Impacts of the annealing profile on AIC thin film solar cell characteristics fabricated by magnetron sputtering

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Abstract. Two different layer orders of p-Si/Al (as structure #1) and Al/p-Si (as structure #2) thin films were deposited on n-type mono-crystalline Silicon wafer and quartz glass by magnetron sputtering at 200 °C. The fabricated films were annealed at different temperatures for various durations. Then, they were analyzed by XRD, Raman and SEM methods. According to XRD results the largest grain size of both structures was smaller than 20 nm. The Raman spectra of the samples annealed at 1000 °C determined a crystallization ratio of 98% and 75% of structures #1 and #2 respectively. SEM images confirmed that the crystallization happened for structure #1 at lower temperatures than for structure #2. The impact of annealing on electrical and photovoltaic performance of the samples were studied after the fabrication of metal contact by sputtering of a few hundred nanometers of aluminium. The highest measured $V_{oc}$ were 360 and 402 mV, and the best $J_{sc}$ were 2.2 and 0.12 mA/cm², for structure #1 and #2 respectively.

1. Introduction
Aluminium inducing crystallization (AIC) is becoming a common method for crystallization and passivation of amorphous Silicon (a-Si) thin films which are used in fabricating low cost photovoltaic (PV) devices and Thin-Film Transistor (TFT) displays [1, 2]. Among different a-Si thin film growth methods like magnetron sputtering, PECVD, LPCVD or EBE; the magnetron sputtering has recently attracted more and more attentions because of its advantages such as being low cost and environment-friendly, and benefiting the high level of uniformity and scalability [3-7]. Poly-Si thin films has been fabricated on various types of substrates such as Si wafer [8], glass [2] and ceramic [9], with inducing different ratios of Al-to-Si for lowering the temperature and shortening the time of annealing [10]. High crystallization ratio is an essential criterion for the thin films which are fabricated for PV applications; either as emitter layer on Si wafers or in the p-i-n structure of thin film solar cells. However, just a few groups have reported the complete fabrication of poly-Si thin film solar cell by AIC and magnetron sputtering, and in majority of research the poly-Si films have been only grown as a primary step to create the so called “Seed Layer” for future growth of high quality films by PECVD or other methods [10, 11]. This paper investigated the AIC of a-Si throughout the fabrication of two simple solar cell structures completely by magnetron sputtering. They were fabricated and annealed at both low and high temperatures for various durations. Subsequently, their material properties were characterized and electrical parameters were measured. Finally, the resulted data were analysed and discussed in detail.
2. Experiments
The sputtering experiments were carried out by a MSP3200P magnetron sputtering machine. A p-type Si disk, with the purity of 99.9999% and resistivity of 1Ω.cm, and an Al disk, with purity of 99.99%, were used as the targets of Si and Al, respectively. All the films were deposited by DC magnetron sputtering power of 250 W, at 200 °C. The base vacuum pressure before sputtering was lower than 10⁻³ Pa. During the sputtering the pressure was raised to 1.2 Pa by flowing Ar inside the chamber at a rate of 40 sccm. The deposition rates of 0.5 nm/sec and 0.33 nm/sec were achieved for Al and Si respectively. Al and Si were used as the targets of sputtering and Quartz glass and n-type Czochralski <100> mono-Si wafer with the thickness of 300 μm and typical resistivity of 20-30 Ω.cm, were used as the substrate. All AIC processes were done in vacuum (<10⁻⁴ Pa) or N₂ atmosphere (~10 Pa). To measure the electrical parameters metal contacts were created on the front and back surfaces of the deposited thin films by sputtering of 150-250 nm of Al.

3. Results and Discussions
Two thin film structures are shown in the inset diagrams of figure 1. The first structure is an example of (1:1) ratio of Si/Al layers that typically has been reported as a typical ratio in AIC method for good poly-Si film fabrication [11]. The second one, which is usually called “Invert” structure [12], is an instance of highly unequal Al/Si layers’ ratio (1:50) and it was investigated to see if such layer order and thin Al layer leads to good crystallization and PV property or not.

3.1. Material Properties
The XRD spectra are presented in figure 1. As shown in the left graph, the peak of Si <111> plane became observable after annealing at 550 °C or above. By extending the annealing time from 1.5 to 6 hours not only the peak intensity of Si <111> plane increased but also <200> and <311> peaks appeared in the XRD spectra. At 1000 °C these peaks became visible even for the annealing times as short as 2 hours. In the right-side graph, the peaks of poly-Si of structure #2 were observable only at the higher temperatures than 800 °C. The grain size of both structures were smaller than 20 nm.

