



Article Surface Passivation of Boron Emitters on n-Type Silicon Solar Cells

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Abstract: Al_2O_3/SiN_x stack passivation layers are among the most popular layers used for commercial silicon solar cells. In particular, aluminum oxide has a high negative charge, while the SiN_x film is known to supply hydrogen as well as impart antireflective properties. Although there are many experimental results that show that the passivation characteristics are lowered by using the stack passivation layer, the cause of the passivation is not yet understood. In this study, we investigated the passivation characteristics of Al_2O_3/SiN_x stack layers. To identify the hydrogenation effect, we analyzed the hydrogen migration with atom probe tomography by comparing the pre-annealing and post-annealing treatments. For chemical passivation, capacitance-voltage measurements were used to confirm the negative fixed charge density due to heat treatment. Moreover, the field-effect passivation was understood by confirming changes in the Al_2O_3 structure using electron energy-loss spectroscopy.

Keywords: surface passivation; hydrogenation; silicon solar cells; aluminum oxide; field-effect passivation; chemical passivation

1. Introduction

As the interest in renewable energy has recently increased, solar energy, in particular, has attracted attention as an energy source that can meet the explosive growth in energy demand. Of the various types of solar cells, silicon-based solar cells account for more than 90% of the total market. To secure the price competitiveness of silicon solar cells due to the recent decline in module prices, studies on highly efficient structures have been carried out, in addition to other efforts to lower the production costs [1,2]. To improve the conversion efficiency of silicon solar cells, wafer thickness reduction and surface passivation characteristics with increased emitter doping concentration are becoming more important. The surface passivation layer has two major roles. First, it eliminates dangling bonds on the surface, thus reducing surface re-defect losses. Second, an effect occurs due to the formation of an interfacial electric field by a fixed charge in the passivation layer. The main passivation layer comprises silicon oxide (SiO_2) and silicon nitride (SiN_x) with a positive fixed charge, and aluminum oxide (Al₂O₃) with a negative fixed charge [3,4]. Of these, Al_2O_3 is mainly used as a passivation film with a high density of fixed negative charge for lowly doped p-type or n-type silicon and highly doped p-type emitters [5,6]. Al₂O₃ thin films deposited by atomic layer deposition (ALD) are known to improve the characteristics of surface passivation by decreasing density of interface defect states (D_{it}) and increasing the fixed charge density (Q_f) through heat treatment [7–9]. SiN_x, which is mainly used as a capping layer, contains a large amount of hydrogen; therefore, hydrogen is used to passivate the dangling bonds present on the silicon surface [10,11]. It is used as a source to supply hydrogen and, at the same time, acts as an antireflective coating on the entire surface of a solar cell. This study was carried out to verify the passivation characteristics of Al_2O_3 and SiN_x stack structures. We compared the implied Voc using pre-annealing and post-annealing treatments. To confirm the effects of chemical passivation, we compared the migration of hydrogen through atom probe tomography (APT) [12,13]. We also used capacitance-voltage (C-V) measurements to determine the field-effect passivation characteristics. The structural changes in Al_2O_3 were analyzed to determine the increase in the fixed charge after the heat treatment.

2. Materials and Methods

2.1. Preparation of Samples

To investigate the chemical and field-effect passivation qualities of the Al₂O₃/SiN_x film, n-type Czochralski (Cz) wafers were used (6 in diameter, 180 µm thickness, 3–4 Ω ·cm resistivity). After cleaning the wafers by the standard Radio Corporation of America (RCA) cleaning procedure, they were textured with a KOH solution. An emitter with a sheet resistance of 110 Ω /cm² was formed on both sides using boron tribromide (BBr₃) in a liquid propane furnace. To remove the borosilicate glass and native oxide, all samples were subjected to wet-chemical cleaning with a dilute HF solution before the deposition of Al₂O₃. To perform the C-V, electron energy-loss spectroscopy (EELS), and APT measurements, n-type semiconductor wafers were used (6 in diameter, 500 µm thickness). The passivation layers were deposited on one side.

