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Impurity Gettering by Atomic-Layer-Deposited Aluminium Oxide Films on Silicon at Contact Firing Temperatures

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Aluminium oxide (Al_2O_3) thin films deposited on silicon surfaces, synthesised by plasma-assisted atomic layer deposition, are recently reported to possess impurity gettering effects for the silicon wafer bulk during annealing at 425 °C, a typical temperature used for activating the surface passivation quality of the Al_2O_3 films. This paper investigates the gettering effects of Al_2O_3 films at higher temperatures of 700–900 °C, which are commonly used for contact firing in silicon solar cell fabrication. Iron is used as a marker impurity in silicon to study the gettering effectiveness. Results show that Al_2O_3 films also generate strong impurity gettering effects at 700–900 °C, through a segregation gettering mechanism. The as-deposited Al_2O_3 films are found to be more effective at gettering than the 425 °C-activated Al_2O_3 films, demonstrating gettering processes that are largely limited by the impurity diffusivity in silicon. For both as-deposited and activated Al_2O_3 films, gettering during high temperature annealing occurs by impurity accumulation at the Al_2O_3/Si interfaces, similar to the gettering action at 425 °C. However, some iron is found to redistribute into the bulk of the Al_2O_3 films after long annealing at a high temperature.

Aluminium oxide (Al_2O_3) thin films have outstanding passivation quality for silicon surfaces, and have been widely adopted in recent years for the fabrication of high efficiency silicon solar cells.[1–5] A high negative fixed charge density and a low interface defect density contribute to the excellent passivation properties of the Al_2O_3 films on silicon.[6] Al_2O_3 films are commonly synthesised via atomic layer deposition (ALD).[5] Plasma-enhanced chemical vapour deposition (PECVD) has also been used,[7–9] mainly for large-scale cell fabrication, usually in conjunction with PECVD silicon nitride (SiN_x) capping layers.

It was recently reported that the dielectric passivation thin films commonly used in silicon solar cells, namely the ALD Al_2O_3 and PECVD SiN_x films, also possess strong gettering effects for bulk impurities in silicon.[10,11] For ALD Al_2O_3 films, gettering during typical moderate-temperature (425 °C) surface passivation activation anneals was demonstrated, and gettering was found to be caused by impurity accumulation at the Al_2O_3/Si interface.[10] The precise physical gettering mechanisms, however, remain unclear.

In standard industrial silicon solar cells, Al_2O_3 thin films are generally used on the rear-side of p-type Passivated Emitter and Rear Cell (PERC) solar cells, capped with a layer of SiN_x as Al_2O_3/SiN_x stacks. A deliberate Al_2O_3 passivation activation anneal at moderate temperatures is typically not performed, although some activation effects could be achieved during the SiN_x deposition processes at moderate temperatures.[5] In cell fabrication, a rapid, high temperature firing process is subsequently carried out to form metal contacts in solar cells.

This work aims to study the gettering effects of ALD Al_2O_3 films at the high temperatures (700–900 °C) typically used for contact firing in solar cell production. The impact of a preceding moderate-temperature activation anneal on the gettering effectiveness is also investigated, which is not only process-relevant for the Al_2O_3/SiN_x stacks in industrial solar cells, but also provides insights into the possible gettering mechanisms of Al_2O_3 films. Iron (Fe) is used as a marker impurity in silicon to quantify the gettering effectiveness. Changes in the bulk Fe concentrations after various annealing conditions are monitored via using a lifetime-based Fe-B pair breaking technique.[12,13] The near-surface distributions of the gettered Fe atoms are assessed by secondary ion mass spectrometry (SIMS) depth profiling.

Experimental Section: This work used high quality boron-doped p-type float-zone (FZ) silicon wafers with a resistivity of 0.9 Ωcm and a thickness of 180 ± 10 μm after saw damage etch. The wafers were intentionally contaminated with Fe in the silicon wafer bulk via ion implantation and a distribution anneal, as detailed in Ref. [10]. The distribution anneal was carried out in dry oxygen at 1000 °C to enable the growth of silicon oxide (SiO_2) surface layers. The implanted Fe concentrations were 10^{13} and 10^{14} cm^{-3} for the 180-μm wafers after the distribution anneal.

