Investigation on blistering behavior for n-type silicon solar cells

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Abstract

Thermal treatment with different gas environment before the Al_2O_3 ALD passivation process plays a key role to the presence of blistering. The specific silanol group vibration peaks in FT-IR spectra confirm the mechanism of the blistering free surface formation. The blistering affects not only the appearance but also the implied Voc of the cells, that is to say, the quality of the passivation [10]. The hydrogen containing species (by-product of the ALD process) will bond to the SiO_2 (both Si and O atom site) which grows after the thermal treatment with oxygen. Due to the good diffusivity within the SiO_2 layer, the amount of hydrogen out-diffusing towards the SiN_X ARC layer after firing can be reduced to achieve blistering free silicon solar cells.

1. Introduction

Al_2O_3 films are often used in n-type silicon solar cells for passivation of p+ doped surface. The thermal stability of the Al_2O_3 is important as the film would go through a high temperature firing process. The deterioration in passivation quality after firing is due to an increase in interface trap density, D_{it} [1], resulting from the dissociation of interfacial Si-H bonds during the firing process, with hydrogen released from the passivation film. Blistering occurs [2] when hydrogen species (atom, ion or H_2 molecules) can't diffuse out during firing, locally accumulating in the SiN_X capping layer, which acts as a barrier. Not only the cell appearance is affected (white dots present on SiN_X surface) but also the passivation performance is impacted. Most of the previous research works used post

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deposition anneal [3], PDA, to solve the blistering issue. In this article, a thermal treatment in specific gas environment is proposed to eliminate blistering.

2. Experiment

In this study, 6-inch n-type Cz silicon wafers with a thickness of 180 μm were used. After texturing, the wafers were then doped with boron for front emitter, and with phosphorous for back surface field. The samples were then deposited with Al_2O_3 using Atomic Layer Deposition (ALD) [4]. Finally, a SiN_X ARC layer was deposited on the samples using PECVD. The samples were fired in an industrial belt driven fast firing furnace at a set peak temperature. We surveyed the appearance of our samples by ZETA's 3D-OM, and analyzed the bonding configuration by BRUKER's FT-IR spectrometer. We also used Sinton Instrument's Suns-Voc to monitor the implied Voc.

3. Results and discussion

3.1. Optical properties

Fig. 1 shows the microscope observations of the sample surface, after firing, with a 20X objective. The white spots in Fig. 1(a) indicate local blistering of the dielectric stack with thermal treatment A (N_2 rich gas environment). No blistering is observed in Fig. 1(b) for the samples with thermal treatment B (O_2 rich environment).
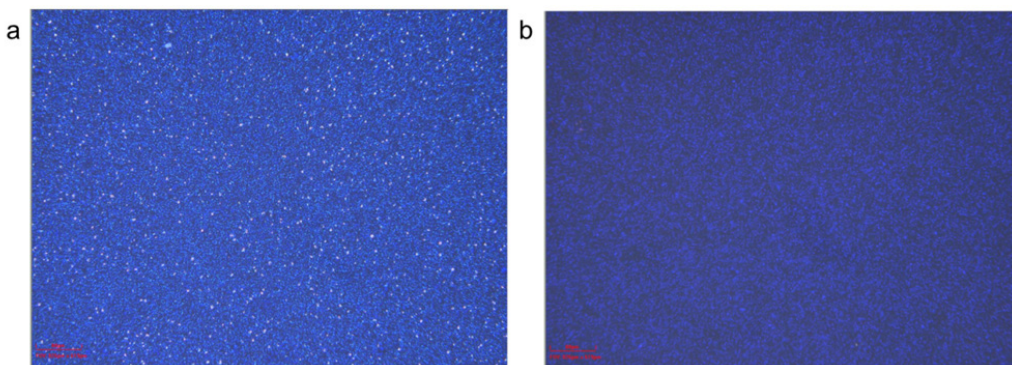

Fig. 1. The microscope observations of the surface after firing: (a) thermal treatment A (N_2 rich environment) and (b) thermal treatment B (O_2 rich environment).

