesses were 10 nm, 4.5 μm , and 10 nm, respectively, were prepared for fabrication of p-i-n poly-Si solar cells. The defect density of the precursor i-a-Si films, measured by electron spin resonance, was less than $10^{16} / \text{cm}^3$, and the films' hydrogen content, estimated by means of Fourier-transform infrared spectroscopy (FT-IR), was less than 3%. FLA was performed under a fixed pulse duration of 5 ms with only one shot of irradiation for each sample, whereas the lamp irradiance was systematically changed on the order of several tens of J/cm^2 in order to find the optimum irradiance, “optimum” meaning no serious peeling of the Si films and complete crystallization of the a-Si films

over the $20 \times 20 \text{ mm}^2$ area. Because of the low hydrogen content, no prior dehydrogenation process is required [16]. We have found that the poly-Si films consist of 10-nm-sized fine grains and relatively larger grains a few hundred nm size, and show high crystallinity close to unity. Detailed microstructures of the poly-Si films and their formation mechanisms have been reported elsewhere [17].

HPWVA was carried out at various annealing temperatures to improve the minority carrier lifetime. Quality of the poly-Si films was characterized by a differential microwave photo-conductivity decay (μ -PCD) system (Kobelco Research Institute, Inc., LTA-1510EP) [18]. This μ -PCD system can coincidentally detect microwave reflections from two areas with and without excess carriers generated by pulse laser illumination, and decay curves with high signal/noise ratio can be obtained from the difference of the two signals, even in the case of thin films. Furthermore, this system can tune the phase of microwaves, which enables us to measure microwave decay curves of thin films even on metal films that could reflect microwaves. We used a pulse laser of 349 nm in excitation wavelength and with a photon density of $2 \times 10^{13} \text{ /cm}^2$, which results in the generation of excess carriers only in poly-Si films. The Si surfaces were chemically passivated by iodine/ethanol solution during the μ -PCD measurement to eliminate the effect of surface recombination. The poly-Si films were also characterized by photoluminescence (PL) spectroscopy using a cw excitation laser (wavelength 532 nm) with the intensity of 0.3 W/cm^2 at 4.4 K.

The p-i-n poly-Si films were processed to solar cells by sputtering of indium tin oxide films and by evaporation of aluminum (Al) electrodes, followed by formation of $2 \times 2 \text{ mm}^2$ mesa structures, whose schematic diagram is shown in Fig. 1. The reason of choosing a substrate-type configuration is that a Cr film is necessary to suppress the

peeling of Si films during FLA. The current-voltage (I-V) characteristics of the devices were measured in dark and AM 1.5-illuminated conditions.

3. RESULTS AND DISCUSSION

Figure 2 shows typical microwave decay curves obtained in the μ -PCD measurement of the poly-Si films before and after HPWVA, in which two decay components are clearly confirmed. The time constants obtained from them are about 10 μ s and 120 μ s, respectively. To determine the origins of the two decay components, we first discuss Auger recombination. The penetration depth of the excitation pulse of 349 nm in wavelength is approximately 10 nm. Hence, the excess carrier density is estimated to be $2 \times 10^{19} / \text{cm}^3$ immediately after the pulse irradiation, which is high enough to trigger Auger recombination [19]. The excess carriers, however, rapidly diffuse into surrounding poly-Si. The carrier mobility is estimated to be $14 \text{ cm}^2/\text{Vs}$, obtained by Hall measurement of 1- μm -thick n^+ -poly-Si films with carrier concentration of approximately $10^{20} / \text{cm}^3$ separately prepared by FLA directly on quartz substrates. The carrier diffusion length of the poly-Si film is thereby approximately 0.5 μm in 10 ns. This time is much shorter than the time interval between the data points in the decay curve, which is 200 ns. The first quick decay component, continuing over 5 μs , is probably not due to Auger recombination, since the carrier diffusion of 0.5 μm in distance reduces the excess carrier concentration of $4 \times 10^{17} / \text{cm}^3$, which is small enough to eliminate domination of recombination by Auger effect [19]. The first decay therefore probably results from Shockley-Read-Hall recombination. The second slow decay component is thought to be due to long-lived excess carriers through trapping-detrapping effects via shallow levels [20]. Since the second slow decay is

