Poly-Si Films with Long Carrier Lifetime Prepared by Rapid Thermal Annealing of Cat-CVD Amorphous Silicon Thin Films

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Abstract

Polycrystalline silicon (poly-Si) films thicker than 1.5 μm, consisting of dense small grains called nano-grain poly-Si (ngp-Si), are formed by flash lamp annealing (FLA) of amorphous silicon (a-Si) films prepared by catalytic chemical vapor deposition (Cat-CVD) method. Crystallinity of the ngp-Si films can be controlled by changing lamp irradiance. Secondary ion mass spectroscopy (SIMS) profiles of dopants in the ngp-Si films after FLA shows no serious diffusion. A minority carrier lifetime of over 5 μs is observed from these ngp-Si films after defect termination process using high pressure water vapor annealing (HPWVA), showing possibility of application for high-efficient thin film solar cells.

Keywords

Annealing, Crystallization, Raman scattering, secondary ion mass spectroscopy (SIMS), Silicon, Solar cells, Microcrystalline, Minority carrier lifetime, Flash lamp annealing

1. Introduction

Microcrystalline Si (μc-Si) is an attractive material for high-efficient solar cells since it has no light-induced degradation, unlike a-Si films. However, there have been some issues in current μc-Si films formed by deposition techniques such as plasma-enhanced chemical vapor deposition (PECVD) and catalytic CVD (Cat-CVD). If highly crystallized μc-Si films are deposited by CVD method, oxygen atoms diffuse into grain boundaries in the films, which deteriorates electronic properties [1, 2]. In order to suppress this, amorphous Si (a-Si) is usually remained around grain boundaries by controlling deposition conditions. However, photo-generated carriers have to flow across a-Si with lower carrier mobility and higher defect density as well as μc-Si, resulting in serious reduction of diffusion length.

On the other hand, poly-Si films formed by rapid thermal annealing (RTA) of a-Si films prepared by Cat-CVD with hydrogen content of lower than 3% show no oxygen diffusion and thus have high carrier mobility of several ten cm^2/Vs [3]. We named this special μc-Si nano-grain poly-Si (ngp-Si) since it consists of closely packed small crystalline Si grains with a size of several ten nm. The dangling bonds generated due to desorption of hydrogen atoms can be effectively terminated by high pressure water vapor annealing (HPWVA) after RTA [4]. However, for fabrication of high-efficient thin-film solar cells using this ngp-Si films, crystallization time should be reduced down to about 10 milliseconds in order to avoid serious dopant diffusion as well as to suppress thermal damage to glass substrates.

Flash lamp annealing is a millisecond treatment using lamp irradiation and thus can be a candidate for a new process to form ngp-Si films and to fabricate ngp-Si solar cell structures without damage to glass substrates. There have been some reports for crystallization of amorphous Si (a-Si) with thickness of several hundred nm or less aiming to apply them to thin-film transistor [5], whereas no reports for formation of crystallized films over 1 μm for the purpose of application to solar cells.

In this study, we have investigated crystallization of Cat-CVD a-Si films over 1 μm by FLA. Their fundamental properties such as dopant diffusion and minority carrier lifetime of the formed films have also been investigated.

2. Experiments

Intrinsic a-Si thin films as precursors having thickness from 100 nm to 1500 nm were formed by Cat-CVD method on quartz substrates using SiH_4 and H_2 gases with flow rates of 50 and 10 sccm, respectively. Tungsten wires heated at 1750 ºC were used as catalyzers. Quartz substrates were heated at 250 ºC during deposition. The hydrogen contents of deposited a-Si films estimated by FT-IR measurements are about as low as 3 %, resulting in low hydrogen desorption during FLA. For investigation of dopant diffusion, p-i-n structures with each thickness of 20 nm, 700 nm, and 20 nm, respectively, were also formed in this order on SnO_2 films formed on glass substrates. Diborane (B_2H_6) and phosphine (PH_3) gases were used to form p- and n-type a-Si layers, respectively.