A subset of the SiO_2-coated Fe-implanted silicon wafers had the thermally grown SiO_2 layers removed in dilute HF solution,

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and were subsequently coated with Al_2O_3 films on both sides of the wafers using plasma-assisted ALD. This work used a Beneq TFS-200 ALD reactor. Trimethylaluminium (TMA) was the precursor, and oxygen plasma was the oxidant for plasma-assisted ALD. The deposition temperature was 175 ± 5 °C, and the deposition rate was around 0.14 nm/cycle.

The Fe-implanted silicon wafers, with either ALD Al_2O_3 films or thermally grown SiO_2 films, were then co-annealed at 700–900 °C. Interstitial Fe concentrations ($[Fe_i]$) in the silicon wafer bulk were measured after each annealing step. FZ-Si control wafers with no Fe implantation, but with the same ALD Al_2O_3 or thermal SiO_2 surface layers, were also included. The Fe-implanted samples had an initial bulk $[Fe_i]$ of 10^{13} cm^{-3}. The Al_2O_3 samples were coated with 30-nm Al_2O_3 films on both sides.

With as-deposited Al_2O_3 films or thermal SiO_2 films, one group of the samples were directly annealed at 700, 800 or 900 °C, for 5 min in N_2. The samples were loaded in and unloaded from the furnace at the respective annealing temperatures. Note that a 5-min anneal is much longer than typical firing durations, and it is used here in order to cause large changes in the bulk Fe concentrations, as Fe has a moderate diffusivity in silicon. The as-deposited Al_2O_3 films degraded severely in terms of their surface passivation quality after the 5-min high temperature anneals. To allow bulk lifetime and $[Fe_i]$ measurements, the degraded films were etched off, and the wafers were re-coated with fresh 30-nm Al_2O_3 films. The passivation effect of the fresh Al_2O_3 films was activated by a 5-min 425 °C anneal in N_2. Gettering of Fe during a 5-min activation anneal at 425 °C is expected to be less than 20%.[10]

The other group of samples were first subjected to an activation anneal at 425 °C before being subsequently annealed at 700, 800 or 900 °C in N_2. The 700 and 800 °C annealed samples had a 5-min 425 °C activation anneal, while the 900 °C annealed sample had a 30-min activation (for better thermal stability during subsequent 900 °C anneals). Degradation of the Al_2O_3 surface passivation quality upon high temperature anneals was less severe for these samples with a preceding 425 °C activation anneal, and hence re-coating after each cumulative annealing step was not required.

The bulk interstitial Fe concentrations were measured by the Fe-B pair breaking technique[12,13] via quasi-steady-state photoconductance (QSSPC) lifetime measurements.[14] A WCT-120 tool from Sinton Instruments was used. Strong illumination was employed to dissociate the Fe-B pairs, as detailed in Ref. [10]. Error bars in the bulk Fe_i concentrations presented in this work were estimated by assuming a 5% uncertainty in lifetime measurements[15] before and after dissociating Fe-B pairs.

SIMS depth profiling of the total Fe concentration was used to study the Fe redistribution from the silicon wafer bulk to the surface regions. SIMS measurements were conducted by EAG Laboratories. The samples for SIMS had a higher initial bulk Fe_i concentration of 10^{14} cm^{-3}, in order to improve sensitivity. The samples were coated with thicker Al_2O_3 films of 80 nm on both sides, to enable surface contamination effects to be discriminated from gettered impurities in the bulk of the Al_2O_3 films and at the Al_2O_3/Si interfaces. One of the SIMS samples was directly annealed at 900 °C for 15 min in N_2 with as-deposited Al_2O_3 films. The other two samples underwent a 30-min 425 °C activation anneal before being annealed at 900 °C for either 15 min, or 2.5 h, in N_2.