notably seen in the decay curve obtained from the poly-Si after HPWVA, as shown in Fig. 2, the shallow levels may be formed through HPWVA. Figure 3 shows the PL spectra from the poly-Si films before and after HPWVA. Clear band-to-band transition can be seen at 1.09 eV in the spectra, indicating excellent crystal quality [11]. Broad emissions in the range of 0.85 to 1.0 eV appear after HPWVA. Judging from the emission energies, these peaks probably come from dislocations [21], and these levels might act as the shallow trapping levels, resulting in observation of the slow decay. Since these trapping levels tend to be filled with excited carriers under sunlight irradiation, negative influence of these traps on solar cell operation may be small. The increase in the PL integral intensity indicates reduction of dangling bonds, which act as non-radiative recombination centers.

Figure 4(a) shows the measured minority carrier lifetime of the poly-Si films after HPWVA at various temperatures, at a pressure of 1 MPa for 1 hour. The lifetime first increases with increase in annealing temperature, and then decreases over 400 °C. The peak intensity of the decay curves, which directly corresponds to the photosensitivity, is also plotted in Fig. 4(b), indicating a similar tendency to the carrier lifetime. The optimum temperature is probably in the range of 350 to 400 °C. Sameshima *et al.* reported tendency of reduction in defect density of poly-Si films as the HPWVA temperature increases [13], which is consistent with our result in the low temperature range. The decreases in the lifetime and the peak intensity might be due to the effect of dehydrogenation during HPWVA, since the poly-Si contains hydrogen atoms on the order of $10^{21} /cm^3$, according to secondary ion mass spectroscopy (SIMS) measurements using Cs^+ ions (5 keV, 20 nA), some of which probably passivate defects, and hydrogen atoms generally start to desorb at temperatures over 500 °C. Thus, the

optimum HPWVA temperature would be different in the case of poly-Si structures originally containing a negligibly small number of hydrogen atoms. Assuming carrier mobility of $14 \text{ cm}^2/\text{Vs}$, measured by Hall measurement, the lifetime obtained corresponds to the minority carrier diffusion length of $19 \mu\text{m}$, which is 4 times longer than the poly-Si film thickness, and hence, effective carrier collection is expected during solar cell operation.

Figure 5 shows I-V characteristics of the solar cells formed using the poly-Si films before and after HPWVA at a pressure of 1 MP for 10 min at 400°C . According to SIMS measurements, the poly-crystallization of the stacked p-i-n a-Si films is performed keeping abrupt profiles of dopant and Cr atoms, as has been reported elsewhere [22]. Use of poly-Si films before HPWVA does not result in devices which work well. This is probably due to the existence of defects in the poly-Si films acting as leakage current passes as well as recombination centers. On the other hand, the devices fabricated from the poly-Si films after HPWVA function as diodes and solar cells. This solar cell indicates short circuit current density (J_{sc}) of 7.15 mA/cm^2 , open circuit voltage (V_{oc}) of 0.21 V , fill factor (FF) of 0.404 , and conversion efficiency of 0.606% . The solar cell properties seem not to be sufficient despite long carrier lifetimes shown above, which would be due to active surface recombination. The poly-Si surfaces whose surfaces are not passivated actually show significantly small lifetimes compared to the temporarily passivated poly-Si films. The introduction of a surface passivation structure, such as a thin intrinsic a-Si film, would lead to much better solar cell properties. The characteristics firstly obtained are comparable to those in the other first reports on the thin-film solar cells based on post-crystallization technologies [4, 23]. We believe that the performance will be improved by optimizing

poly-Si structures, solar cell processes, and HPWVA conditions, because of the excellent fundamental properties of the poly-Si films, such as the long carrier lifetime and high crystallinity.

4. CONCLUSIONS

We have clarified that HPWVA is effective in improving the carrier lifetime of the poly-Si films formed by FLA of precursor a-Si films on Cr-coated glass substrates. The minority carrier lifetime can be improved up to over 10 μ s, together with increase in peak intensity of microwave reflection, and the optimized HPWVA temperature is in the range of 350 to 400 °C for the case of the poly-Si films discussed in this study. P-i-n stacked poly-Si films, formed by FLA of stacked p-i-n a-Si films, can be processed to substrate-type solar cells using bottom Cr adhesion layers as back electrodes. We have demonstrated actual operation of the devices after HPWVA, indicating high feasibility of using the poly-Si films formed on glass substrates as thin-film solar cells.

