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Hydrogen induced passivation of Si interfaces by Al$_2$O$_3$ films and SiO$_2$/Al$_2$O$_3$ stacks

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The role of hydrogen in Si surface passivation is experimentally identified for Al$_2$O$_3$ (capping) films synthesized by atomic layer deposition. By using stacks of SiO$_2$ and deuterated Al$_2$O$_3$, we demonstrate that hydrogen is transported from Al$_2$O$_3$ to the underlying SiO$_2$ already at relatively low annealing temperatures of 400 °C. This leads to a high level of chemical passivation of the interface. Moreover, the thermal stability of the passivation up to 800 °C was significantly improved by applying a thin Al$_2$O$_3$ capping film on the SiO$_2$. The hydrogen released from the Al$_2$O$_3$ film favorably influences the passivation of Si interface defects. © 2010 American Institute of Physics. [doi:10.1063/1.3497014]

Aluminum oxide (Al$_2$O$_3$) films afford a high level of Si surface passivation with ultralow surface recombination velocities ($S_{eff} < 5$ cm/s) after postdeposition annealing. These films exhibit a high fixed negative charge density located near the Si interface that generates field-effect passivation. Moreover, the significant reduction in the interface defect density $D_{it}$ to $< 10^{11}$ eV$^{-1}$ cm$^{-2}$ during postdeposition annealing is vital for their passivation performance. The actual processes that lead to the decrease in $D_{it}$ during annealing are not fully understood yet. However, there are indications that the hydrogen (2–3 at. %) in the Al$_2$O$_3$ films plays an important role in passivating defects at the Si/SiO$_2$ interface which is formed when Al$_2$O$_3$ is applied on an H-terminated Si surface.

In this letter, we will experimentally identify the role of hydrogen in the passivation of interface defects during the postdeposition annealing of Al$_2$O$_3$ films. For this purpose we employ a model system comprising a stack of thermally grown SiO$_2$ and a deuterated Al$_2$O$_3$ (Al$_2$O$_3$ :D) film. The use of a thicker thermally grown SiO$_2$ layer, instead of the interfacial (1–2 nm) SiO$_x$, enables the separation between chemical and field-effect passivation. As reported below, SiO$_2$/Al$_2$O$_3$ stacks with a relatively thick SiO$_2$ layer provide negligible field-effect passivation different from Al$_2$O$_3$ films directly deposited on Si. Moreover, these SiO$_2$/Al$_2$O$_3$ stacks are highly technologically relevant as Si passivation scheme, which has recently been demonstrated by results on solar cells. The surface passivation mechanism of such stacks, however, remains poorly understood. The first principal result of this letter is that it is experimentally established that hydrogen diffuses from the Al$_2$O$_3$ thin film toward the Si interface at the relatively low temperature of 400 °C typically employed during postdeposition annealing. By passivating dangling bonds, the hydrogen provides effective chemical passivation of the Si interface. Second, we demonstrate that the effective hydrogenation under influence of the Al$_2$O$_3$ capping film leads to a significantly enhanced thermal stability for the stacks, compared to a single layer of SiO$_2$.

The Al$_2$O$_3$ films were deposited by plasma atomic layer deposition (ALD) at a substrate temperature of $\sim$200 °C. The deuterated films were grown by using Al(CD$_3$)$_3$ as metal precursor. Deuterium was used to facilitate the tracing of hydrogen by secondary ion mass spectrometry (SIMS, carried out at Philips Material Analyses) and thermal effusion measurements. Elastic recoil detection, used to calibrate the SIMS results, revealed that the density of D in the Al$_2$O$_3$:D films was $2.2 \times 10^{13}$ cm$^{-3}$ ([D] = $\sim$ 2.4 at. %, similar to [H] in the Al$_2$O$_3$:H films normally employed), and contained only a small density of H of $\sim$ 1.5 $\times 10^{20}$ cm$^{-3}$. The latter can be attributed to the isotopic purity of the Al(CD$_3$)$_3$ precursor. The high quality SiO$_2$ layers (thickness $\sim$ 200–300 nm) were grown using wet thermal oxidation (at 900 °C) and floatzone Si (100) wafers were used as substrates. Annealing was carried out in an N$_2$ environment, unless otherwise indicated. The upper level of $S_{eff}$ was determined from the effective lifetime, as measured with photoconductance decay (Sinton WCT 100) at an injection level of $5 \times 10^{14}$ cm$^{-3}$ by assuming an infinite bulk lifetime.