Results: The remaining bulk Fe_i concentrations after annealing Fe-contaminated silicon wafers with different surface films are shown in **Figure 1**. Both as-deposited and 425 °C-activated Al_2O_3 films, from plasma-assisted ALD, demonstrate strong gettering effects at 700–900 °C. On the other hand, thermally grown SiO_2 films provide no gettering action at 700–900 °C during the cumulative annealing times

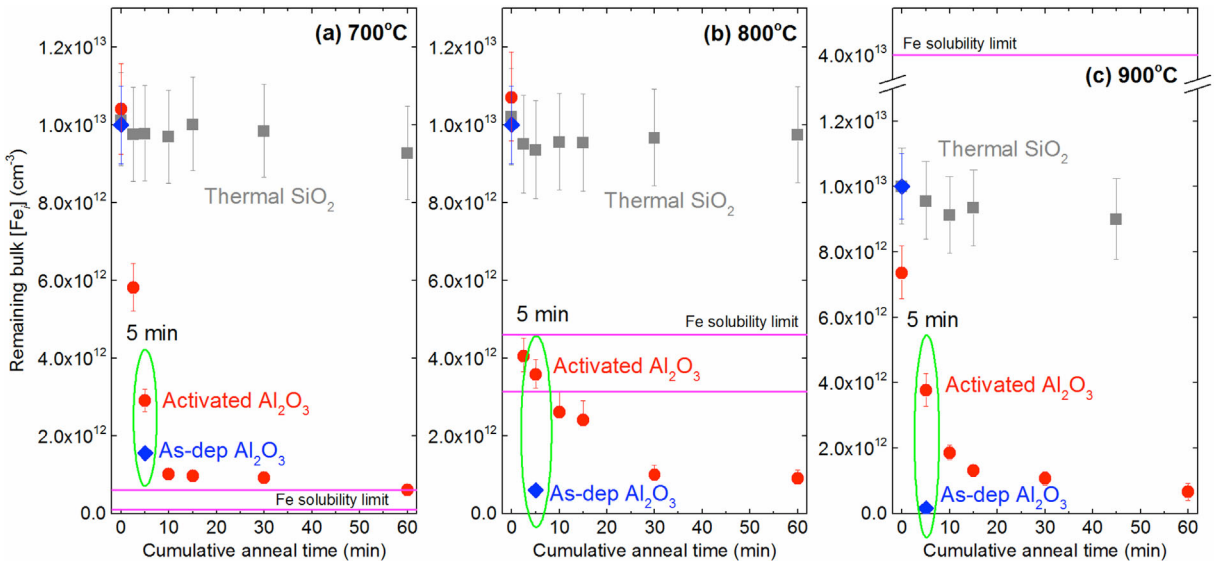

Figure 1. Interstitial Fe concentrations remaining in the silicon wafer bulk after cumulative anneals at (a) 700 °C, (b) 800 °C, and (c) 900 °C. The Fe-implanted silicon wafers were coated with either thermally grown SiO_2 films, as-deposited ALD Al_2O_3 films, or ALD Al_2O_3 films that had undergone a preceding 425 °C activation anneal. The solubility limits of Fe in silicon at the respective annealing temperatures[16,17] are marked.

examined here (less than 2 h in total). This indicates that gettering is caused by the Al_2O_3 films.

The solubility limits of Fe in silicon are $(1–6) \times 10^{11}$ cm^{-3} at 700 °C,[16,17] $(3–5) \times 10^{12}$ cm^{-3} at 800 °C,[16,17] and 4×10^{13} cm^{-3} at 900 °C.[16] As shown in Figure 1, for the Al_2O_3 coated samples, the Fe solubility limits in silicon are either above the initial bulk [Fe_i] at 900 °C, or above the remaining bulk [Fe_i] at 800 °C, which clearly demonstrate a segregation gettering mechanism of the Al_2O_3 films.