Pulse width of flash lamp irradiation was less than 10 milliseconds, while its irradiance, that is, incident energy, was systematically changed. HPWVA was performed to some of films after FLA under 3 MPa and 350 ºC in 60 min. The impurity profiles for p-i-n structures both before and after FLA were observed by secondary ion mass spectrometry (SIMS). Fundamental properties of the films were characterized by X-ray diffraction (XRD), and Raman spectroscopy. Minority carrier lifetimes were measured by microwave photoconductivity decay (μ-PCD) with an excitation laser wavelength of 770 nm.

3. Results

Raman spectra of films having a thickness ranging from 100 nm to 1500 nm after FLA are summarized in Fig. 1. Broad peaks centered at 480 cm^{-1} originating from a-Si are dominant in

the spectra for 100 and 300 nm-thick films, which is due to insufficient optical absorption for crystallization. By contrast, sharp peaks located at 520 cm^{-1} indicating crystallization of the film can be seen in the spectra of 1000 and 1500 nm films. This result is an indication of a possibility that a-Si films with thickness of over 1 μm, which is necessary for sufficient absorption of sunlight, can be crystallized by FLA.

Figure 2 shows grain size estimated by XRD measurement of μc-Si contained in the crystallized films with thickness of 1.5 μm as a function of relative irradiance. Although the grain size gradually increases with increasing lamp irradiance, it is still less than 60 nm, which is equivalent to that in ngp-Si formed by RTA for several ten seconds.

Figure 3 shows Raman spectra of crystalline Si films with thickness of 1.5 μm formed by FLA with different irradiance. Films annealed with low irradiance exhibit a broad peak associated with a-Si, whereas the film annealed with high irradiance at 1.48 in Fig. 2 exhibits no such signal. The results suggest that ngp-Si structure was formed in the case of high irradiance.

Figure 4 shows a microwave reflection decay of the 1.5 μm-thick ngp-Si film after HPWVA. Amazingly long minority carrier lifetime of 5-10 μs is seen. This lifetime is comparable to that of μc-Si formed by selective nucleation and solid phase epitaxy [6]. Only highly crystallized poly-Si films formed by high irradiance FLA show lifetime of this length.

Figures 5 (a) and (b) show SIMS profiles for phosphorus and boron atoms in a p-i-n structure before and after FLA, which is treated after formation of whole structure. Although both of dopants have slightly diffused into intrinsic layers, p-i-n structure has still maintained. This larger impurity diffusion compared with that reported in ref. 7 is probably due to too much lamp irradiance and can be suppressed by optimization of the annealing conditions.

4. Discussion

According to minority carrier lifetime of 5-10 μs, the diffusion length can be estimated to be over 10 μm assuming minority carrier mobility of 10 cm^2/Vs, using equations of $L = (D\tau)^{1/2}$ and

$D/\mu = kT/q$, where L, D, τ, μ represent minority carrier diffusion length, diffusion coefficient, lifetime and mobility, respectively. The assumption of mobility of 10 cm^2/Vs is based on the measured Hall effect mobility of ngp-Si formed by RTA for several ten seconds [3]. This minority carrier diffusion length is much longer than the film thickness. Without HPWVA treatment, such significant signals cannot be seen, which is probably because minority carriers generated by a laser pulse are immediately annihilated due to a large number of unpassivated defects. Therefore, this result also indicates that HPWVA is essential for forming high-quality ngp-Si films with long minority carrier lifetime.

5. Conclusions

The study demonstrated the possibility that a-Si films formed by Cat-CVD deposited on quartz substrates with thickness of the order of micrometer can be crystallized by FLA. High irradiance resulted in ngp-Si film consisting of high quality grains smaller than 60 nm. HPWVA treatment is effective to terminate defects for these ngp-Si films and consequently a long minority carrier lifetime of 5-10 μs is observed from the ngp-Si films. The long carrier lifetime corresponds to the minority carrier diffusion length of over 10 μm assuming minority carrier mobility of 10 cm^2/Vs. Dopant diffusion during the FLA treatment is so small that p-i-n structures have been maintained, indicating that the FLA process and ngp-Si films formed by it are applicable for high-efficient thin film solar cells.

Acknowledgments

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Figure Captions

Fig. 1 Raman spectra of Si films with various thickness after FLA.

Fig. 2 Grain size in crystallized Si films with thickness of 1.5 μm as a function of relative lamp irradiance.

