Solid-Phase Crystallization and Implanted Dopant Activation in PECVD a-Si:H Thin Films

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Index Terms— amorphous silicon, hydrogenated amorphous silicon, a-Si:H, dopant reactivation, Solid-Phase Crstallization

I. Introduction

In the initial stages of the semiconductor industry, much of the focus on silicon remained in the areas of crystalline and polycrystalline materials. For amorphous silicon, high defect density has long prevented and consideration as a material for electronic devices. However, in the 1970s, hydrogenation of amorphous silicon was found to passivate the amorphous material, satisfying dangling bonds and therefore reducing defect density by orders of magnitude. These hydrogenated materials were shown to have good electrical transport properties and reasonably high carrier mobility, and also a high photoconductivity due to low defect density [1].

With a rise in the solar cell industry in the 1970s, this characteristic made amorphous silicon cells a front-runner in early solar technology. Soon after, the first substitutional doping was performed on such layers and hydrogenated amorphous silicon (a-Si:H) was seen as a suitable material for several applications. With the rise of the field-effect transistor in the 1980s, the material has been incorporated with many of these devices, the most notable being the liquid crystal display, the optical scanners and radiation imagers. More recently, a-Si:H has been used in advanced, developing technologies such as photonic waveguides, thin-film transistors and in carbon-silicon alloys for solar cells [2].

The first amorphous films were deposited by use of electric glow discharge and sputtering, however glow discharge soon became dominant since it provided slightly better film properties.

II. Procedure

While a-Si:H is a relatively mature technology, the transition from the amorphous to nano/micro/polycrystalline phase is an active area of research. The goals of this study involved the characterization of solid-phase crystallization and the activation of implanted dopants following a thermal anneal of a-Si:H layers on glass and oxidized silicon.

Ten silicon and four glass wafers were used in the experiments. All silicon wafers received the same first two steps: 1000 Å of TEOS oxide followed by 2000 Å of a-Si:H. For the solid-phase crystallization study, two silicon wafers were cleaved into quadrants and annealed at increasing temperatures to observe re-crystallization. The processing of the two wafers differed only in the final, two-hour 1000 °C anneal, which resulted in very different film properties. Table 1 shows the condensed process flow for these samples. The four glass wafers used also received the 2000 Å thin-film of a-Si:H. These wafers were then annealed in the same steps used on wafer 1 and used for optical characterization. Originally, Rapid Thermal Processes (RTP) was to be used to compare against furnace annealing. However, delamination due to thermal shock was observed even at low RTP temperatures and therefore removed from the experiment.

SUB ID	450°C (48 hrs)	500°C (24 hrs)	600°C (24 hrs)	1000°C (2hrs)
1.1	X			
1.2	X	X		
1.3	X	X	X	
1.4				
2.1	X			X
2.2	X	X		X
2.3	X	X	X	X
2.4				

Table 1: Solid-Phase Crystallization Process Flow

For the dopant activation study, four silicon wafers were used. Two wafers were implanted with phosphorous and two were implanted with boron at high doses. One of each type then received anneals identical to wafer 1 from experiment one, and one of each type received higher temperature anneals (600 - 1000 °C) for shorter time intervals. Table 2 shows the condensed process flow for this experiment.

[400]	69.16°

Table 3: XRD Planes and Silicon Lattices

X ray diffraction was used to observe the re-crystallization of the amorphous films. Through X-ray diffraction, a rotating sample is struck with a fixed x-ray beam. A detector rotates with the sample to obtain a 2D pattern of diffracted x-rays. At certain angles of incidence, intensity peaks are observed (angle vs I) corresponding to specific crystalline planes. Variable Angle Spectroscopic Ellipsometry (VASE) results were also used to confirm the results obtained on crystallography and obtain absorption data. The levels of hydrogen in the films were compared using Fourier Transform Infrared-Radiation (FTIR) Spectroscopy. Through FTIR, H-Si bonding arrangements present in the film can be quantified. Research has shown hydrogen to diffuse out of a-Si when heated above 600 °C. [1] In addition to data on optical properties, sheet resistance measurements were taken using four-point probe measurements to quantify implanted dopant reactivation (i.e. sample 7, 8, 9 and 10).