The inability of thermal SiO_2 films to getter Fe for the given annealing times is consistent with our previous observation that the onset of SiO_2 gettering, via Fe precipitation at the SiO_2/Si interface, takes place only after 3–5 h for the high quality FZ-Si wafers, which possibly relates to the nucleation time required for forming precipitation sites.[10] At 900 °C, Fe precipitation should not occur as the initial bulk [Fe_i] is below the solubility limit of Fe in silicon,[16] as shown in Figure 1. At 800 and 700 °C, the levels of impurity supersaturation are relatively low, which may also contribute to the very slow Fe precipitation for the SiO_2 coated samples.[18]

Comparing the remaining bulk [Fe_i] after a same anneal time of 5 min, it is evident that the as-deposited Al_2O_3 films exhibit more effective gettering than the 425 °C-activated Al_2O_3 films, and the difference in the gettering effectiveness increases with increasing temperature (Figure 1). As was already demonstrated in Refs. [10,11], a diffusion-limited surface-loss model[19] is suitable for fitting the measured bulk [Fe_i] as a function of annealing time, yielding apparent Fe diffusivities in silicon. For the as-deposited Al_2O_3 films, the fitted apparent Fe diffusivities at 700–900 °C are found to be smaller than the reported Fe diffusivities in silicon[16] by only a factor of 2–3, indicating a largely diffusion-limited gettering process. On the other hand, for the activated Al_2O_3 films, the gettering processes are much slower than the diffusion-limited kinetics, particularly at 800–900 °C. This clearly shows that a moderate-temperature activation anneal changes the gettering kinetics of the Al_2O_3 films.

To understand the different gettering kinetics of the as-deposited and activated Al_2O_3 films, SIMS was used to examine the Fe distributions in and near the two different Al_2O_3 films after a same 900 °C 15-min anneal, with and without a preceding 425 °C activation anneal. As shown in **Figure 2**, the two samples exhibit the same SIMS Fe profiles. The quantitative Fe concentration within the surface region, from SIMS measurements, corresponds to a bulk Fe concentration of 1.5×10^{14} cm^{-3} for a 180-μm thick silicon wafer. This agrees reasonably well with the implanted Fe concentration of 10^{14} cm^{-3}, considering that the Al_2O_3 used in SIMS calibration standards may exhibit a different ion yield, and the 900 °C anneals could also potentially change the crystal structure of the Al_2O_3 films.[20,21] The Fe peaks at the Al_2O_3/Si interfaces, for the two 900 °C 15-min annealed samples with and without a prior activation step, therefore clearly come from the relocation of Fe from the silicon wafer bulk to the Al_2O_3/Si interfaces, as was previously found for Al_2O_3 gettering at 425 °C.[10] Although about half of the initial bulk Fe is gettered to the Al_2O_3/Si interface during a 30-min 425 °C activation anneal[10] for the activated sample, its Fe profile in Figure 2 shows that the further gettering action during the 900 °C 15-min anneal also takes place

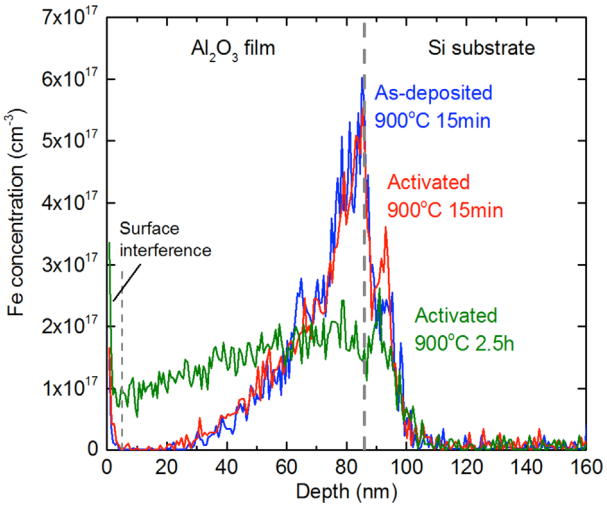

Figure 2. SIMS measurements of the Fe distribution in Al_2O_3 films and the near-surface regions of the silicon wafer bulk for the samples with initial bulk Fe contamination and subsequently being annealed with Al_2O_3 films at 900 °C. One of the samples was annealed with as-deposited Al_2O_3 films for 15 min (blue), and the other two were first annealed at 425 °C for 30 min to activate the passivation quality of the Al_2O_3 films before being annealed at 900 °C for either 15 min (red) or 2.5 h (green).