2.2. Passivation

 Al_2O_3 films of thickness 10 nm were deposited on both sides of the substrate by thermal ALD with trimethyl aluminum (TMA, Al(CH₃)₃) and H₂O as precursors at 220 °C. After the deposition of the Al_2O_3 films, the samples were divided into two groups to confirm the effects of chemical and field-effect passivation. On half of the samples, 80 nm SiN_x films were directly deposited onto the Al_2O_3 on both sides of the wafers using plasma-enhanced chemical vapor deposition (PECVD). After the deposition of the SiN_x films, the samples were annealed under N₂ for 15 min with a rapid thermal process in the temperature range of 400–600 °C, at intervals of 50 °C. On the other half of the samples, the annealing treatment was performed before deposition of the SiN_x layer. The processing sequence is illustrated in Figure 1.



Figure 1. Processing sequence for pre-annealed and post-annealed samples.

2.3. Measurements

The *implied Voc* values were obtained from quasi-steady-state photoconductance (QSSPC, WCT-120) measurements and were used to compare the passivation characteristics of the pre-annealed and post-annealed samples. The sample structures are shown in Figure 2. The wafers used for the C-V, EELS, and APT measurements were polished on both sides and were 500 µm thick.



Figure 2. Cross-sectional schematics of the samples prepared for (**a**) quasi-steady-state photoconductance (QSSPC), (**b**) atom probe tomography (APT), and (**c**) electron energy-loss spectroscopy capacitance-voltage (EELS C-V) measurements.

3. Results and Discussion

3.1. Implied Voc

Figure 3 shows the *implied Voc* values of the pre-annealed and post-annealed samples with respect to the annealing temperature. The *implied Voc* values of the pre-annealed and post-annealed samples were higher than those of the deposited Al₂O₃. Excluding the samples treated at 600 °C, the post-annealed samples showed higher *implied Voc* values than the pre-annealed samples. One peculiar aspect is that the pre-annealed samples showed similar *implied Voc* values over the entire temperature range. On the contrary, the post-annealed samples showed a maximum *implied Voc* value at a certain temperature, above which the *implied Voc* tended to decrease with increasing temperature.



Figure 3. *Implied Voc* values of pre-annealed and post-annealed samples with different annealing temperatures.

This can be understood as a decrease in the passivation property due to the blistering phenomenon in the Al_2O_3/SiN_X stack structure [14,15]. To confirm the effects of chemical and field-effect passivation on the pre-annealed and post-annealed samples, we compared the migration of hydrogen through APT and examined the structural change of Al_2O_3 through EELS. Moreover, Q_f was compared through the C-V measurements.

3.2. Chemical Passivation: Atom Probe Tomography

Research on hydrogen has been actively conducted to understand chemical passivation [16–19]. However, as hydrogen has a small mass and small size, the analysis methods are limited and difficult to perform. Therefore, through an analysis different from existing research methods we were able to understand the behavior of hydrogen. APT was performed to confirm the distribution of hydrogen at the interface between the silicon and Al₂O₃. The samples were polished to alleviate surface morphology issues. Figure 4a,b show the transmission electron microscopy (TEM) images after pre-annealing and post-annealing, respectively. Meanwhile, Figure 4c,d show the atomic distributions of the pre-annealed and post-annealed samples treated at 500 °C. The sample structure was SiN_x-Al₂O₃-Si, in sequence from