Fig. 3 Raman spectra for crystallized Si films with thickness of 1.5 μm treated under various lamp irradiance.

Fig. 4 Microwave reflection decay of the ngp-Si with thickness of 1.5 μm measured after HPWVA.

Fig. 5 SIMS profiles for (a) phosphorus and (b) boron atoms before and after FLA.

Figure 1

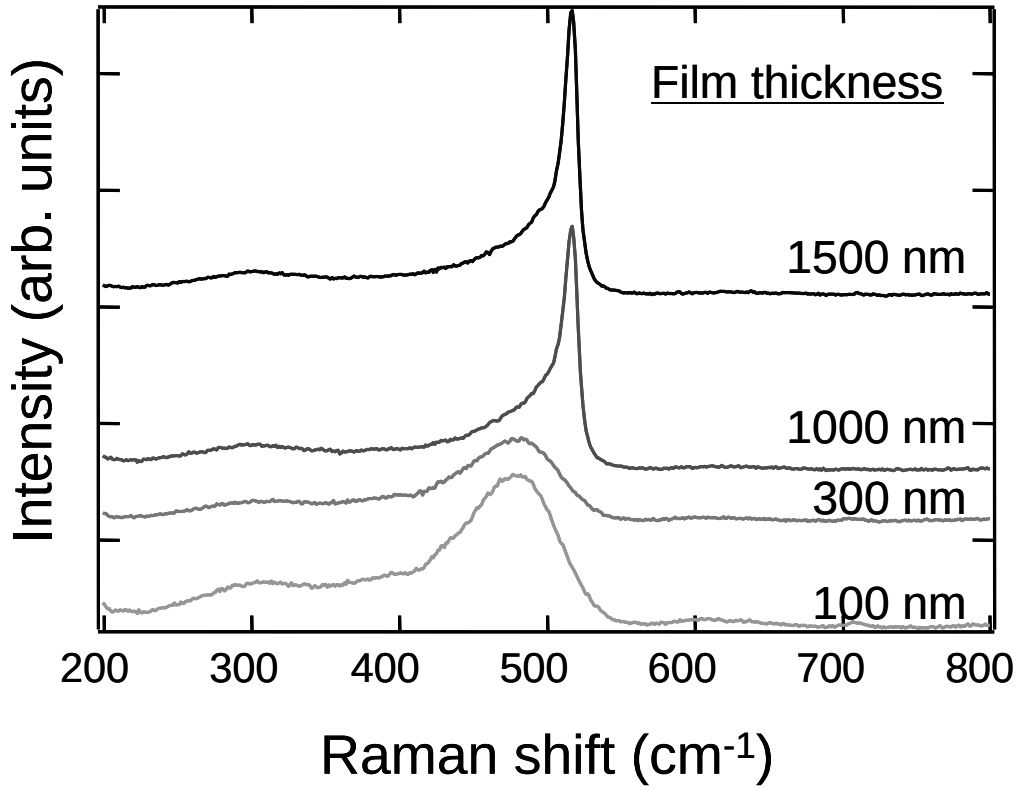

Film thickness
1500 nm
1000 nm
300 nm
100 nm
Intensity (arb. units)
200
300
400
500
600
700
800
Raman shift (cm-1)

