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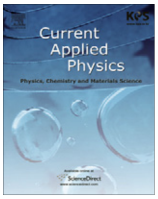

Flash-lamp-crystallized polycrystalline silicon films with remarkably long minority carrier lifetimes

Keisuke Ohdaira [a,b,*], Hiroyuki Takemoto [a], Takuya Nishikawa [a], Hideki Matsumura [a]

[a] Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan
[b] PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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ABSTRACT

Polycrystalline silicon (poly-Si) films formed by flash lamp annealing (FLA) of precursor a-Si films are found to hardly lose hydrogen (H) atoms during crystallization and keep the initial H concentration on the order of $10^{21}/\mathrm{cm}^3$. Short annealing duration and sufficient Si film thickness would lead to the suppression of H desorption. A characteristic lateral crystallization mechanism, referred to as explosive crystallization (EC), may also contribute to the prevention of H desorption due to rapid lateral heat diffusion into neighboring a-Si. Poly-Si films after annealing under N_2 or forming gas ambient shows remarkably long minority carrier lifetime compared to untreated films, indicating effective defect termination by H atoms remaining in the poly-Si films.

1. Introduction

Thin-film polycrystalline silicon (poly-Si) solar cells have advantages that they need much less amount of Si material than bulk crystalline Si (c-Si) cells, and are stable against light soaking, unlike thin-film cells using amorphous Si (a-Si) and microcrystalline Si (μc-Si) with low crystalline fraction. One of the most often-used approaches for the formation of poly-Si films is the deposition of precursor a-Si films on low-cost substrates such as glass substrates and following crystallization by annealing [1–4]. Solar cells with conversion efficiencies over 10% have been realized by using poly-Si films formed by solid-phase crystallization (SPC) of a-Si films through conventional furnace annealing [1], demonstrating the high potential of the concept of the thin-film poly-Si solar cells. For further cost reduction and improvement in throughput, rapid annealing techniques are expected to be applied, instead of the furnace annealing which requires temperature of approximately 600 °C and duration more than 10 h. The time-consuming annealing process also induces the desorption of hydrogen (H) atoms from Si films, resulting in defect generation, and thus, an additional defect termination process should be performed after the crystallization process.

Flash lamp annealing (FLA), with millisecond-order duration [5–7], is capable of crystallizing a-Si films a few micrometer thick without thermal damage to glass substrates due to its appropriate pulse duration, and would therefore be one of the candidates for the rapid crystallization process [8,9]. The short pulse duration might also realize the suppression of significant H desorption and resulting formation of poly-Si films with low defect density. In this study, we have investigated the H density of poly-Si films formed by FLA, the result of which clearly indicates that H atoms are hardly desorbed from Si films during FLA. We have also attempted defect termination by conventional furnace annealing using the high-density H atoms, on the order of $10^{21}/\mathrm{cm}^3$, remaining in poly-Si films, and observed significant enhancement in the minority carrier lifetimes with the furnace annealing temperature.

2. Experimental details

Fig. 1 shows a sample structure and the schematic of a FLA system used in this study. Cr films 200 nm thick were first deposited by sputtering on quartz glass substrates with a size of $20 \times 20 \times 0.7\ \mathrm{mm}^3$. n^+- and intrinsic (i-) a-Si stacked films 10 nm and 4.5 μm thick, respectively, were then deposited as precursor films on the Cr-coated quartz glass substrates in this order by catalytic chemical vapor deposition (Cat-CVD), whose detailed deposition conditions have been summarized elsewhere [10]. The FLA system used in this study equipped a Xe lamp array, which emits a pulse light with millisecond-order duration. A typical spectrum

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* Corresponding author. Address: Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan. Tel.: +81 761 51 1563; fax: +81 761 51 1149.
E-mail address: ohdaira@jaist.ac.jp (K. Ohdaira).

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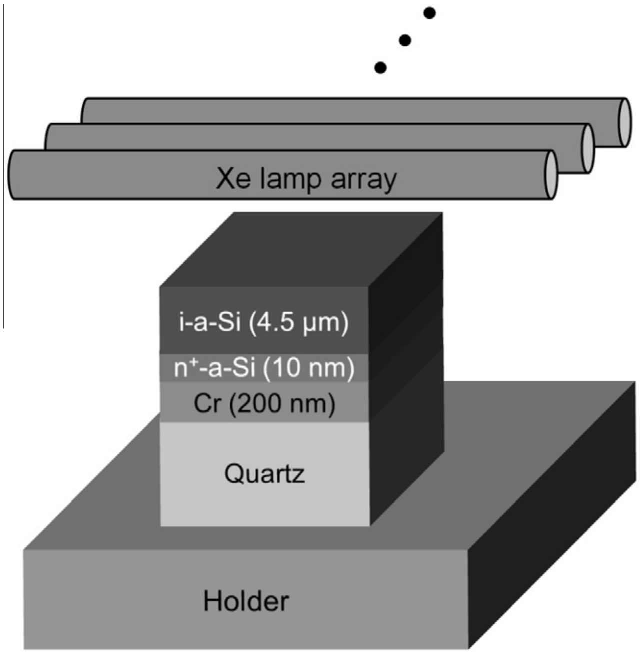