at the Al_2O_3/Si interface, resulting in the same Fe profile as the as-deposited Al_2O_3 films. The different gettering effectiveness of the as-deposited and activated Al_2O_3 films therefore relates to the Al_2O_3/Si interfaces.

It is interesting to note that the Fe distribution changes after a longer annealing time at 900 °C, as shown by the Fe profile of a 2.5-h annealed sample in Figure 2. The Fe concentration under this profile also gives rise to a bulk Fe concentration of 1.5×10^{14} cm^{-3} for a 180-μm wafer, indicating that the flatter Fe profile results from the redistribution of the gettered Fe from the Al_2O_3/Si interface to the bulk of the Al_2O_3 film during the longer anneal at 900 °C. This is different to the Fe distribution at 425 °C, in which case the gettered Fe seems to remain at the Al_2O_3/Si interfaces even after a long cumulative annealing time of 18 h.[10] This may explain the broader Fe peaks after a 900 °C 15-min anneal at the Al_2O_3/Si interfaces (Figure 2) compared to the SIMS Fe peaks at 425 °C reported in Ref. [10], as Fe redistribution may have already occurred during the 15-min anneal.

The cause for this difference in Fe distribution after long annealing time at 900 and 425 °C is unknown at this stage. The crystal structure change of the Al_2O_3 films at temperatures above 850 °C[20,21] might contribute to this difference. The temperature-dependent Fe diffusivity in the ALD Al_2O_3 films might also be a contributing factor, although this is highly speculative at present, as no such diffusivity data is available in the literature, and much further work is required to understand the interaction of Fe, and other impurities, with the Al_2O_3 films.

Discussion: The high temperature gettering results presented in this work not only reveal the gettering kinetics and effectiveness at contact firing temperatures, which is relevant for solar cell applications, but also help understand the reported

gettering effects at moderate temperatures[10] and the possible gettering mechanisms.

The ALD Al_2O_3 films demonstrate a two-stage gettering kinetics at 425 °C, with the initial stage being fast and largely diffusion-limited, followed by a second slow gettering phase.[10] As with the fast gettering stage at 425 °C, as-deposited Al_2O_3 films at 700–900 °C also exhibit largely diffusion-limited gettering kinetics. In addition, both SIMS Fe profiles at 425 °C[10] and 700–900 °C (Figure 2) reveal Fe accumulation at the Al_2O_3/Si interfaces. The initial fast gettering stage at 425 °C is possibly dominated by the same segregation gettering mechanism as at high temperatures. Given the similarity of the second slow gettering kinetics with the thermal SiO_2 gettering kinetics,[10] and Fe precipitation at the SiO_2/Si interfaces is a well-known phenomenon,[22] the slow gettering stage at 425 °C may be dominated by Fe precipitation at the SiO_x/Si interfaces (an interfacial thin SiO_x layer is known to exist in-between Al_2O_3 and Si[2]).

As shown by the SIMS results in Figure 2, the gettering action for both as-deposited and 425 °C-activated Al_2O_3 films takes place at the Al_2O_3/Si interfaces. The different gettering kinetics of the two are therefore likely caused by the different interface properties. For plasma-assisted ALD Al_2O_3 films, it has been consistently reported that a moderate-temperature activation anneal significantly decreases the interface defect density (D_{it}), while the fixed negative charge density (Q_f) is only slightly improved, as summarised in Ref. [5]. Q_f is also reported to remain unaffected after high temperature firing.[23] The different gettering effectiveness of the as-deposited and activated Al_2O_3 films is therefore more likely related to the different densities of the interface defect, that is, a more defective interface generates better gettering effects.