After deposition of a 30 nm thick Al$_2$O$_3$ capping film on the as-grown SiO$_2$, a low level of surface passivation was obtained ($S_{eff} < 280$ cm/s). The passivation by the stacks could however be activated by annealing (400 °C, 10 min), and typically very low $S_{eff}$ values $< 4$ cm/s and $S_{eff} < 2$ cm/s were obtained for $\sim 2.5$ Ω cm and $\sim 10$ Ω cm n-type c-Si wafers, respectively. Reference samples with Al$_2$O$_3$ capping films synthesized with thermal ALD, using H$_2$O instead of O$_2$ plasma as the oxidant, led to similar results. The annealed SiO$_2$/Al$_2$O$_3$ stacks generally afforded a higher level of passivation compared to SiO$_2$ reference samples annealed in forming gas. Second-harmonic generation experiments, performed on the thermal SiO$_2$/Al$_2$O$_3$ stacks demonstrated that no significant field-effect passivation was present for the SiO$_2$ thicknesses employed. The passivation performance of the stacks can therefore be attributed to a high level of chemical passivation. A high level of chemical passivation, in addition to effective field-effect passivation, was previously also reported for Al$_2$O$_3$ applied directly on Si as indicated by a $D_{it}$ of $<10^{11}$ eV$^{-1}$ cm$^{-2}$ obtained after the same annealing treatment. Another important observation was that the thermal stability of the...
SiO$_2$ was significantly enhanced by the use of an Al$_2$O$_3$ capping film. Figure 1 compares the thermal stability of the passivation afforded by a SiO$_2$/Al$_2$O$_3$ stack (after annealing at 400 °C) with that of (hydrogenated) SiO$_2$ only. The latter sample underwent the same treatment as the SiO$_2$/Al$_2$O$_3$ stack but the Al$_2$O$_3$ capping film was removed after annealing by etching in HF. This SiO$_2$ sample (prepared with “sacrificial” Al$_2$O$_3$) and the SiO$_2$/Al$_2$O$_3$ stack resulted in a similar level of passivation, which remained high for temperatures up to 400 °C. Above 500 °C a rapid deterioration was, however, observed for the SiO$_2$, whereas the passivation induced by the stack was less affected. The stack exhibited improved thermal stability, and only after annealing at 700 °C (for 1 min), the surface passivation deteriorated. The stability of the stacks was also examined for an industrial firing process as used for the metallization of solar cells, which is consistent with the improved thermal stability of the Al$_2$O$_3$ films initially, diffused into the SiO$_2$ layer during annealing in the near surface region has been observed before during forming gas annealing studies.15 This is consistent with the high mobility of molecular hydrogen in SiO$_2$ in combination with the Si substrate acting as a diffusion barrier,16 which promotes the diffusion of hydrogen along the interface and significantly increases its interaction with electronically active recombination centers,16,17 and other defects present in this interfacial region.15,16,17 Overall, the data indicate that approximately 4% of the D present in the Al$_2$O$_3$ films initially, diffused into the SiO$_2$ layer during annealing, which is approximately a quarter of the total amount of D that was removed from the Al$_2$O$_3$ film. After a subsequent high temperature step (800 °C, 30 s), a strong reduction in [D] in both the Al$_2$O$_3$ and SiO$_2$ layers was observed. Interestingly, the decrease in [D] at Si/SiO$_2$ interface was significantly lower than that in the SiO$_2$ bulk. To summarize, these SIMS results clearly demonstrate the release, and subsequent diffusion, of hydrogen from the Al$_2$O$_3$ toward the interface region during annealing.