Infrared spectroscopy is sensitive to OH-related functional groups and gives information about hydrogen's bonding state. Fig. 2 shows FTIR spectra of the samples. Silanol groups (Si-OH) [5, 6, 7] are one of the major indicators that the hydrogen species are trapped by the oxide layer, which formed after the thermal treatment. The assignations for the four spectral components in Fig. 2(a) are listed in Table 1, and the corresponding bonding configurations are shown in Fig. 3(a)-(c). In Fig. 2(b), the specific IR peak is due to the intra-molecular cyclic hydrogen bonding (Fig. 3(d)), consistent with the observation of the 2360 cm^{-1} band in [8] [9]. The absorbance intensity of 3745 cm^{-1}(germinal OH vibration) is higher than 3652 and 3622 cm^{-1} (inter-molecular cyclic configuration OH vibration). This can be supported by the following argument; due to the large O··H distance and HO··H angles, the steric effect increases the difficulties to form an inter-molecular cyclic configuration.
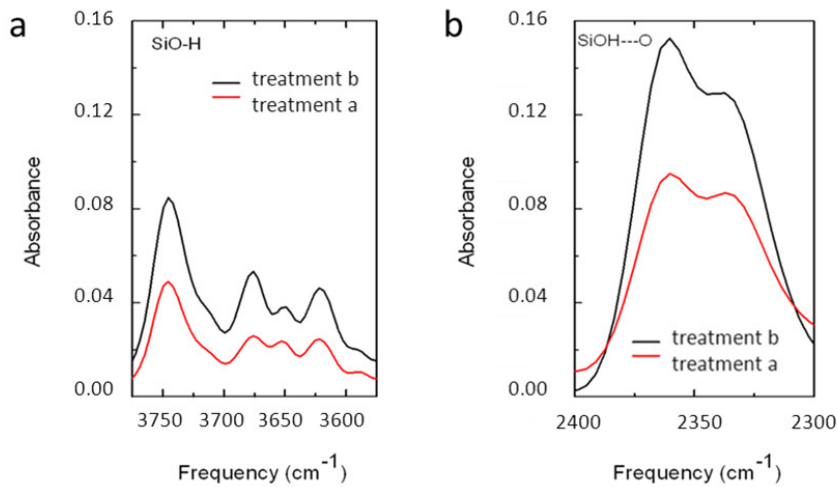
Fig. 2. FTIR spectra results of the samples with silanol group

Table 1. Peak positions of the silanol groups IR absorption band (cm^{-1})

| Components position (cm^{-1})	Band assignation
3745 cm^{-1}	Germinal OH vibration
3676 cm^{-1}	Free OH vibration
3652 cm^{-1}	out-of-phase OH vibration of adjacent SiOH groups in inter-molecular cyclic configuration
3622 cm^{-1}	in phase OH vibration of adjacent SiOH groups in inter-molecular cyclic configuration
2360 cm^{-1}	OH vibration in SiO_2H intra-molecular cyclic configuration
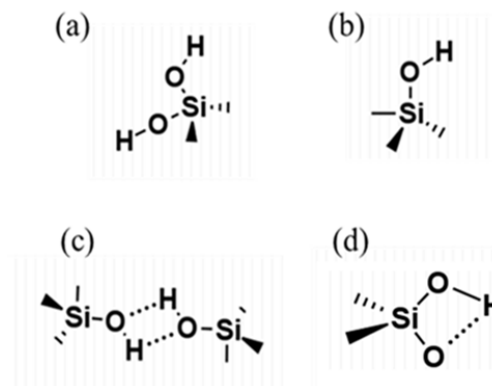
Fig. 3. The possible bond configurations of a couple of adjacent Si-OH units: (a) germinal structure (b) free structure (c) inter-molecular cyclic structure (d) intra-molecular-cyclic structure

Comparing the intensity of these specific vibration modes, it can be noted that the samples with treatment B showed stronger absorbance than the samples with treatment A. We supposed that with treatment B, hydrogen species preferentially moved into the oxide layer since molecular hydrogen has a higher diffusivity [11] within SiO_2 than in SiN_X. The hydrogen will out-diffuse from the Al_2O_3 layer due to the high firing temperature. If the oxide layer is thick enough to trap or "dissolve" the hydrogen species, the hydrogen will not out-diffuse to the ARC layer and stuck on the top of the surface, resulting in blistering.