SUB ID	450°C	500°C	600°C	furnace act.
7.1	X			
7.2	X	X		
7.3	X	X	X	
7.4				
8.1				X
9.1	X			
9.2	X	X		
9.3	X	X	X	
9.4				
10.1				X

Table 2: Dopant Reacivation Process Flow

III. DISCUSSION OF RESULTS

The x-ray crystallography results showed re-crystallization to varying degrees from the samples annealed at 600 °C to those annealed to 1000 °C. Figure 1 shows an example of an x-ray diffraction plot for a silicon sample. Where the annealed sample at 600 °C is shown in blue has a higher level of recrystallization. Table 3 shows the planes considered in the graph where all other peaks are forbidden peaks or peaks from the film that do not relate to crystallization data. The gradual increase of XRD data for the [111] shows the greatest level of recrystallization. In addition, this gradual increase corresponds to smaller grain boundaries, whereas a sharp peak (observed later) corresponds to larger grain size.

plane	2θ
[111]	28.45°
[220]	47.32°
[311]	56.14°

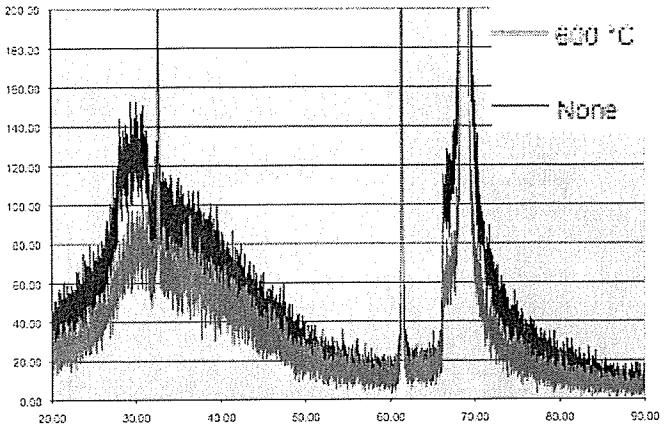

Figure 1: XRD Data for 600 °C and Non-annealed a-Si:H

The x-ray crystallography results for higher anneals showed higher degrees of crystallization. Samples given 600 °C and the additional 1000 °C are shown plotted against the same 600 °C in order to show the differences in properties of these films. Figure 2 shows these results.

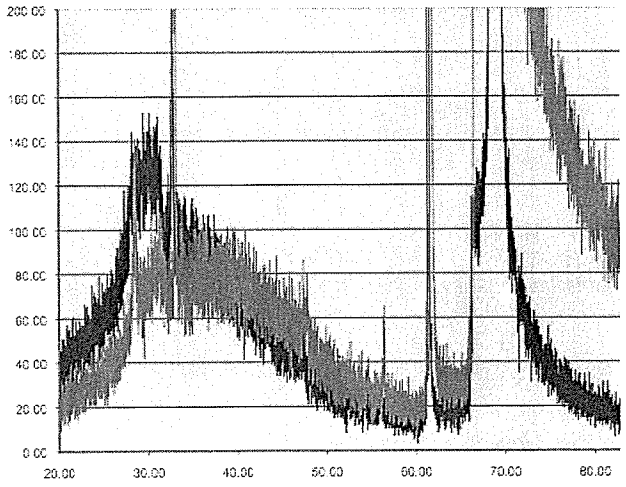

Figure 2: XRD Data for 600 °C and 600+1000 °C a-Si:H

For the glass samples, the crystallization process was not as apparent. Since these samples could not be taken above 600 °C, high temperature anneals were not observed. However, as shown in Figure 3, a higher degree of crystallization was observed for the 600 °C sample with respect to 450 °C and non-annealed a-Si:H.

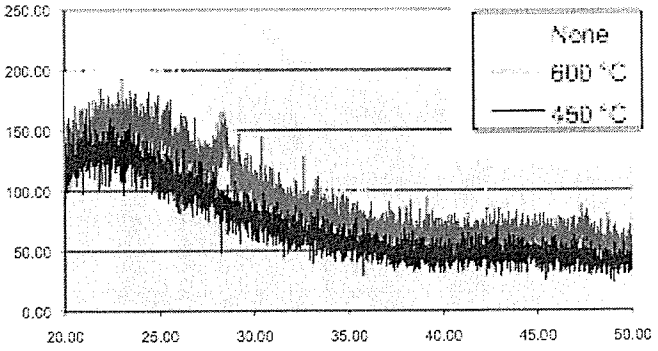

Figure 3: XRD Data for 450 °C, 600 °C and non-annealed a-Si:H Layers on Glass Substrates

VASE data further confirmed the crystallization data obtained from XRD data. Figure 4 shows the obtained data for varying anneal temperatures. In general, a trend was seen towards the crystalline silicon model as anneal temperature and time were increased. The most effective in crystallizing the a-Si:H was the up to 600 °C anneal followed by the short 1000 °C anneal.