Figure 2

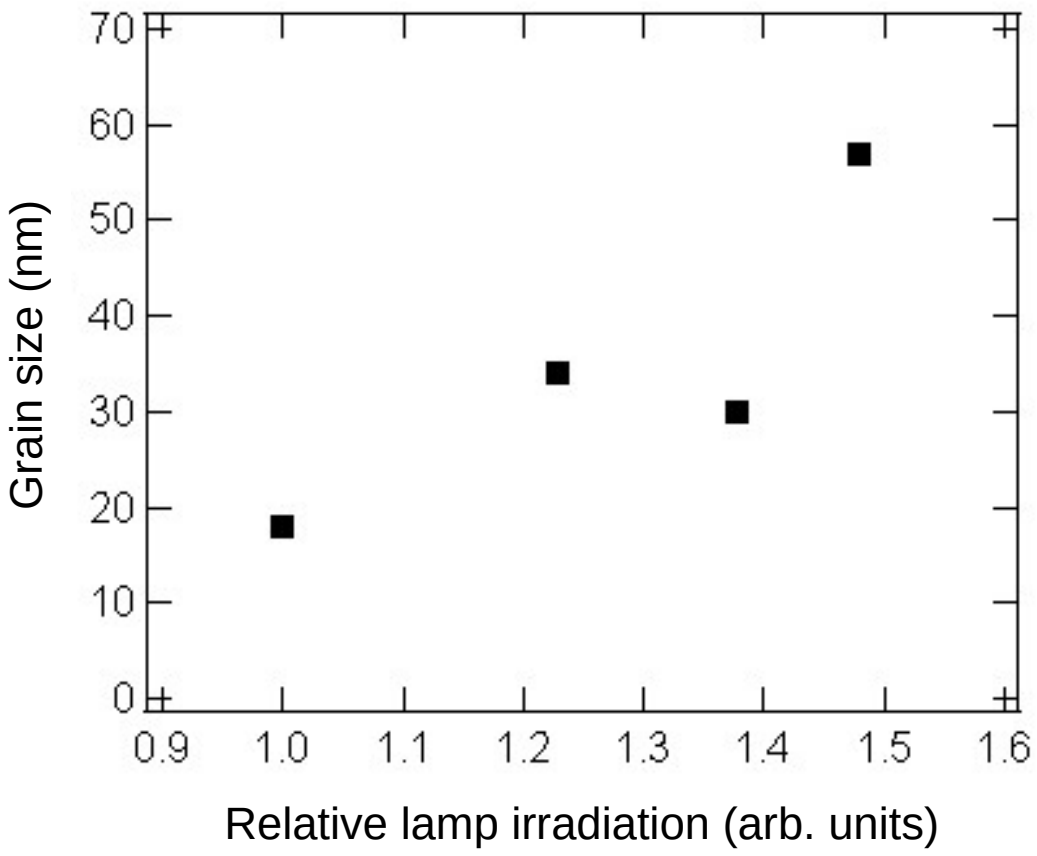

Grain size (nm)
70
60
50
40
30
20
10
0
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
Relative lamp irradiation (arb. units)