the surface to the silicon; the hydrogen, nitrogen, aluminum, and silicon atoms are represented by the pink, yellow, blue, and green colors, respectively. In the case of the pre-annealed sample, the interfaces between $SiN_x/Al_2O_3/Si$ are clearly distinguished. However, in the case of the post-annealed sample, the interfaces are not, and hydrogen is widely distributed throughout the silicon. Figure 4e,f show the hydrogen concentration along the depth direction from the surface. In the case of the post-annealed sample, the hydrogen concentration at the silicon and Al_2O_3 interface was approximately 20–30%, which is higher than the hydrogen content (~2%) in the pre-annealed sample. Because SiN_x was deposited using SiH_4 and NH_3 gas by PECVD, the SiN_x film contains a high concentration of hydrogen. The post-annealing process was performed after the deposition of SiN_x ; therefore, some of the hydrogen and Al_2O_3 interface, passivating the dangling bonds. However, it cannot be said that the pre-annealed sample did not undergo chemical passivation by hydrogen. Because the Al_2O_3 is deposited using TMA and H_2O sources, it also contains a small amount of hydrogen.



Figure 4. Atom probe tomography. Focused ion beam transmission electron microscopy images of (a) pre-annealed and (b) post-annealed samples. Three-dimensional atomic maps of (c) pre-annealed and (d) post-annealed samples. One-dimensional hydrogen concentration profiles of (e) pre-annealed and (f) post-annealed samples.

Distance (nm)

3.3. Analysis of Al₂O₃ Structure

C-V measurements were performed to confirm the characteristics of field-effect passivation with and without the heat treatment of Al_2O_3 . The samples were characterized after the 10 nm thick Al_2O_3 was deposited and annealed at 500 °C, the results of which were compared. The fixed charge was calculated by changing the flat band voltage based on the C-V graph. Figure 5a shows the change in the negative fixed charge before and after annealing. By comparing these results, it is observed that the Al₂O₃ film shows increased negative fixed charge after the heat treatment. Similar results were reported in many papers [19–23]. According to these, the negative fixed charge of Al₂O₃ results from its structural change. This can be confirmed by the bonding change of Al-O, Al-O-H and Si-O with X-ray photoelectron spectroscopy (XPS) analysis, as well as an analysis of the TEM images [2,4,19,20,24]. We confirmed the structural change of Al_2O_3 through EELS, showing it has both octahedral and tetrahedral structures. The closer to the silicon interface, the more tetrahedral sites exist owing to the effects of silicon oxide. When the structure changes from an electronically neutral octahedral structure to a tetrahedral structure, Al vacancies are formed and the vacancy of Al^{3+} provides a negative charge. In this study, we compared the relative amounts of the tetrahedral and octahedral structures of Al₂O₃ with respect to the depth from the surface before and after annealing. It can be seen from Figure 5b that the ratio of Tetrahedral/Octahedral varies depending on the heat treatment. In the case of the sample without heat treatment, the tetrahedral ratio gradually increases from the surface to the interface. On the contrary, in the case of the heat-treated sample, the tetrahedral ratio is high for the entire Al_2O_3 film. The structural change to tetrahedral structure increases the negative fixed charge and increases the field-effect passivation effect.



Figure 5. (a) C-V results for negative fixed charge density (Q_f); (b) EELS depth analysis results for as-deposited 500 °C annealed samples.

4. Conclusions

To investigate the surface passivation characteristics of the Al_2O_3/SiN_x stack layer, two aspects of chemical passivation and field effect passivation were studied using common analytical methods such as C-V and QSSPC and new analytical methods such APT and EELS. In order to verify the characteristics of passivation by heat treatment, *implied Voc* was measured and compared, and it increased at all heat treatment temperature ranges. To understand the chemical passivation, the hydrogen behavior was studied and the 3D mapping analysis showed that hydrogen was supplied from SiN_x. Particularly, when a sufficient amount of hydrogen was supplied from SiN_x through post annealing, the hydrogen distribution increased to approximately 20% at the interface of Al_2O_3 and silicon. However, although hydrogen supply through post-annealing is also important, properties due to the heat treatment temperature must be considered. From C-V measurements and EEL results, it was confirmed that the negative fixed charge of Al_2O_3 came from the structural change of it. The ratio of the tetrahedral structure inside the Al_2O_3 film was increased about 1.5 times by the heat treatment.

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