Fig. 1. Schematics of the structure of precursor a-Si films and a FLA system used in this study.

of flash lamp light can be seen elsewhere [7]. Each sample received only one shot of flash irradiation with 5 ms pulse duration and with an irradiance of approximately 20 J/cm^2. No dehydrogenation process was performed prior to FLA. The crystalline fraction (X_c) of the poly-Si films was checked by means of Raman spectroscopy, and was close to unity, as has been previously reported [8,9]. The poly-Si films have no preferred orientation, as shown in an X-ray diffraction (XRD) rocking curve of Fig. 2. The mobilities of the poly-Si films are typically 1–10 cm^2/V/s, according to Hall measurement. The densities of H atoms in the Si films before and after FLA were characterized by secondary ion mass spectroscopy (SIMS), and the H atom density of precursor a-Si films was approximately 5×10^{21}/cm^3.

The poly-Si surface regions 500 nm in depth were etched off using a mixed acid consisting of HF and HNO_3 since the regions contain a large number of voids formed during crystallization which would cause the recombination of excess carriers [11]. The poly-Si films were then put into a conventional furnace under forming gas (2% H_2, 98% N_2) or pure N_2 atmosphere 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 (Kobelco Research Institute, Inc., LTA-1510EP) [12]. This system can coincidentally detect microwave reflections from two areas with and without pulse laser illumination, and a decay curve corresponding only the variation of the number of carriers in a poly-Si film can be obtained from the difference of the two signals. Furthermore, this system can tune the phase of microwaves, which enables us to measure microwave decay curves of poly-Si films even on metal films that could reflect microwaves. We used a pulse laser of 349 nm in wavelength and 2×10^{13}/cm^2 in a photon density for carrier excitation, and a Gunn diode emitting microwave with a frequency of 26 GHz. The surfaces of the poly-Si films were temporarily passivated using iodine/ethanol solution during the μ-PCD measurement to eliminate the effect of surface recombination.

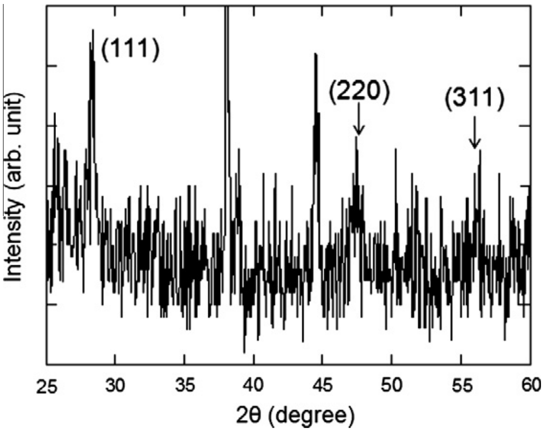

Fig. 2. Typical XRD rocking curve of a poly-Si film formed by FLA.

3. Results and discussion

Fig. 3 shows the density of H atoms, measured by SIMS, contained in poly-Si films formed by FLA, together with reported values for poly-Si films formed by other crystallization techniques such as furnace annealing [13], plasma-jet crystallization (PJC) [3], and excimer laser annealing (ELA) [14], for comparison. In the case of poly-Si films formed by means other than FLA, the number of hydrogen atoms drastically decreases to the order of 10^{20}/cm^3 or less, meaning the desorption of H atoms from the Si films during crystallization. On the other hand, flash-lamp-crystallized poly-Si films hardly lose H atoms and keep the initial concentration on the order of 10^{21}/cm^3. There would be some factors for the suppression of H atom desorption in the case of FLA. The first would be the shortness of annealing duration, particularly compared with furnace annealing. H atoms have to diffuse onto the surface of Si films within annealing duration for their desorption, and the shorter annealing duration would result in more suppression of H desorption, even annealing temperature is much higher. The second would be the difference of Si film thickness. From the viewpoint of H diffusion, thicker films would be better for the suppression of H desorption due to longer distance to reach the surface of Si, which would explain the difference of H atom density from poly-Si formed by ELA which has shorter pulse duration of less than 100 ns. Also in the case of poly-Si films formed by FLA, the surface region of the films, approximately 200 nm in depth,

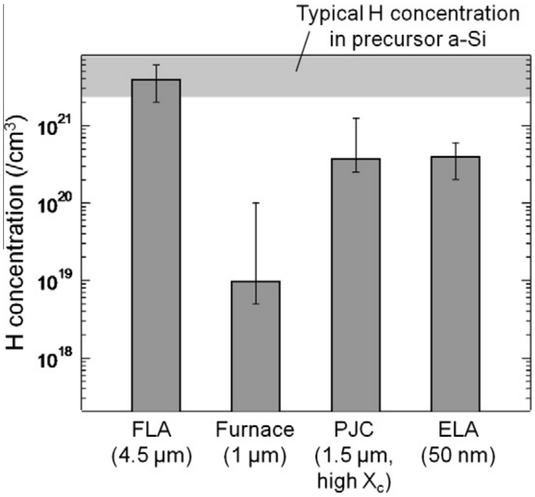

Fig. 3. H atom density in a poly-Si film formed by FLA. Reported values for poly-Si films formed by furnace annealing, PJC and ELA are also shown.