To investigate the mechanism underlying the effective chemical passivation induced by Al$_2$O$_3$ and the enhanced thermal stability of the SiO$_2$/Al$_2$O$_3$ stacks, SIMS measurements were performed on three similarly-prepared SiO$_2$/Al$_2$O$_3$-Si stacks that only differed in postdeposition annealing. The D depth-profiles are displayed in Fig. 2. For the as-deposited stack, the deuterium concentration, [D], was relatively constant in the Al$_2$O$_3$ film, as expected for films prepared by ALD. D atoms were also detected in the SiO$_2$ film, with significant accumulation near the SiO$_2$/Si interface,13 prior to annealing of the stack. It is likely that the D atoms were incorporated into the SiO$_2$ during the oxidation step in the Al$_2$O$_3$ ALD cycle, when atomic deuterium originating from the metal precursor is present in the plasma, as we have corroborated by optical emission spectroscopy.14 The activation of the surface passivation during annealing at 400 °C, led to a significant drop of the total [D] by ~3.3 with that of (hydrogenated) SiO$_2$ only. The latter sample underwent the same treatment as the SiO$_2$/Al$_2$O$_3$ stack but the Al$_2$O$_3$ capping film was removed after annealing by etching in HF. This SiO$_2$ sample (prepared with “sacrificial” Al$_2$O$_3$) and the SiO$_2$/Al$_2$O$_3$ stack resulted in a similar level of passivation, which remained high for temperatures up to 400 °C. Above 500 °C a rapid deterioration was, however, observed for the SiO$_2$, whereas the passivation induced by the stack was less affected. The stack exhibited improved thermal stability, and only after annealing at 700 °C (for 1 min), the surface passivation deteriorated. The stability of the stacks was also examined for an industrial firing process as used for the metallization of solar cells, which is consistent with the improved thermal stability of the Al$_2$O$_3$ films initially, diffused into the SiO$_2$ layer during annealing in the near surface region has been observed before during forming gas annealing studies.15 This is consistent with the high mobility of molecular hydrogen in SiO$_2$ in combination with the Si substrate acting as a diffusion barrier,16 which promotes the diffusion of hydrogen along the interface and significantly increases its interaction with electronically active recombination centers,16,17 and other defects present in this interfacial region.15,16,17 Overall, the data indicate that approximately 4% of the D present in the Al$_2$O$_3$ films initially, diffused into the SiO$_2$ layer during annealing, which is approximately a quarter of the total amount of D that was removed from the Al$_2$O$_3$ film. After a subsequent high temperature step (800 °C, 30 s), a strong reduction in [D] in both the Al$_2$O$_3$ and SiO$_2$ layers was observed. Interestingly, the decrease in [D] at Si/SiO$_2$ interface was significantly lower than that in the SiO$_2$ bulk. To summarize, these SIMS results clearly demonstrate the release, and subsequent diffusion, of hydrogen from the Al$_2$O$_3$ toward the interface region during annealing.

To study the influence of the annealing treatment on the release of hydrogen from the Al$_2$O$_3$ films in more detail, effusion experiments were carried out in an ultrahigh vacuum quartz tube with a constant heating rate of 20 °C/min.18 The effusion measurements on a Al$_2$O$_3$-D stack, as displayed in Figs. 3(a) and 3(b), demonstrated that D is released from the film into the vacuum in different forms. Analyses of the cracking patterns revealed the following prominent species; D$_2$O (mass over charge ratio m/z=20), HDO (m/z=19), D$_2$O (m/z=4), and HD (m/z=3). The maxima in the effusion transients were detected at temperatures of $T_{max}$~670–715 °C. The onset of the signals, however, already occurred at temperatures as low as ~400 °C. These observations indicate that hydrogen is released from the Al$_2$O$_3$ films over a relatively broad temperature range, which is consistent with the improved thermal stability of the

![FIG. 1.](Image) (Color online) Maximum effective surface recombination velocity ($S_{eff,max}$) for cumulative annealing treatments (in steps of 1 min) for float-zone Si wafers (n-type, ~10 Ω cm) with SiO$_2$/Al$_2$O$_3$:H stack and SiO$_2$ layer. The latter sample was hydrogenated by using a sacrificial Al$_2$O$_3$ film during annealing at 400 °C for 10 min. Prior to this experiment, also the stack was annealed under the same conditions. Lines serve as guide for the eye.

