## P-67: Investigation on the Hydrogen-Assisted Al Induced Metal Crystallization Poly-Si

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#### Abstract

The hydrogen plasma-assistant Al induced crystallization (HAIC) technology has been proposed in this paper. This technology integrates the crystallization and passivation into one process. The annealing time has been reduced by almost half of the traditional AIC technology. Additionally, the HAIC technology can also improve the resulted poly-Si performance obviously. This technology makes the AIC technology more suitable for the industrial application.

#### **1.** Introduction

Poly-si thin films prepared on glass substrate at the temperature lower than 600°C is a promoting technology applied in flat panel displays<sup>[1]</sup>, solar cells<sup>[2]</sup>, sensor, etc. Among the crystallization technologies, AIC (Aluminum Induced Crystallization) is a promising method for its lower cost than LA (laser annealing) and lower annealing temperature than NI-MIC (nickel metal induced crystallization), which makes it more suitable for industrial application. Furthermore, AIC can prepare the high preferential (100) orientation p-type poly-Si which can be used as the seed laver in poly-Si thin film solar cells. However, AIC still need a relatively long annealing time. Besides, the poly-Si crystallized by AIC technology always has grain boundary defects <sup>[3]</sup> and/or intra-grain defects <sup>[4]</sup> in it, which would severely deteriorate the performance and stability of their devices. The hydrogen passivation was one of the most effective methods to passivate the defects in poly-Si thin film.

In this paper, the aluminum induced crystallization assisted by hydrogen plasma technology (HAIC) has been proposed. This technology integrates the crystallization and passivation into one process, which can not only reduce the annealing time of AIC but also passivate the defects in the material simultaneously.

#### 2. Methods

1000 Å a-Si was deposited by LPCVD on Eagle 2000 Corning glass, followed by deposition of 10nm SiO<sub>2</sub>. Then, 1000 Å Al was evaporated on the a-Si thin film. The glass/ a-si/ Al stack was put into a PECVD chamber and annealed in hydrogen plasma with the substrate temperature of 450°C. To investigate the structure of the crystallized Si films, the residual of Al on the top surface was etched using standard Al etching solution (80% phosphoric acid+5% nitric acid+15% DI water). In order to compare, we also prepared the poly-Si thin film by the traditional AIC method. The glass/ a-si/ Al stack was annealed in vaccum at 450°C.

#### 3. **Results**

#### 3.1. AIC in H plasma

Figure1 shows the optical micrograph images of the sample surface after being annealed for different time under hydrogen plasma condition at 450°C. It can be observed that with the time goes by, the grain size become lager and larger. After 4 hours, the adjacent grains meet, forming a continuous Si layer.

This growth behavior indicates that the mechanism of HAIC is probably similar with that of the traditional AIC, but the crystallization rate is quicker. In order to compare, the crystalline volume fraction of the sample prepared by HAIC and traditional AIC method as a function of annealing time is shown in fig 2. Here, the crystalline volume fraction (Xc) measured by Raman spectra was used to describe the crystalline degree of the films. As well known, the Xc of the sample can be deduced from its Raman scattering spectra by the Gaussian fitting. Xc is given by the ratio of the integrated intensities of the Gaussian curves at 510 and 520



Fig. 1 The optical microscope images of sample surface after different time annealing and Aletching

to the total integrated intensity. As shown in Fig 2, after being annealed for 4 hours, the sample prepared by HAIC is fully crystallized, well, that by traditional AIC is still amorphous. The latter need nearly 10 hours to be fully crystallized. That is to say, the crystallization rate of the HAIC is quicker than that of traditional AIC by almost 2.5 times with the same annealing temperature. Additionally, the hall mobility of the fully crystallized poly-si prepared by HAIC is 42.5cm<sup>-1</sup>/V·S, which is

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almost twice higher than that by AIC. This illustrates that HAIC technology integrates the crystallization and passivation into one process, as a result, the annealing time is reduced and the defects in the poly-Si is passivated simultaneously.