Figure 3

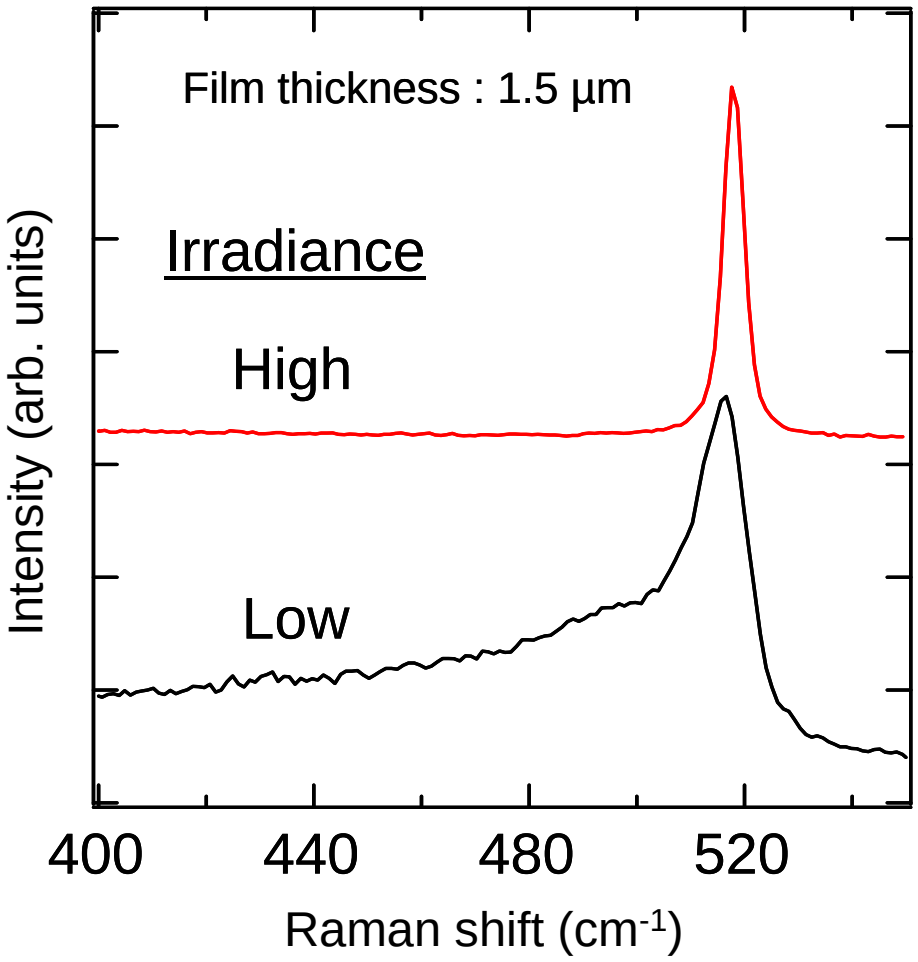

Film thickness : 1.5 μm
Irradiance
High
Low
Intensity (arb. units)
400
440
480
520
Raman shift (cm-1)