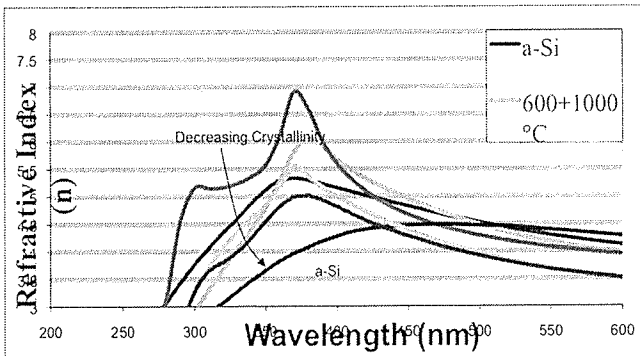

Figure 4: VASE Data for Various Anneal Temperatures a-Si:H Layers on Silicon Substrates

For electrical characterization, as previously mentioned, sheet resistance measurements were taken. The two annealing areas (long, low temperature and short, high temperature) were found to have different results. Figure 5 shows the sheet resistance measurements plotted vs. annealing temperature. The point results at 600 °C were the only observable sheet resistances for the low temperature anneals. That is to say that 450 °C and 500 °C were not efficient in activating the phosphorous and boron dopants within the film. However, a long, low temperature anneal up to 600 °C (from 450 and 500 °C) was more successful than a short two hour anneal at 600 °C. As shown in Figure 5, for the high temperature samples, 600 °C for two hours was not sufficient to reactivate any dopant in the films to a measureable degree. However, when carried to higher temperatures, these samples activated much better.

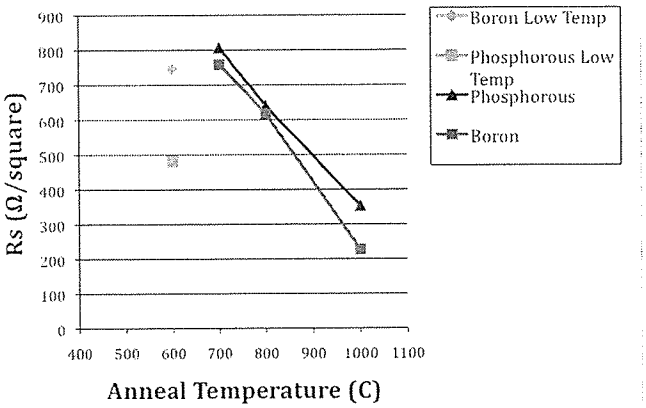

Figure 5: Four-Point Probe Data for Various Anneal Temperatures of a-Si:H Layers on Silicon Substrates

IV. Conclusion

For the optical characterization XRD and VASE data, these results showed crystallization of a-Si:H when annealed. Crystalliation has a direct relationship with annealing temperature however these films weren't quantified. Optical microscopes do not have the magnification capability to observe such small grain sizes. This Solid-Phase Crystalliation (SPC) process could be a substitute for LPCVD of polysilicon when smooth surfaces or high repeatability are necessary. However, a more likely process – and active area of research – is Pulsed Rapid Thermal Annealing (PRTA) or Excimer Laser Annealing.

The dopant reactivation study showed observable sheet resistances and a reactivation to varying degrees. A linear inverse relationship, resistance decreases with an increase in annealing temperature. The effects at 600 °C for different processing techniques may be due to hydrogen leaving the film. A future user might be able to take results seen here and further explore film properties at and around 600 °C by use of Fourier Transform IR Spectroscopy. However, thicker films are needed for such characterization and results may differ from thin-film characteristics.

Acknowledgment

Nathaniel R. Lozier thanks Dr. Karl Hirschman, Dr. Al Raisanen, Dr. Vinnie Gutpa, Eryk Glowacki, Ryan Rettmann, RIT SMFL Staff

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