Fig. 2 Crystalline volume fraction (Xc) of the sample prepared by HAIC and traditional AIC method as a function of annealing time



Fig. 3 The SIMS result of poly-si prepared by HAIC

#### 3.2. The analysis of HAIC mechanism

From Fig3, we can see that in the HAIC process, the H really participates in the crystallization process. The key problem is how the H improves the crystallization process involves two distinct steps: the first step is the incubation period during which the nuclei forms and no crystallization occurs; the second step is the crystal growth period during which the crystal becomes to grow from the nuclei until the crystallization completes. As for AIC, there are five important steps in this process: (1) Si transport across the oxide layer (2) Si diffusion in the Al-layer (3) nucleation probably appears at grain boundaries in the Al (4) grain growth and (5) Al transport across the oxide layer.

In order to know which step the H plays its role, we did experiment as follow: firstly, the sample was annealed in hydrogen plasma (HAIC) for 2.5 hours, and then, the RF power for the H plasma was turned off, keeping the annealing at 450°C in vaccum, during this period, there is no H plasma. In this experiment, the time for HAIC is only 2.5 hours which is just in the nuclei step. Therefore, if the role of H plasma contributed to the nuclei step, then, the crystallization time should be shorter than that of the traditional AIC process and the obtained curve of Xc vs. annealing time is similar as curve A (HAIC) in fig 4, otherwise, if the role of H plasma contributed to the crystal growth step, then the crystallization time should be similar as that of the traditional AIC process and the obtained curve of Xc vs. annealing time is similar as curve B(traditional AIC) in fig 4. In Fig.4, curve C refers to the result of the experiment mentioned above. As can be observed that curve C is almost the same as curve A, which illustrates that the H plasma plays its role mainly during the nuclei step. Because the plasma power has been turned off at 2.5 hours, it would not play its role in the next step. So, the H plasma can reduce the nuclei time in the crystallization process. Why? We supposed that the H plasma can break lots of the Si-Si bonds in the a-Si network and form into Si-H bond.



Fig. 4 The crystalline volume fraction (Xc) of the sample prepared by HAIC, traditional AIC and verify experiment method as a function of annealing time

Moreover, the enthalpy of Si-H bond is lower than that of Si-Si



Fig. 6a SIMS results of HAIC samples after annealed at different temperature

bonds. Consequently, Si–H bond is easier to be broken than Si-Si bond by the thermal energy. As a result, more Si atom can diffuse into the Al, and the Si concentration in Al will be easier to exceed the critical concentration for the nuclei forming, leading to reduction of crystallization time.

# **3.3.** The enhancement of the performance of the resulted poly-Si by HAIC

The advantage of HAIC is not only reducing the annealing time but also improving the resulted poly-Si performance. To compare, we also prepared the AIC sample with the H plasma post treatment (named AIC+H). And then, the poly-Si samples prepared by HAIC and AIC+H were annealed at different temperature in vacuum. From fig. 5, we can observe the hall mobility of the resulted poly-Si. The hall mobility of HAIC poly-Si is higher than that of AIC+H poly-Si, which indicates that the defect passivation in HAIC technology is more effective than that in the traditional H plasma post treatment technology. It has been reported that the H in the Si thin film will escape when the temperature is higher than 350°C, which will cause the instability of the poly-Si. As can be seen from the SIMS results in fig 6, the change of H concentration in the HAIC poly-Si is smaller by almost one magnitude than that in the AIC+H poly-Si after different annealing. This indicates the better stability of the HAIC poly-Si.



Fig. 6b SIMS results of AIC+H samples after annealed at different temperature

#### 4. Impact

The hydrogen plasma-assistant Al induced crystallization (HAIC) technology has been proposed in this paper. This technology integrates the crystallization and passivation into one process. The annealing time has been reduced by almost half of the traditional AIC technology. Additionally, the HAIC technology can also improve the resulted poly-Si performance obviously.

Furthermore, the equipment used in this technology is compatible with the traditional PECVD equipment except the relatively high temperature substrate holder, so, the cost is low. This technology makes the AIC technology more suitable for the industrial application.

## 5. Acknowledgements

This research is jointly supported by the Project of China's NSFC (Project No. 61076006) and the Flat-Panel Display Special Project of China's 863 Plan (Project No.2008AA03A335).

## 6. References

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