Following the XRD test, Raman spectra was measured to determine the crystallization ratio of the sputtered thin films. According to the Raman results of structure #1, shown in the left graph of figure 2, the crystallization ratio was not considerable for the annealing temperatures below than 550 °C. For the sample annealed at 550 °C for 6 hours, the crystallization ratio was about 44%. After annealing at 1000 °C for 2 hours, the poly-Si peak was very sharp and strong (shown by dash line) that didn’t fit to the graph. The crystallization ratio for this sample was more than 98%. The Raman spectra of structure #2, right-side graph of figure 2, shows small peaks due to Si crystallization after annealing below 800 °C, while annealing at higher temperatures resulted in the stronger peaks. However, the crystallization ratio was less than 75% even after annealing at high temperatures up to 1000 °C.
Figure 2. The Raman spectra of different samples of structure #1 (left) and #2 (right), after applying of different annealing profiles

Next part of the analysis was the study of thin films surface morphology by SEM images. The top row of figure 3 shows three different samples of structure #1. The left picture shows the smooth surface of the as-deposited sample, cover by a-Si. The middle one belongs to the sample annealed for 0.5 hour at 500 °C, wherein the surface roughness increased and some dark areas appeared. At 1000 °C, and due to the diffusion of Al into a-Si, the extra Al transferred to the top layer and formed an almost continuous layer on the top surface of the sample that prevented the film surface from receiving the light. In the second row, the as-deposited sample of structure #2 is displayed in the left-side, which expectedly was smooth. The middle picture shows that after annealing at 800 °C for 2 hours, dark poly-Si area was formed and surface roughness increased a little bit due to the diffusion of Al into the a-Si. The last picture belongs to the sample annealed at 1000 °C for 2 hours, wherein the phase-change obviously took place because the number and dimension of the dark areas increased.

3.2. Electrical Properties

Figure 4 shows the J-V curves of structure #1 samples in dark condition (left) and under the irradiance of 50 mW/cm² (right). All samples showed good rectification properties in dark condition. The reverse saturation current obviously reduced with longer annealing and at higher temperatures, while the corresponding threshold voltages increased. Furthermore, the PV performance of the samples under the illumination improved with increasing the annealing time and/or temperature, as shown in figure 4-right. The J-V curves of structure #2, shown in figure 5, are very different than of the structure #1. In dark condition (figure 5-left), the rectification took happen only after annealing at temperatures higher than 800 °C. Under the illumination (figure 5-right), the PV effect was very weak for all the samples annealed at temperatures lower than 600 °C and the voltage polarity of the solar cell was the inverse of the cell voltage annealed at higher temperatures, probably due to the metal-semiconductor junction formed at the top layer (besides the main p-n junction). Annealing with longer durations and at higher temperatures resulted in larger open circuit voltage ($V_{oc}$). However, the short circuit current density ($J_{sc}$) was reduced.
for the samples annealed at very high temperature for longer time than 1 hour. Finally, measurements in AM1.5 condition showed that structure #2 generated higher $V_{oc}$ up to 402 mV but its $J_{sc}$ was limited to 0.12 mA/cm$^2$, while structure #1 generated lower $V_{oc}$ (about 360 mV) however its best measured $J_{sc}$ was almost 20 times larger than of the structure #2 (about 2.2 mA/cm$^2$).

**Figure 4.** The J-V curves of structure #1 solar cell in dark (left) and under illumination of 50mW/cm$^2$ (right).

**Figure 5.** The J-V curves of structure #2 solar cell in dark (left) and under illumination of 50mW/cm$^2$ (right).

4. Conclusions
In this research we fabricated two different solar cell structures, i.e. (Al/p-Si) and (p-Si/Al) thin film layers on n-type Si wafer, by AIC and magnetron sputtering. Fabricated samples were annealed in an electrical annealing furnace at different temperatures and for various durations. The poly crystal films grain size, measured by XRD peak analysis, showed that the largest grain size is smaller than 20 nm in both structures. The crystallization ratio, determined by Raman peaks intensity measurement, was about 98% and 75% for structure #1 and #2 respectively. SEM images confirmed that the crystallization took place at higher temperatures for structure #2 (>600 $^\circ$C), while it happened at 500 $^\circ$C for structure #1. The I-V curve measurements showed the $J_{sc}$ up to 2.2 mA/cm$^2$ for solar cells of structure #1 with a $V_{oc}$ of 360 mV, whilst the best $V_{oc}$ measured structure #2 was 402 mV with a $J_{sc}$ of 0.12 mA/cm$^2$.

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