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Description	

Drastic Improvement of Minority Carrier Lifetimes Observed in Hydrogen-Passivated Flash-Lamp-Crystallized Polycrystalline Silicon Films

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Polycrystalline silicon (poly-Si) films 4.5 μm thick, formed on glass substrates by flash lamp annealing (FLA) of precursor amorphous Si (a-Si) films, show remarkably long minority carrier lifetimes of approximately 100 μs after post-furnace annealing under N_2 ambient. Even after crystallization by FLA, there remain a large number of H atoms, on the order of $10^{21} / \text{cm}^3$, which probably effectively act to passivate dangling bonds in the poly-Si films. A minority carrier diffusion length of approximately 60 μm , estimated using the lifetime value, indicates high feasibility of realizing thin-film solar cells using this material.

Polycrystalline silicon (poly-Si) films formed by post-annealing of precursor amorphous Si (a-Si) films on low-cost substrates have attracted significant interest as solar cell material, because they have the advantages of high stability against light-induced degradation, long carrier diffusion length and resulting high carrier mobility originating from the absence of a-Si, and lower Si material usage than bulk crystalline Si (c-Si) solar cells. There have been a number of advanced investigations based on thermal equilibrium treatment such as furnace annealing¹⁾ and metal-induced crystallization.^{2,3)} Conventional glass substrates with poor thermal tolerance, such as soda lime glass, however, cannot be utilized, because of the high annealing temperature, which induces thermal damage to the glass substrates. This problem can be solved by applying non-thermal equilibrium annealing, which enables us to selectively heat precursor a-Si films, keeping the glass temperature sufficiently low. Flash lamp annealing (FLA) seems to be one of the best methods to crystallize a-Si films, from the viewpoint of solar cell application. This is because the FLA has proper pulse duration on the order of ms, corresponding to thermal diffusion lengths of several tens of μm in a-Si and in glass. This pulse duration is not realized in conventional rapid thermal annealing (RTA) with s-order duration, which results in thermal damage to glass substrates, nor in excimer laser annealing (ELA) with less than 1 μs duration, which results in incomplete crystallization of thick a-Si films. We have succeeded in forming high-quality poly-Si films on glass substrates by FLA. These films have minority carrier lifetimes of approximately 10 μs after termination of the dangling bonds, which were generated during FLA, by using high-pressure water-vapor annealing (HPWVA).⁴⁻⁷⁾ In this letter, we report an important improvement of the carrier lifetimes of the flash-lamp-crystallized poly-Si films, up to 100 μs , by simple furnace

annealing under nitrogen (N₂) ambient.

Chromium (Cr) adhesion layers were first deposited on quartz glass substrates by sputtering, followed by deposition of n⁺- and intrinsic (i-) a-Si films, in this order, with thicknesses of 10 nm and 4.5 μm, respectively, by catalytic chemical vapor deposition (Cat-CVD), often referred to as hot-wire CVD. The Cat-CVD can provide a-Si films with initially low hydrogen (H) content and with low film stress, resulting in the suppression of Si film peeling during deposition as well as during FLA. The details of the deposition conditions are reported elsewhere.⁸⁾ FLA was performed under fixed pulse duration of 5 ms. Each sample received only one shot of flash irradiation. No dehydrogenation process was performed prior to FLA. The densities of H atoms in the Si films before and after crystallization by FLA were characterized by secondary ion mass spectroscopy (SIMS).

The poly-Si surface regions (approximately 500 nm thick, and containing a number of voids formed during crystallization by FLA) were etched off using a mixed acid consisting of HF and HNO₃. The poly-Si films were then put into a conventional furnace under N₂ ambient for 30 min at various temperatures up to 600 °C. Minority carrier lifetimes of the poly-Si films were measured using a differential microwave photoconductivity decay (μ-PCD) system equipped with a pulse laser of 349 nm excitation wavelength and with a photon density of 2×10^{13} /cm². The poly-Si surfaces were temporarily passivated by iodine/ethanol solution during the μ-PCD measurement to eliminate the effect of surface recombination.