Acknowledgements

The authors acknowledge T. Owada and T. Yokomori of Ushio Inc. for their expert operation of and fruitful discussion on FLA, and Professor M. A. Mooradian of JAIST for improvement of English. This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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Figure captions

Figure 1 Schematic diagram of the p-i-n poly-Si solar cell.

Figure 2 Typical microwave decay curves of the poly-Si films before and after HPWVA obtained by μ -PCD measurement.

Figure 3 PL spectra from the poly-Si films before and after HPWVA.

Figure 4 Minority carrier lifetimes (a) and peak intensities of the microwave reflection (b) of the poly-Si films as a function of HPWVA temperature.

Figure 5 Dark and illuminated I-V characteristics of the stacked poly-Si p-i-n structures before and after HPWVA.

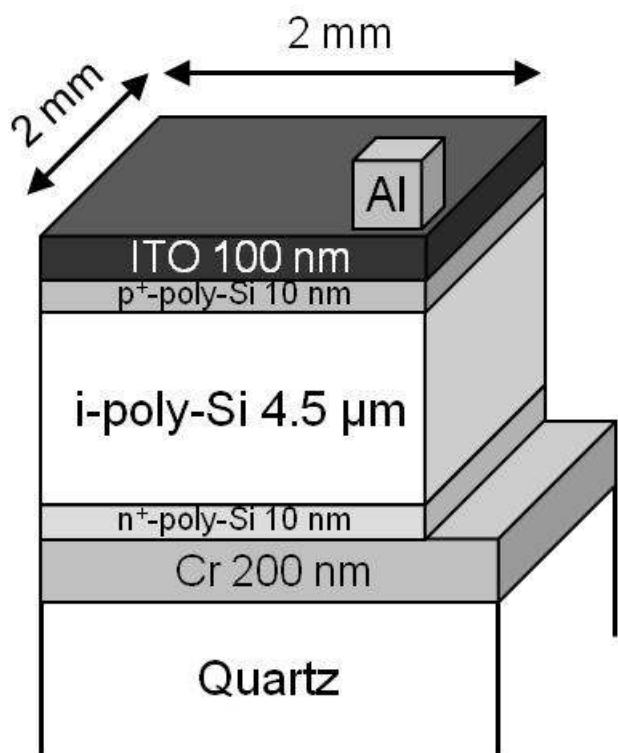


Figure 1 Y. Endo *et al.*,

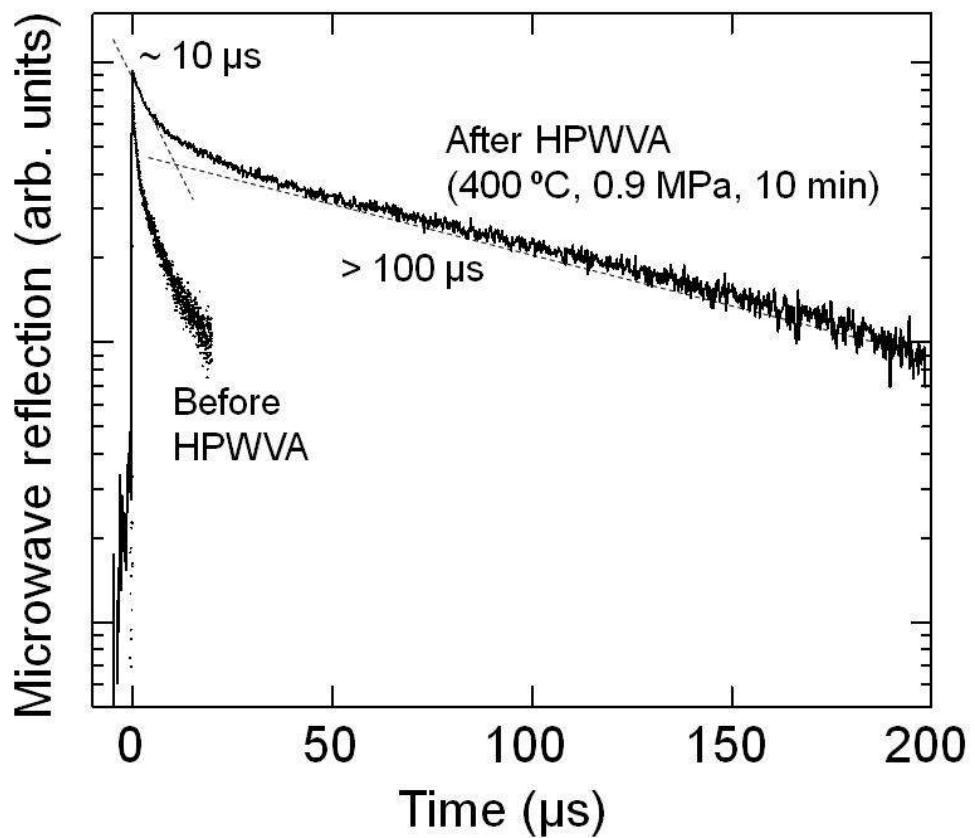


Figure 2 Y. Endo *et al.*,

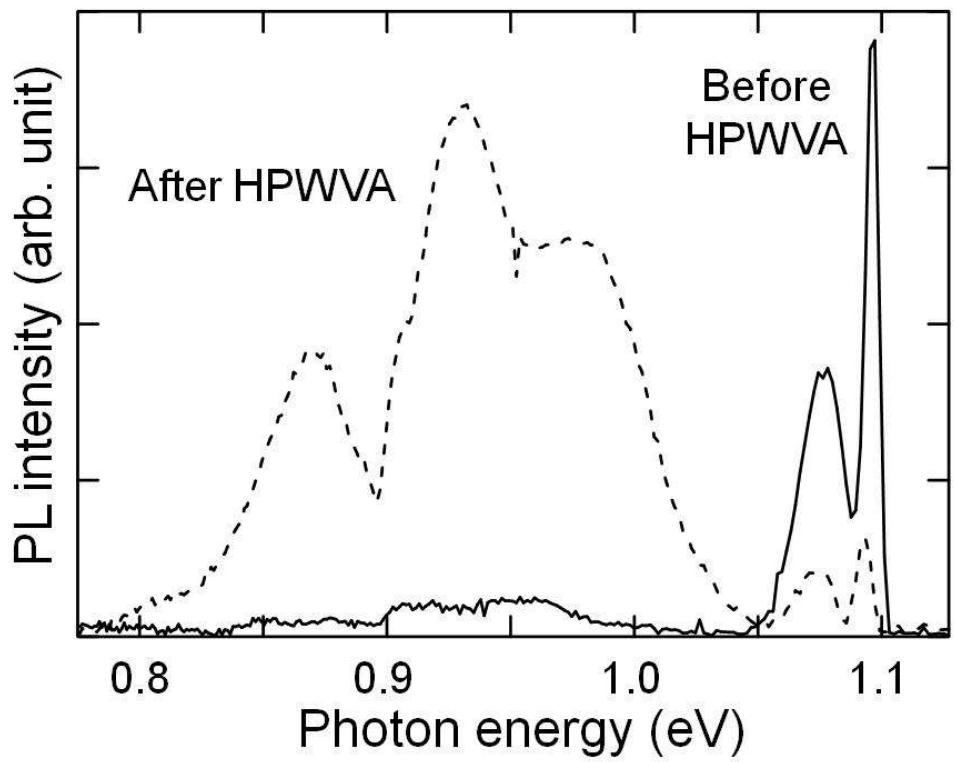


Figure 3 Y. Endo *et al.*,

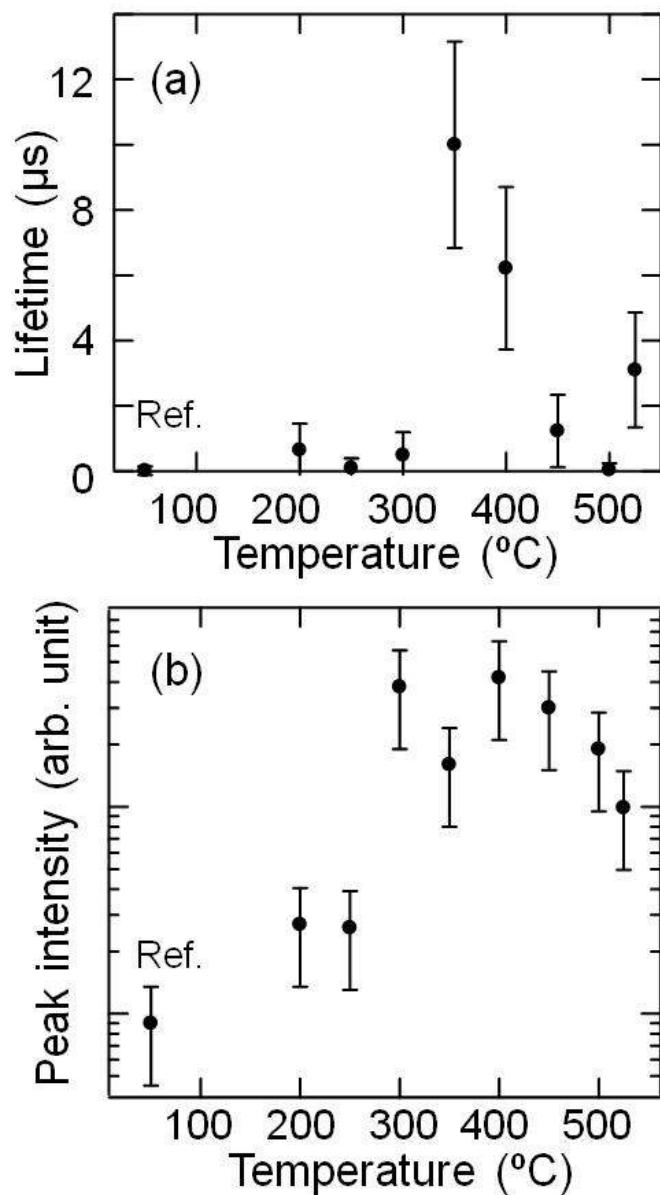


Figure 4 Y. Endo *et al.*,

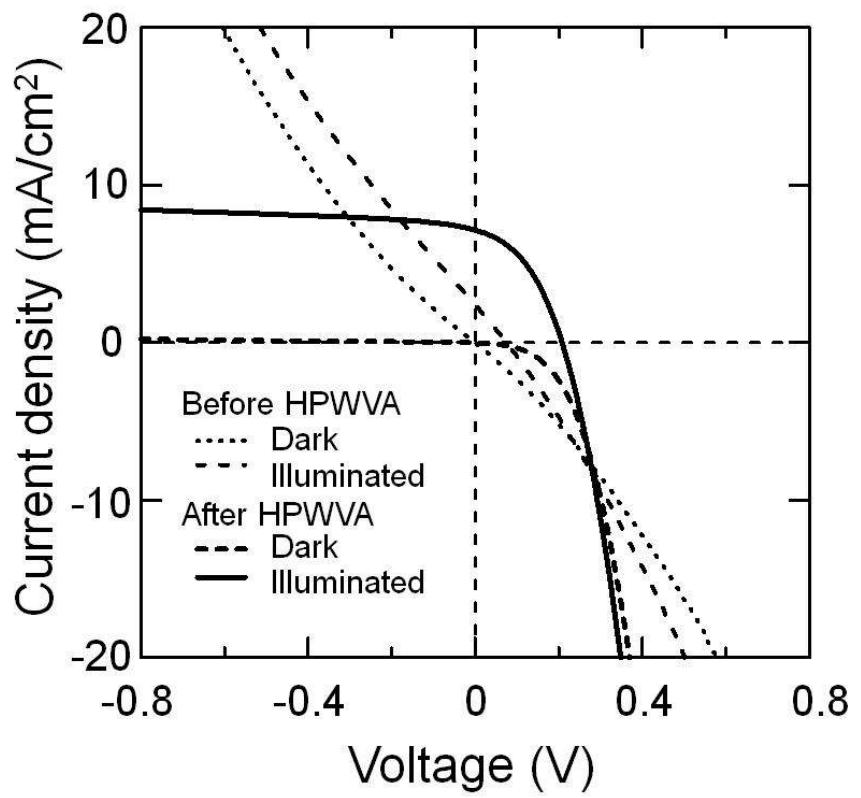


Figure 5 Y. Endo *et al.*,