![FIG. 2.](Image) (Color online) Deuterium depth profiles measured with SIMS for Al$_2$O$_3$:D/SiO$_2$ stacks on Si. (1) as-deposited, (2) after annealing at 400 °C (10 min), and (3) after annealing at 400 °C (10 min) and subsequent annealing at 800 °C (30s). The vertical axis displays the calibrated [D] in the Al$_2$O$_3$ films. For the SiO$_2$ and Si, calibrations revealed that [D] is a factor 1.7 higher than indicated on the axis. For (1), the lower apparent D signal for short sputtering times is a measurement artifact.
SiO$_2$/Al$_2$O$_3$ stack (Fig. 1). Although these effusion results warrant a more detailed discussion outside the scope of this Letter, we would like to point out that the HDO signal is significantly stronger than the D$_2$O signal. Because $[H]/[D]$, this suggests an effusion process with a surface-enhanced desorption component in which diffusion in the Al$_2$O$_3$ film and the subsequent isotope exchange at the surface (with H$_2$O adsorbed from the ambient) play a role.

To investigate the role of hydrogen in the thermal stability of the stacks, and the depassivation of Si/SiO$_2$ interface defects,$^{19}$ thermal effusion experiments were carried out on a deuterated SiO$_2$ sample. The deuterium was incorporated into the SiO$_2$ using a sacrificial Al$_2$O$_3$-D layer during annealing as described earlier. The effusion signals of HDO and HD originating from this “SiO$_2$:D” film, which were not detected for a reference SiO$_2$ sample, corroborate the SIMS results by confirming the presence of D in the SiO$_2$ film [Fig. 3(c)]. H$_2$O and H$_2$ were also detected [Fig. 3(d)], with comparable transients for a SiO$_2$ film which received forming gas annealing (not shown). Maxima in the effusion signals were detected at $T_{M1} \sim 425$ °C, $T_{M2} \sim 520$ °C, and $T_{M3} \sim 750$ °C. The existence of multiple peaks indicates various activation energies and suggests a variety of corresponding bonding configurations of hydrogen. While the low temperature ($T_{M1}$) features may be explained by surface desorption of (hydrogen-bonded) H$_2$O and by dehydroxilation reactions,$^{20}$ the effusion at higher temperatures can be attributed to hydrogen originating from the bulk and interface. In fact, comparison with Fig. 1 strongly suggests that the release of hydrogen at $T_{M2}$ is indicative of the depassivation of interface defects, coinciding with a strong decrease in surface passivation performance for single layer SiO$_2$. It is likely that the reverse process, the interface hydrogenation, also involves the diffusion of H$_2$ in SiO$_2$. A possible role of atomic hydrogen, as has been reported for dense α-SiN$_x$:H layers,$^{21}$ cannot be conclusively established on the basis of the presented data as the effusion measurements only detect stable molecules.

The combination of experimental results demonstrates that the high level of chemical passivation induced by the Al$_2$O$_3$ capping layer on SiO$_2$ is related to effective transport of hydrogen from the Al$_2$O$_3$ toward the Si interface during annealing. The effective hydrogenation is reminiscent of the annealing effect employing an Al capping layer.$^{22}$ Furthermore, it was shown that the significantly enhanced thermal stability of the SiO$_2$/Al$_2$O$_3$ stacks can be related to a supply of hydrogen from the Al$_2$O$_3$ film that balances the depassivation of defects at the SiO$_2$/Si interface at elevated temperatures. The Al$_2$O$_3$ capping may simultaneously serve as a diffusion barrier and impede the rapid effusion of hydrogen from the SiO$_2$. As the interface of Al$_2$O$_3$ applied directly on c-Si is essentially Si/SiO$_2$-like,$^{23}$ it is likely that a similar hydrogen-induced passivation mechanism can also explain the low interface defect density for single-layer Al$_2$O$_3$ after annealing. Moreover, the important role of hydrogen can be linked to reported trends concerning, for example, the Al$_2$O$_3$ film thickness and deposition temperature.$^{4,10}$ Finally we note that the insights revealed by this study may have major implications for the optimization of postdeposition treatments and for defining specific passivation schemes comprising Al$_2$O$_3$ for industrial-type solar cells.

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