Figure 1 shows SIMS profiles of H atoms before and after crystallization by FLA. The crystallized Si film has high crystalline fraction close to unity.⁴⁾ Surprisingly, many H atoms, on the order of 10^{21} /cm³, still remains in the film even after

crystallization. The inset of Fig. 1 shows Raman spectra of Si films before and after FLA at a Si-H peak position. The Si-H signals are clearly seen even after crystallization, which is also an indication of high-density H atoms remaining in the poly-Si film. The intensity of the Si-H peak, however, decreases after FLA, probably due to the disconnection of some Si-H bonds during the crystallization process.

One of the possible reasons for the suppressed H desorption is the thickness of the Si films. Thicker films generally require longer duration for dehydrogenation, and the sufficient thickness of 4.5 μm may result in keeping the hydrogen density high in the Si films. Another possible reason is a characteristic crystallization mechanism. The crystallization discussed here is based on “explosive crystallization (EC)”, which is governed by heat generation through phase change from metastable a-Si to stable c-Si and by its transfer to neighboring a-Si regions, resulting in lateral crystallization.⁹⁾ Judging from the microstructure of the poly-Si films, with a large number of fine grains on the order of 10 nm in size, the flash-lamp-induced crystallization is mainly dominated by solid-phase nucleation.⁹⁾ In the phase transition directly from a-Si to c-Si, the possible maximum temperature of Si is limited to the Si melting point of 1414 °C, due to a large latent heat of fusion in c-Si (1803.75 J/g).¹⁰⁾ Furthermore, because of the rapid lateral heat transfer into neighboring a-Si, thermal holding time of c-Si at a peak temperature is quite short, roughly estimated to be less than 1 μs . These facts probably lead to suppression of H desorption. The large amount of H atoms remaining in the poly-Si films are expected to terminate defects during post-annealing.

Figure 2 shows the result of μ -PCD measurement for the poly-Si film after furnace annealing at 450 °C. The carrier lifetime, estimated from the initial, relatively fast decay component, is approximately 100 μs long, which is much longer than the

lifetime of poly-Si films after HPWVA defect termination, as shown in the inset of Fig. 2. Although the high effectiveness of HPWVA for defect termination in Si films is well-known,¹¹⁻¹³⁾ it also probably induces dislocations in the flash-lamp-crystallized poly-Si films, evidenced by observation of four D lines in the photoluminescence spectrum of the poly-Si films after HPWVA.⁷⁾ The generation of dislocations might be due to high pressure, and defect termination under atmospheric pressure might be better for the suppression of damage to the poly-Si microstructures during the defect termination process. The drastic improvement in carrier lifetimes of the furnace-annealed poly-Si films must be due to effective termination of dangling bonds by the remaining H atoms.

The remarkably long carrier lifetimes we obtained in the poly-Si films with no back-surface passivation structures can be understood as follows. The poly-Si films have in-depth distribution of a crystalline fraction, and the crystalline fraction drops considerably in the vicinity of the Si/Cr interface.¹⁴⁾ The Si films must therefore have a graded band gap, a wider gap at some distance from the surface, which might prevent photo-generated carriers from approaching the defective Si/Cr interface. Another possibility is the effect of a thin n⁺-Si layer inserted between Cr and i-Si films, which may act as a blocking layer for holes.

The second relatively slow decay component might be due to trapping-detrapping effects via shallow levels, as has been reported previously.^{7,15)} Another possible explanation is that the first decay component is dominated by Auger recombination and the second decay is the actual Shockley-Read-Hall (SRH) recombination. Neglecting radiative recombination, the measured lifetime τ_{eff} can be expressed as

$$\tau_{eff}^{-1} = \tau_{SRH}^{-1} + \tau_{Auger}^{-1}, \quad (1)$$

where τ_{SRH} and τ_{Auger} represent lifetimes governed by SRH and Auger processes, respectively. With a photon density of $2 \times 10^{13} / \text{cm}^2$ and a penetration depth of 10 nm for incident light of 349 nm in wavelength, the photo-excited carrier density is estimated to be $2 \times 10^{20} / \text{cm}^3$ immediately after the pulse incidence, which rapidly decreases to $4 \times 10^{17} / \text{cm}^3$ because of carrier diffusion downward. τ_{Auger} for high-level injection can be written as

