

H-plasma-assisted aluminum induced crystallization of amorphous silicon*

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Abstract: A technique to improve and accelerate aluminum induced crystallization (AIC) by using hydrogen plasma is proposed. Raman spectroscopy and secondary ion mass spectrometry of crystallized poly-Si thin films show that hydrogen plasma radicals reduce the crystallization time of AIC. This technique shortens the annealing time from 10 to 4 h and increases the Hall mobility from 22.1 to 42.5 cm²/(V·s). The possible mechanism of AIC assisted by hydrogen radicals is also discussed.

Key words: poly-silicon; H-plasma; aluminum induced crystallization

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1. Introduction

Poly-Si thin films prepared on glass substrate at temperatures lower than 600 °C are of scientific interest because of their application in flat panel displays^[1] and solar cells^[2].

However, each preparation technique for poly-Si thin films, such as solid phase crystallization (SPC) and rapid thermal annealing (RTA), laser crystallization and metal-induced crystallization (MIC), has restrictive factors. For example, SPC and RTA need high temperatures, which sometimes exceed the glass substrate limit, and laser crystallization requires expensive equipment. In contrast, MIC using Al as the inducing metal (called AIC) is a promising method because of its low cost and relatively short annealing time^[3]. Furthermore, AIC can yield a large grain size^[4] and the high preferential (100) orientation^[5] p-doped^[6] material is useful as a high quality seed layer for solar cells.

However, AIC still would profit from shortening its relatively long annealing time of about ten or more hours at low temperatures (around 450 °C^[7]). Furthermore, poly-Si thin films crystallized by any crystallization method always contain many defects, resulting from grain boundaries^[7] or intragrain^[8], which severely affect the performances and stabilities of the devices made by such poly-Si thin films. Hydrogen plasma treatment is one of the most common ways to deal with these problems due to its low cost and simple technique^[9].

In this paper, AIC in hydrogen plasma surroundings is proposed. This technique combines crystallization and passivation into one process, which not only reduces the crystallization time but also passivates the defects in the material.

2. Experimental procedure

At first, 1000 Å a-Si was deposited by low pressure chemical vapor deposition (LPCVD) on Eagle 2000 Corning glass.

This was followed by a less than 10 nm SiO₂ separation layer and a 1000 Å thick evaporated Al film. The glass/a-Si/SiO₂/Al stack was put into a hydrogen plasma enhanced (PECVD) chamber with H₂ of 30 sccm at 800 mTorr and T_s = 450 °C for several hours. The RF power is 40 W. This process is called HAIC. After completed crystallization, the residual Al on the top surface is etched off using a standard Al etching solution.

In order to evaluate the effect of the H-plasma on crystallization we also carried out traditional AIC by just heating the samples in vacuum at 450 °C for crystallization. That means the glass/a-Si/SiO₂/Al stack has been annealed in a vacuum chamber without H-plasma. The other experimental condition was the same as with HAIC. We compared the passivation effect of HAIC and AIC.

The poly-silicon films were characterized by Raman spectroscopy (Renishaw inVia), secondary ion mass spectrometry (SIMS) and Hall mobility measurements (Bio-Rad Model HL5500PC). The results were compared and analyzed.

3. Results and discussion

3.1. Effect of promotion crystallization using Al as the inducing source in H plasma^[10]

Figure 1 shows the Raman spectra of the samples annealed for 2–4 h in hydrogen plasma. We found the typical TO mode of a-Si at 480 cm⁻¹ after 2 h in the hydrogen plasma, which indicated that the sample did not crystallize. After 3 or 4 h annealing in the same condition, we can see a peak at about 520 cm⁻¹ in both figures. Using three Gaussian curves with peaks at 480, 510 and 520 cm⁻¹ to fit the Raman spectra, the crystalline volume ratio (X_c) was calculated. The peak at 510 cm⁻¹ is commonly attributed to the presence of tensile strained Si–Si bonds at grain boundaries^[11]. The X_c is given by the ratio of the inte-