3.2. Electrical properties

In the following part, we compared the implied V_{OC} between the two annealing recipes just after the simulated firing process. Fig. 4 shows that the thermal treatment B has a higher implied Voc than A. This is because the firing temperature will induce the out-diffusion of the species containing hydrogen from the AlO_X layer. The O_2 rich gas environment will form a thicker oxide layer between the silicon substrate and AlO_X layer. Table 2 shows the order of the hydrogen diffusion coefficients in the dielectric films [12-14]. The diffusivity of the hydrogen in the SiO_2 under such a high firing temperature is two orders higher than in the AlO_X. So, obviously most of the species containing hydrogen will diffuse into the SiO_2 layer. This forms a hydrogen rich SiO_2 film, and furthermore reduces the defect density between the Si/ SiO_2 interface.

In thermal treatment A, the N_2 rich gas environment results in a thinner SiO_2 layer. There is not enough space to accommodate the hydrogen species. So, most of the species will out-diffuse from the AlO_X layer and are then stuck in the SiN_X, which acts as barrier layer. This makes the blistering and meanwhile a lower implied V_{OC} appear. We supposed that blistering leads to a degradation of the passivation properties.

Table 2. Molecular hydrogen diffusion in dielectric films with different temperatures [11]

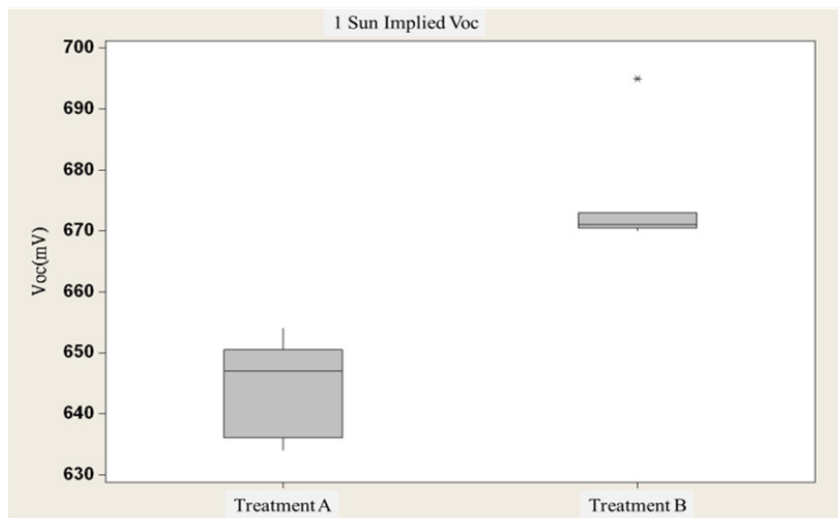| Order of the magnitude in different temperatures		
Diffusion Coefficients(cm^2/s), D	400 $^\circ$C	800 $^\circ$C
H$_2$ in SiO$_2$	3.50E-06	8.00E-06
H$_2$ in Al$_2$O$_3$	5.00E-12	1.30E-08
H$_2$ in SiN$_X$	3.00E-17	4.00E-13
$D_{SiN_X} << D_{Al_2O_3} << D_{SiO_2}$		

Fig 4. Implied Voc of the two different gas environments

4. Conclusion

In this work, we investigated the thermal treatment before Al_2O_3 ALD with two different gas environment to avoid the surface blistering after high temperature fast firing. A clear correlation between the blistering behavior and thermal treatment is in existence. Blistering-free samples have better passivation and results in a higher implied Voc than those with blistering. We use OM to monitor the surface blistering, and FT-IR to confirm that the hydrogen species react with the oxide, resulting in less out-diffusion to the ARC layer. So, the out-diffusion of the hydrogen can be controlled by various treatments, and oxide growth by the thermal treatment before ALD plays a key role to the formation of the blistering behavior and the passivation quality.

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