$$\tau_{Auger}^{-1} = (C_p + C_n) \Delta n^2, \quad (2)$$

where C_p and C_n are the Auger recombination coefficients for holes and for electrons, respectively, and Δn is the excess carrier density. Since $C_p + C_n = 2.35 \times 10^{-31} \text{ cm}^6/\text{s}$,¹⁶⁾ τ_{Auger} is estimated to be 2-31 μs when $\Delta n = 4 \times 10^{17} / \text{cm}^3$, which is significantly smaller than the measured τ_{eff} . According to eq. (1), the initial decay could therefore be governed by the Auger process, and the second decay might indicate the τ_{SRH} , which is more than 300 μs .

Figure 3 shows minority carrier lifetime of the poly-Si films after furnace annealing as a function of annealing temperature. The lifetime gradually increases with increase in annealing temperature, then significantly improves at 450 °C, and finally decreases at higher temperatures. One of the possible reasons for the increase in the lifetime is the enhancement of the diffusion length of hydrogen atoms. The significant increase in the lifetime at 450 °C, however, cannot be accounted for only by the H diffusion enhancement because of the sufficient diffusion length of H atoms (L_e) during 30-min annealing at 400 °C of more than 13 μm , according to reported diffusion coefficients for H atoms in poly-Si at 400 °C of $1 \times 10^{-9} \text{ cm}^2/\text{s}$ or more.¹⁷⁻¹⁹⁾ One possible explanation of the drastic lifetime improvement at 450 °C might be the

enhanced dissociation of H₂ molecules, resulting in increase in the number of H atoms to passivate the dangling bonds in the Si film. Sara *et al.*, have demonstrated the significant improvement of bulk poly-Si solar cell performances after 10%-H₂ forming gas annealing, and they have claimed that Al or Al/Si interface assists to dissociate H₂ molecules.²⁰⁾ In our case, some of H atoms might exist as H₂ molecules in the poly-Si films, and the temperature of around 450 °C might be needed for the dissociation of H₂ atoms by the assistance of the backside Cr films or Cr/Si interfaces. When the annealing temperature exceeds 575 °C, at which Si-H bonds break,²¹⁾ the effect of H termination is lost, resulting in significant reduction in the minority carrier lifetime. Further investigation is necessary for more detailed understanding of this temperature dependence.

Assuming that the minority carrier mobility of the poly-Si films is 14 cm²/(V·s), obtained by the Hall measurement of independently prepared flash-lamp-crystallized n⁺-poly-Si films,²²⁾ the minority carrier diffusion length is estimated to be 60 μm when the minority carrier lifetime is 100 μs. This carrier diffusion length is much longer than the poly-Si film thickness, and hence, improvement in the solar cell properties will be realized by applying the improved defect passivation technique.

In summary, we have succeeded in realizing flash-lamp-crystallized poly-Si films with remarkably long carrier lifetime of 100 μs by applying post-annealing under N₂ ambient. The poly-Si contains a large number of H atoms on the order on 10²¹ /cm³ even after crystallization. This phenomenon is probably due to the unique crystallization mechanism of FLA, which results in a significantly shorter holding time of the maximum temperature during the crystallization process. The remaining H atoms effectively act to passivate the dangling bonds in the poly-Si films. This simple

passivation process is quite suitable for the mass-production of flash-lamp-crystallized thin-film poly-Si solar cells.

Acknowledgments

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Figure captions

Fig. 1 SIMS profiles of H atoms in the Si films before and after FLA. The inset shows Raman spectra of these Si films at a Si-H peak position.

Fig. 2 Microwave decay curve measured from the poly-Si film after N₂ annealing at 450 °C, indicating a minority carrier lifetime of 100 μs. The inset shows decay curves obtained from the poly-Si films after N₂ annealing and HPWVA, and the decay curve from the as-crystallized poly-Si film for comparison.