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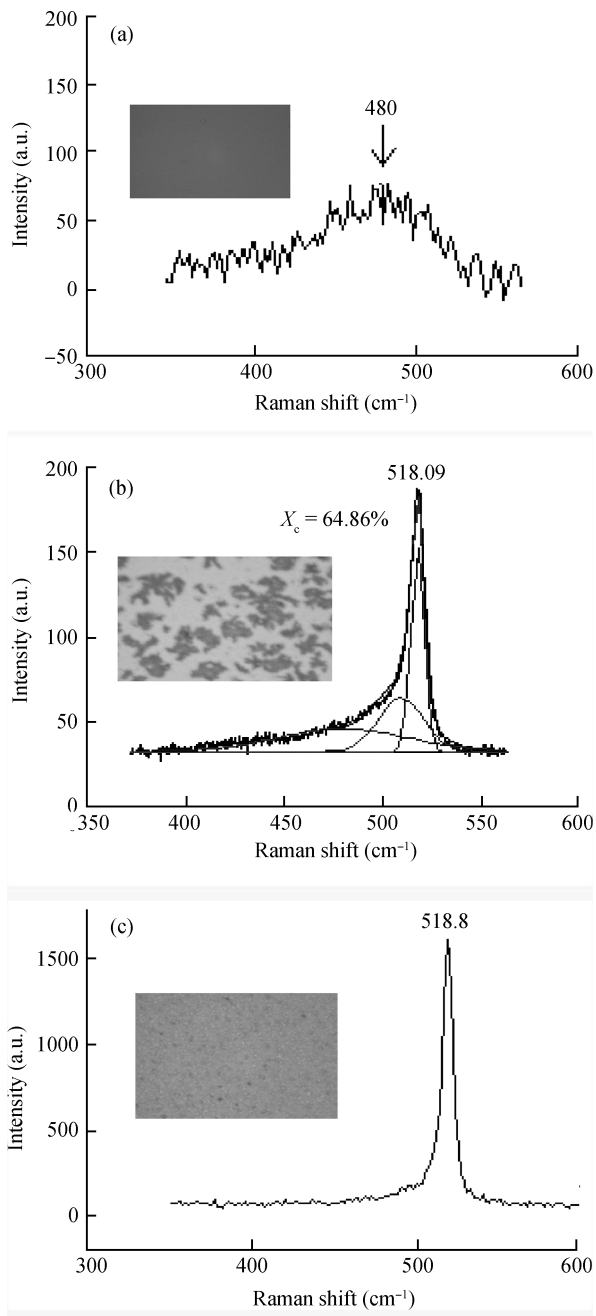


Fig. 1. Raman spectra of the samples after different annealing times. (a) 2 h. (b) 3 h. (c) 4 h.

grated intensities of the Gaussian curves at 510 and 520 cm^{-1} to the total integrated intensity. The peaks at 480 and 520 cm^{-1} are observed in the films after 3 h, which indicates that the samples are partly crystallized with $X_c = 64.8\%$ obtained by a 3-peaks fitting results as shown in the curve labeled “3 h”. After 4 h of treatment, no signal around 480 cm^{-1} can be observed and the peak is very sharp. This indicates that the samples are totally crystallized, which can also be proved by its XRD spectrum, as shown in Fig. 2. The insert in each Raman figure shows a photo of the surface taken with the micro-Raman apparatus microscope. They match up with the crystallization situation shown by the Raman curves. As can be observed in Fig. 2, the XRD peaks are at approximately 28.4°, 47.38° and 56.08°, corresponding with the (111), (220) and (311) orientation, respec-