It has been reported that the as-deposited interfacial SiO_x thin layer at the Al_2O_3/Si interface contains many defects such as the trivalently bonded Si, Si danging bonds, SiO_x interface defects and so on.[5] Such interface defects possibly act as the segregation gettering sites for Fe. A high temperature anneal of the as-deposited Al_2O_3 does not activate the films, meaning that the high level of interface defects offer many gettering sites for Fe, and the gettering kinetics is therefore largely limited by the diffusion of Fe to reach the wafer surfaces. On the other hand, for the previously activated Al_2O_3 films, some interface defects remain passivated during the subsequent high temperature anneals, as surface passivation degradation is found to be less severe in the activated Al_2O_3 compared to the as-deposited Al_2O_3. The gettering reaction is therefore no longer limited by impurity diffusivity but limited by the available gettering sites.

The above hypothesis can also explain the two-stage gettering kinetics and the effect of film thickness at 425 °C.[10] At moderate temperatures, passivation of the interface defects and gettering take place at the same time. As the reactions at the interfacial defect sites become stable, the fast, largely diffusion-limited gettering process slows down, and Fe precipitation at the SiO_x interfaces starts to dominate the second slow gettering stage. Thick Al_2O_3 films tend to become partially activated during the long deposition time,[5] the slow gettering stage therefore starts earlier, as observed in Ref. [10].

One explanation for the reduction of interface defect density upon a moderate-temperature activation anneal is the hydrogen-related passivation of the interfacial SiO_x, as a fraction of hydrogen (in the form of its isotope, deuterium) in the Al_2O_3 film is shown to migrate to the oxide interface after an activation anneal.[24]

An implication of the proposed gettering hypothesis is that impurity gettering and interface passivation are competing processes, and the presence of gettered impurities at the Al_2O_3/Si interfaces may affect the surface passivation effect of the Al_2O_3 films. Further studies are required to examine the impact of gettering on the Al_2O_3 passivation quality.

In industrial solar cells with Al_2O_3/SiN_x stacks, impurity gettering is expected to occur during a high-temperature contact firing process, as both Al_2O_3 and SiN_x films demonstrate gettering effects at 700–900 °C.[10,11] Given that a firing process typically lasts merely a few seconds, only the very fast diffusing impurities, such as copper and nickel, can be gettered during firing. Depending on the deposition conditions of the SiN_x capping layers, the underlying Al_2O_3 films could experience different degrees of passivation activation, which affects its subsequent gettering effectiveness at higher temperatures. During firing, the SiN_x capping layer may affect the amount of hydrogen in the Al_2O_3 layer, which may in turn influence the hydrogen-related interfacial passivation reaction in the underlying Al_2O_3 films. Based on the proposed gettering hypothesis and current understanding of the passivation activation reaction,[24] this could also have an impact on the Al_2O_3 gettering effects.

In summary, results in this work show that the Al_2O_3 films from plasma-assisted atomic layer deposition possess strong impurity gettering effects at typical contact firing temperatures (700–900 °C). Gettering occurs via a segregation mechanism, and iron, a marker impurity in silicon, is found to be relocated from the silicon wafer bulk to the Al_2O_3/Si interfaces during annealing. A longer annealing time at 900 °C redistributes some iron into the bulk of the Al_2O_3 films. The as-deposited Al_2O_3 films demonstrate largely diffusion-limited gettering of Fe. Al_2O_3 films that have a preceding moderate-temperature passivation activation anneal exhibit slower gettering kinetics. A hypothesis is proposed to explain the Al_2O_3 gettering effects at both moderate and high temperatures, based on a competitive gettering and interfacial passivation mechanism.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Al_2O_3, atomic layer deposition, gettering, iron, silicon

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