Fig. 3 Minority carrier lifetime of the poly-Si films after 30-min N₂ annealing as a function of annealing temperature.

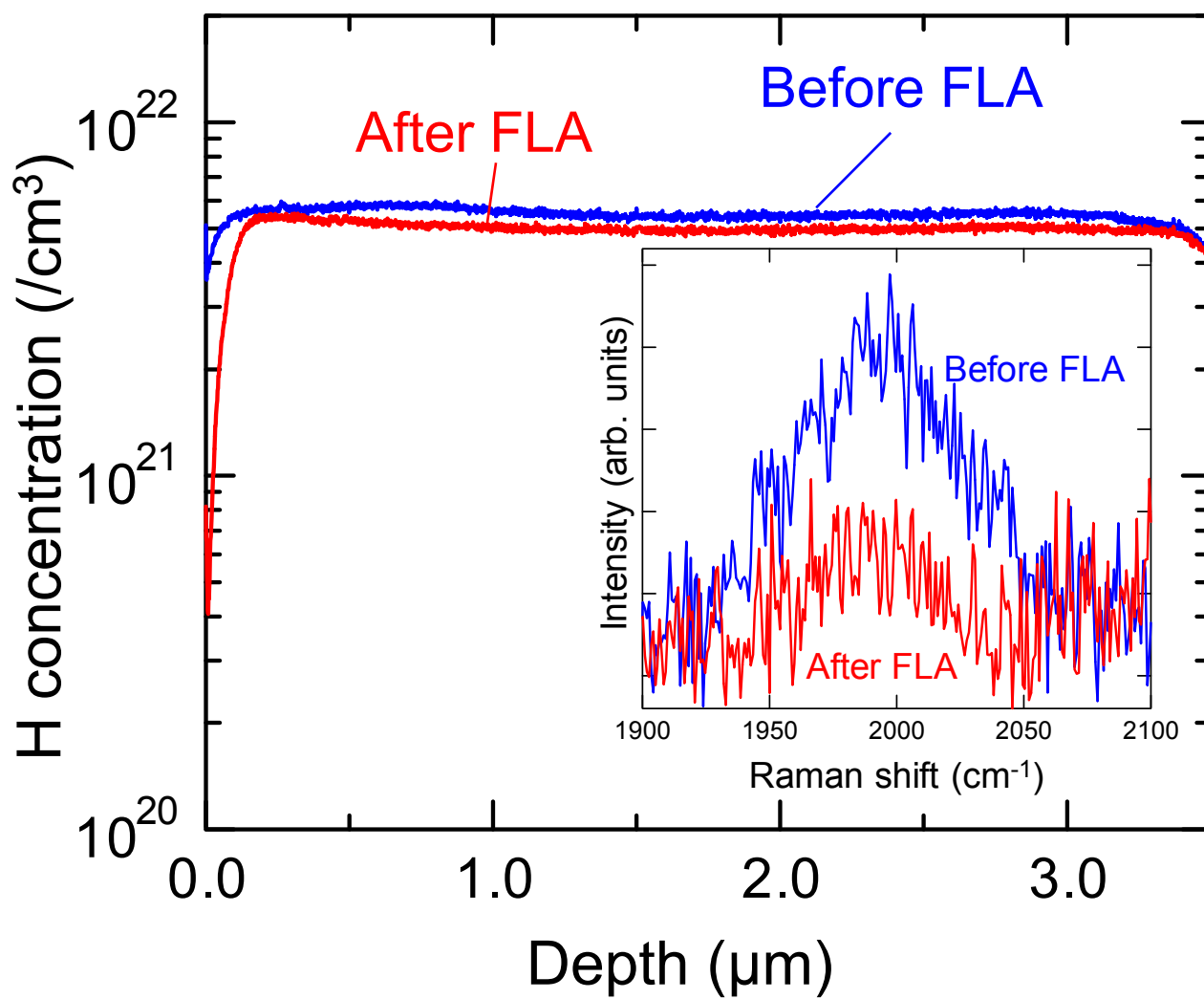


Figure 1 K. Ohdaira *et al.*,

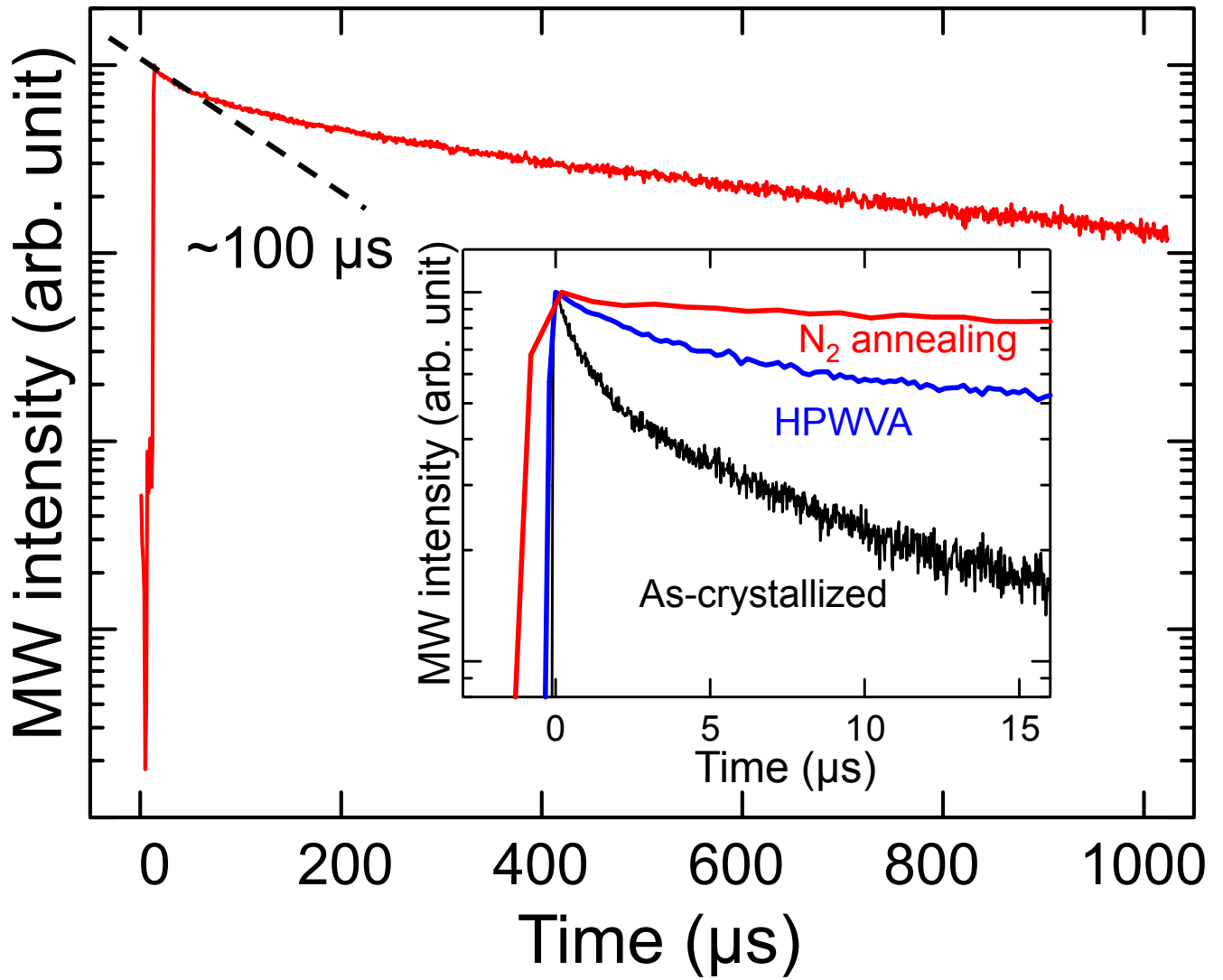