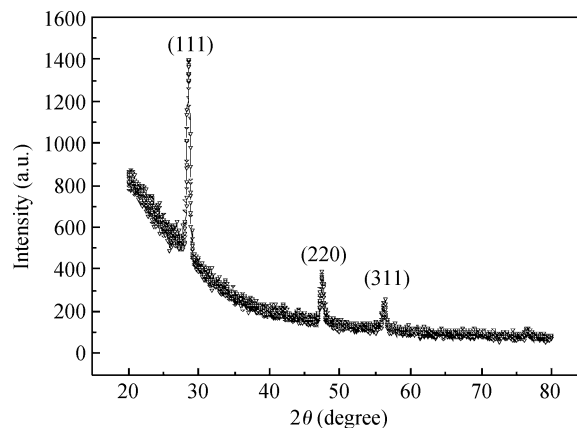


Fig. 2. XRD spectrum of the poly-Si after annealed for 4 h.

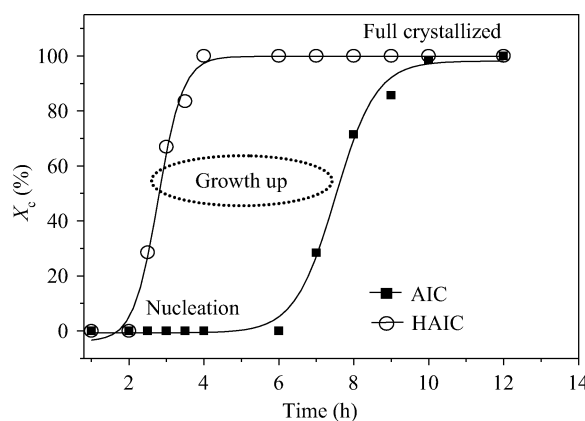


Fig. 3. Crystalline volume factor (X_c) as a function of annealing time for samples exposed to hydrogen plasma (HAIC) or not (AIC).

tively. The (111) is the preferential orientation which is identical to the reported one. The inclination of the first peak in the XDR spectrum is due to the effect of the amorphous glass substrate. Because the Si film is very thin (only 100 nm), lots of X-ray could get into the amorphous glass substrate after penetrating the poly-Si thin film, therefore, an amorphous shoulder could be seen obviously in the XRD spectrum. Nevertheless, this amorphous shoulder has no relationship with the crystallization of the poly-Si film.

In order to compare the time needed for complete crystallization of HAIC with normal AIC, we measured X_c versus annealing time of each sample as shown in Fig. 3. After 6 h, AIC started to crystallize and after 12 h crystallization was fully completed. For the curve named “HAIC”, the nucleation time is just 2 h. After 4 h, the films are crystallized completely while annealing in the H-plasma. Another feature of HAIC is fast crystal growth, as reflected by the rise gradient. That means one obtains short and rapid crystallization by HAIC. Would the short and rapid crystallization under H-plasma damage the performances of the HAIC poly-Si? We compare the Hall mobility of HAIC and AIC poly-Si materials as shown in Fig. 4. The mobility (42.5 $\text{cm}^2/(\text{V}\cdot\text{s})$) of samples crystallized with H-plasma is much higher, and nearly double that (22.1 $\text{cm}^2/(\text{V}\cdot\text{s})$) when no H-plasma accompanied crystallization.

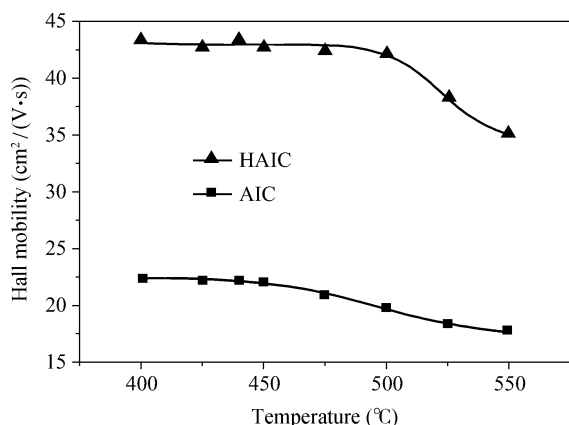


Fig. 4. Comparison of Hall mobility of the poly-Si crystallized by AIC with (HAIC) or not (AIC).