Figure 4

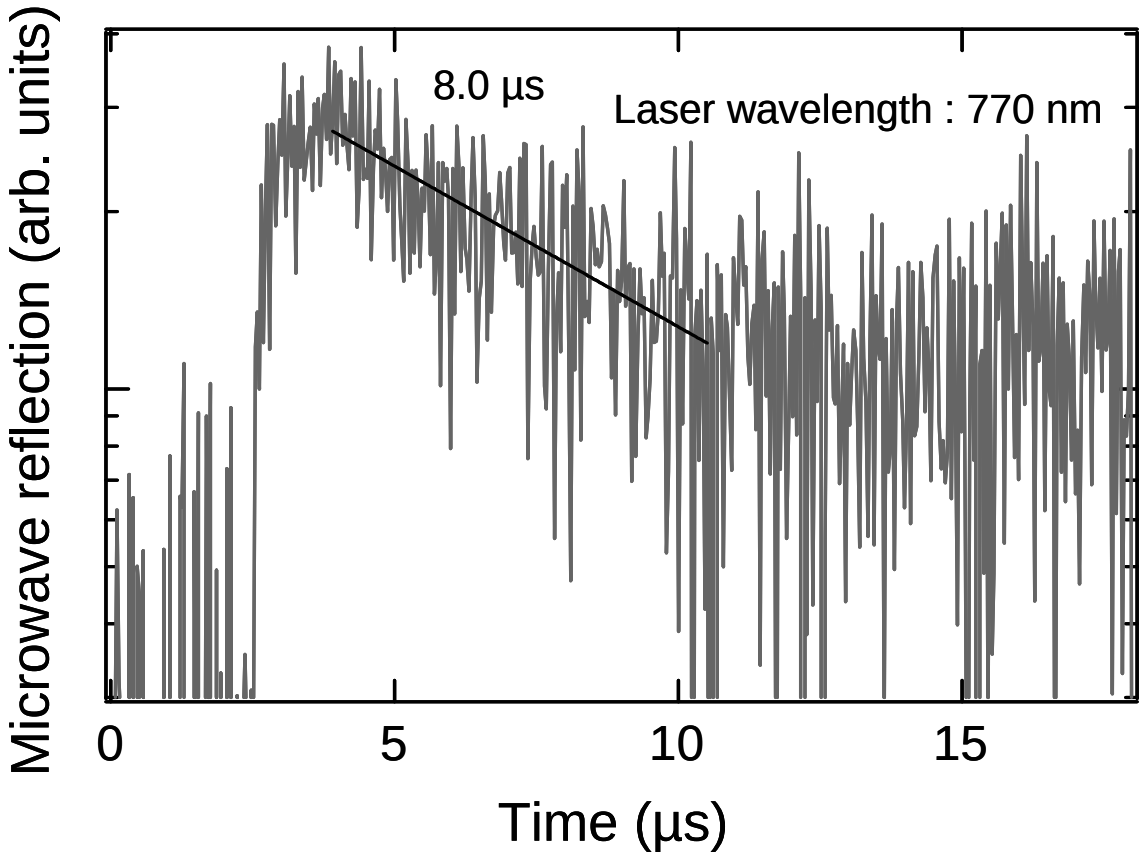
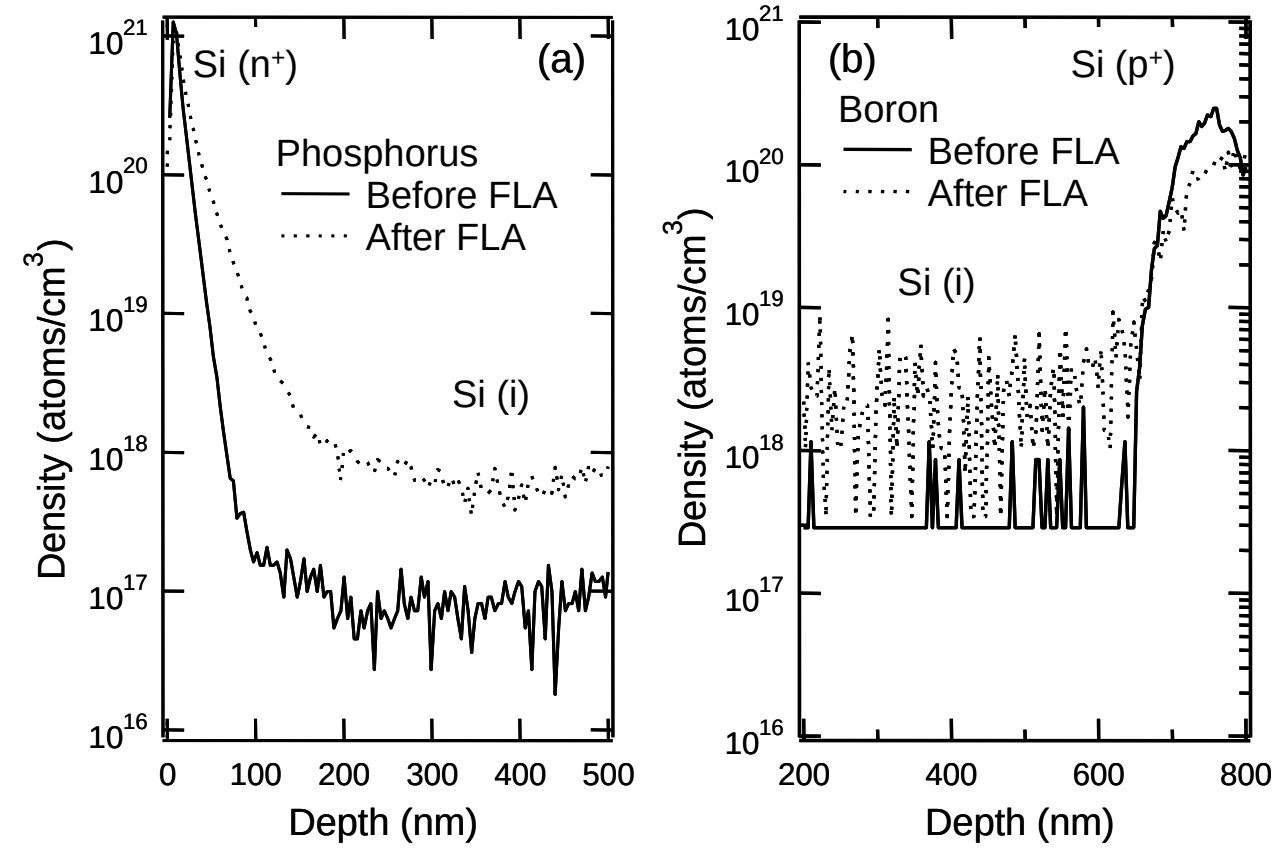

Microwave reflection (arb. units)
8.0 µs
Laser wavelength : 770 nm
0
5
10
15
Time (µs)

Figure 5


Si (n+)
(a)
Phosphorus
Before FLA
After FLA
Si (i)
Density (atoms/cm3)
Depth (nm)
(b)
Si (p+)
Boron
Before FLA
After FLA
Si (i)
Density (atoms/cm3)
Depth (nm)