Figure 2 K. Ohdaira *et al.*,

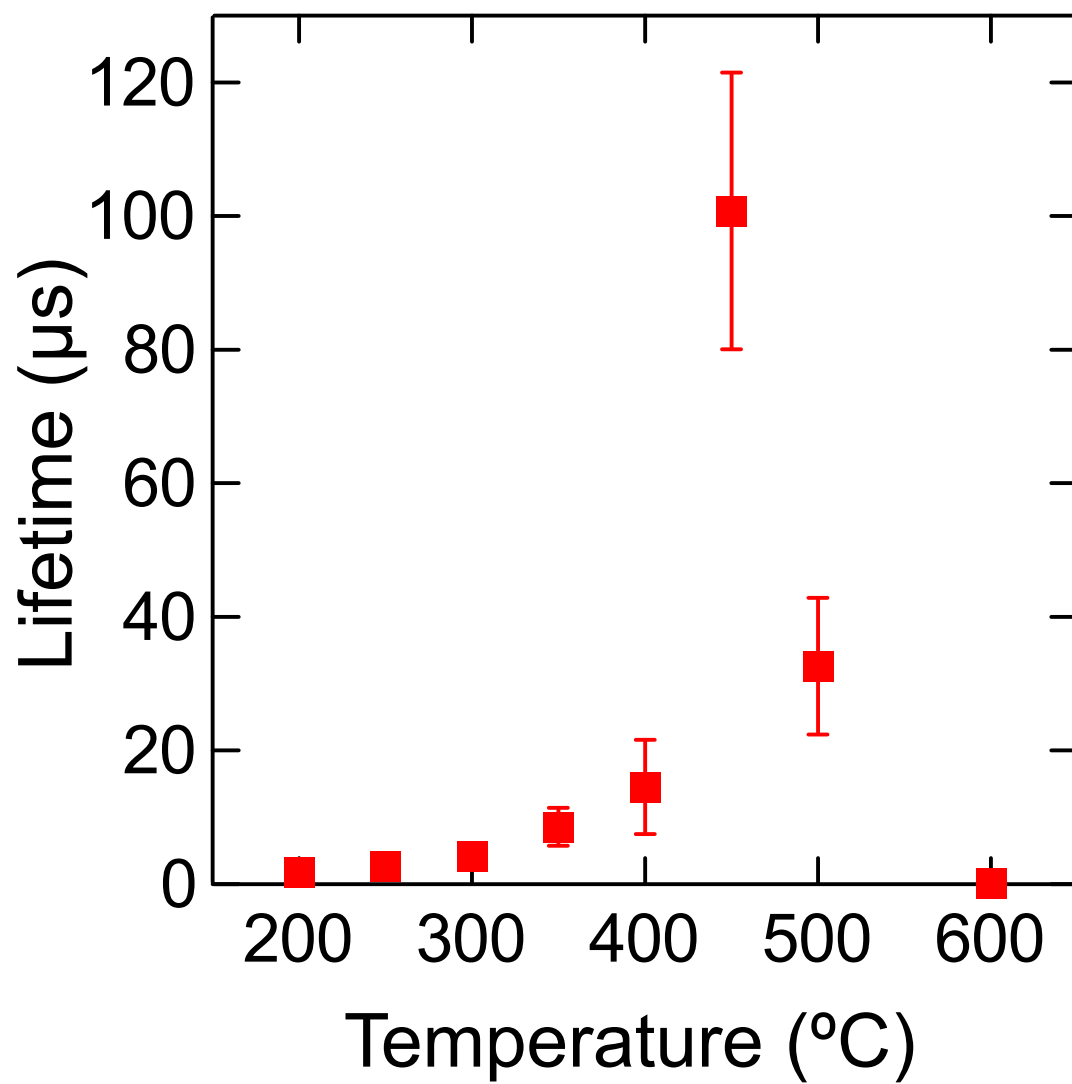


Figure 3 K. Ohdaira *et al.*,