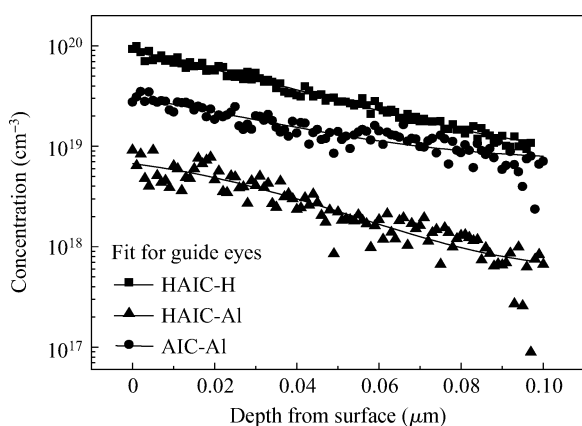


Fig. 5. Comparison SIMS of Al and H in poly-Si crystallized in H plasma or not.

3.2. What is the reason for the accelerating crystallization in H-plasma?

As mentioned in Ref. [12], Al-Si alloy is a lower melting point system, so Al induced-crystallization of Si involves five important steps, as follows: Si atoms migrate (step ①) and dissolve into aluminum (step ②). When the concentration of Si dissolved in Al is higher than its critical concentration then Si will segregate (step ③) and crystallize (step ④) from Al. The Al will also migrate into Si (shown as step ⑤) in the opposite direction. This is a layer-exchange process. In this case the rapid migration and dissolution of Si atoms in the Al film will be an important factor for promoting the nucleation and crystallization.

Al atom distribution in fully crystallized poly-Si samples by HAIC and AIC are shown in Fig. 5. The Al distribution in HAIC is steeper than that in AIC. Because the Al and Si atoms move in opposite directions, the Al distribution in Si film should be similar to that of Si in Al films. The steeper gradient of Al in HAIC poly-Si implies a steeper gradient of Si in the Al part of HAIC poly-Si compared to that in AIC. The gradient is steeper when the diffusion is faster, so it is favorable to rapidly reach and exceed the critical concentration for nucleation, which then shortens the crystallization. Figure 4 also shows an abundance of H in HAIC poly-Si. No H signal

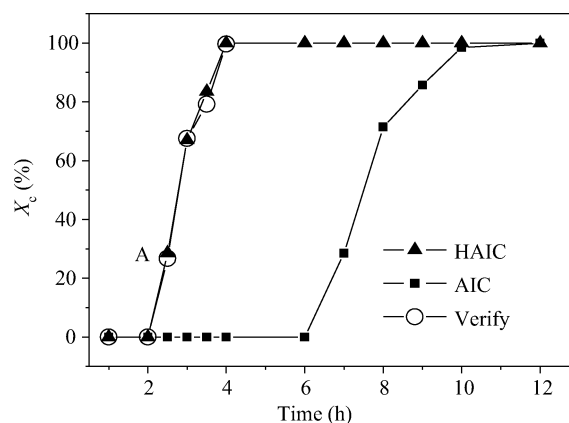


Fig. 6. Verification experiment (Here, curve AIC is just for comparison).

could be found in AIC samples, which indicates that hydrogen plasma radicals could penetrate the Al film, accompanied by vacancies formed at the surface^[13], and migrate through the very thin oxide^[14]. The hydrogen could reach the silicon layer, interact with Si atoms and then passivate the defects in the material during the crystallization process. Finally, Figure 4 shows that the Al content in HAIC poly-Si annealed in H plasma is half an order of magnitude lower than that in AIC poly-Si annealing in vacuum. This means that the H plasma is also active to decrease the Al leftover in poly-Si films. Therefore the electron mobility in HAIC poly-Si is much higher than that in AIC samples, as shown in Fig. 3.

The hydrogen plasma reduces the crystallization time from a-Si to poly-Si thin films. The H-plasma radicals provide an additional thermal budget for crystallization, which can promote the crystal growth. As a result, the crystallization time has been reduced and the performance of the poly-Si film can also be improved.

3.3. Mechanism of AIC enhanced by H plasma

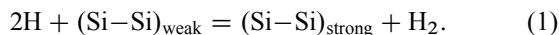
We further explored a hypothesis to explain the mechanism of the enhancement effect of H-plasma.

We first crystallized the sample using Al as an inducing source in hydrogen plasma just for 2.5 h (point “A” in Fig. 6). We then turned off the plasma power and continued annealing at the same temperature in vacuum for several hours to complete the crystallization. We measured the Raman spectrum and calculated X_c . The result is shown in Fig. 6, which includes HAIC and normal AIC results for comparison. We selected the time of 2.5 h because then it just passes the nucleation process and starts crystalline growth, as we know from the earlier results.

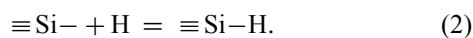
As shown by Fig. 6, the curves labeled as “HAIC” and “Verify (by open circle)” coincide. After 4 h, the sample is totally crystallized after annealing for the last 1.5 h just in vacuum without hydrogen plasma. That means the H plasma has provided enough Si concentration and a gradient of the Si atom distribution in the Al film to maintain subsequent crystalline growth under these experimental conditions. This result supports the view that the hydrogen plasma mainly contributes to Si transportation thereby being beneficial to nucleation and

grain growth.

The hydrogen radicals with higher energy in plasma are able to move through the interstice around the strained bonds of Al or Si and react with Si to form Si–H bonds. The Si–H bonds are subsequently easier to break and release single Si atoms because the enthalpy of Si–H bonds is smaller than that of Si–Si bonds^[15]. Single atoms of Si neighboring Al then dissolve in the Al film and create a steeper gradient of Si atoms there. The steeper slope of Si atoms in the Al film will promote the diffusion of Si and dissolution in Al. The concentration of Si dissolved in the Al film will reach and exceed the critical value of nucleation to form the Si grain nuclei separated out from the Al film thereby shortening the formation time of crystalline-nuclei. The steeper distribution of Al in HAIC shown by SIMS in Fig. 5 implies that its steeper slope will also accelerate the layer-exchange process resulting in a higher growth rate. The rapid layer-exchange of Si and Al films will contribute to Al migration out of the Si film. At the same time, the H in HAIC will passivate the crystallized poly-Si during the crystallization process. As mentioned above, the AIC includes five steps. During step ④, the Si begins to crystallize, at that time, some weak Si–Si and dangling bonds may be created in the Si network structure. These weak Si–Si and dangling bonds in the poly-Si may form defects and trap carriers. In the H-plasma atmosphere, atomic hydrogen plays two roles during HAIC: (1) breaking weak Si–Si bonds, leading to a removal of Si atoms weakly bonded to another Si. And then, this site is replaced with a new film precursor, SiH₃, creating rigid and strong Si–Si bond, giving rise to a more ordered structure as shown in Eq. (1).



(2) Combination with the dangling bonds as shown in Eq. (2), preventing it trapping carriers.



Consequently, the defects in the poly-Si can be passivated during the HAIC process. Thereby, the performance of the crystallized poly-Si has been improved.

4. Conclusion

We propose that aluminum induced crystallization in a hydrogen plasma combines crystallization and passivation into one process. Raman spectroscopy, SIMS and Hall mobility data reveal that it can not only reduce the annealing time of AIC but also enhance the performance of crystallized poly-Si. The mechanism of this technique is mainly that hydrogen plasma radicals penetrate the aluminum and the thick oxide layer resulting in more Si atom diffusing into the Al, and reaching a critical concentration for the acceleration of nucleation thereby causing crystallization. The growth time is also be shortened by hydrogen plasma radicals possibly because of

a steeper gradient of Si in the Al layer of HAIC sample than that in AIC.

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