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Hydrogen induced passivation of Si interfaces by Al₂O₃ films and SiO₂/Al₂O₃ stacks

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The role of hydrogen in Si surface passivation is experimentally identified for Al₂O₃ (capping) films synthesized by atomic layer deposition. By using stacks of SiO₂ and deuterated Al₂O₃, we demonstrate that hydrogen is transported from Al₂O₃ to the underlying SiO₂ 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 Al₂O₃ capping film on the SiO₂. The hydrogen released from the Al₂O₃ film favorably influences the passivation of Si interface defects. © 2010 American Institute of Physics. [doi:10.1063/1.3497014]

Aluminum oxide (Al₂O₃) films afford a high level of Si surface passivation with ultralow surface recombination velocities ($S_{\text{eff}} < 5$ cm/s) after postdeposition annealing.¹⁻⁴ 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.⁵ 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 Al₂O₃ films plays an important role in passivating defects at the Si/SiO_x interface which is formed when Al₂O₃ is applied on an H-terminated Si surface.^{2,6-8}

In this letter, we will experimentally identify the role of hydrogen in the passivation of interface defects during the postdeposition annealing of Al₂O₃ films. For this purpose we employ a model system comprising a stack of thermally grown SiO₂ and a deuterated Al₂O₃ (Al₂O₃:D) film. The use of a thicker thermally grown SiO₂ layer, instead of the interfacial (1–2 nm) SiO_x, enables the separation between chemical and field-effect passivation. As reported below, SiO₂/Al₂O₃ stacks with a relatively thick SiO₂ layer provide negligible field-effect passivation different from Al₂O₃ films directly deposited on Si. Moreover, these SiO₂/Al₂O₃ stacks are highly technologically relevant as Si passivation scheme, which has recently been demonstrated by results on solar cells.⁹ 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 Al₂O₃ 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 Al₂O₃ capping film leads to a significantly enhanced thermal stability for the stacks, compared to a single layer of SiO₂.

The Al₂O₃ films were deposited by plasma atomic layer deposition (ALD) at a substrate temperature of ~ 200 °C.¹⁰ The deuterated films were grown by using Al(CD₃)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 Al₂O₃:D films was 2.2×10^{21} cm⁻³ ($[D] = \sim 2.4$ at. %, similar to $[H]$ in the Al₂O₃:H films normally employed),¹⁰ 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(CD₃)₃ precursor. The high quality SiO₂ layers (thickness ~ 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 N₂ 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 5×10^{14} cm⁻³ by assuming an infinite bulk lifetime.

After deposition of a 30 nm thick Al₂O₃ capping film on the as-grown SiO₂, a low level of surface passivation was obtained ($S_{\text{eff}} < 280$ 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 $S_{\text{eff}} < 2$ cm/s were obtained for ~ 2.5 Ω cm and ~ 10 Ω cm *n*-type *c*-Si wafers, respectively. Reference samples with Al₂O₃ capping films synthesized with thermal ALD, using H₂O instead of O₂ plasma as the oxidant, led to similar results. The annealed SiO₂/Al₂O₃ stacks generally afforded a higher level of passivation compared to SiO₂ reference samples annealed in forming gas. Second-harmonic generation experiments,¹¹ performed on the thermal SiO₂/Al₂O₃ stacks demonstrated that no significant field-effect passivation was present for the SiO₂ 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 Al₂O₃ applied directly on Si as indicated by a D_{it} of $< 10^{11}$ eV⁻¹ cm⁻² obtained after the same annealing treatment.⁵ Another important observation was that the thermal stability of the

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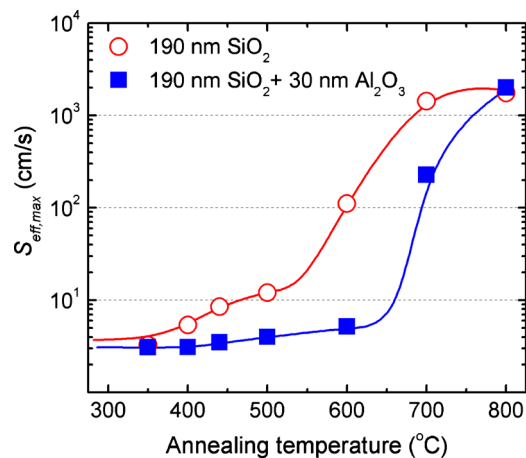


FIG. 1. (Color online) Maximum effective surface recombination velocity ($S_{\text{eff,max}}$) for cumulative annealing treatments (in steps of 1 min) for float-zone Si wafers (n -type, $\sim 10 \Omega \text{ cm}$) with $\text{SiO}_2/\text{Al}_2\text{O}_3:\text{H}$ stack and SiO_2 layer. The latter sample was hydrogenated by using a sacrificial Al_2O_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.

SiO_2 was significantly enhanced by the use of an Al_2O_3 capping film. Figure 1 compares the thermal stability of the passivation afforded by a $\text{SiO}_2/\text{Al}_2\text{O}_3$ stack (after annealing at 400 °C) with that of (hydrogenated) SiO_2 only. The latter sample underwent the same treatment as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ stack but the Al_2O_3 capping film was removed after annealing by etching in HF. This SiO_2 sample (prepared with “sacrificial” Al_2O_3) and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 ($T > 800 \text{ °C}$ for a number of seconds), which resulted in low $S_{\text{eff}} < 9 \text{ cm/s}$. Such increased stability compared to single layer SiO_2 , has also been reported for $\text{SiO}_2/a\text{-SiN}_x:\text{H}$ stacks.¹²

To investigate the mechanism underlying the effective chemical passivation induced by Al_2O_3 and the enhanced thermal stability of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks, SIMS measurements were performed on three similarly-prepared $\text{SiO}_2/\text{Al}_2\text{O}_3:\text{D}$ 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_2O_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_2O_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 $\sim 3.3 \times 10^{20} \text{ cm}^{-3}$ in the Al_2O_3 films, which is approximately $\sim 15\%$ of the initial concentration. The D content in the SiO_2 layer increased by $\sim 9 \times 10^{19} \text{ cm}^{-3}$ ($\sim 100\%$ increase), dem-

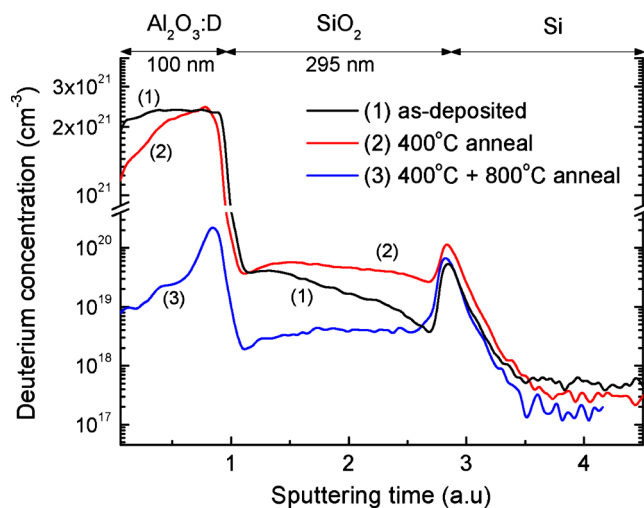


FIG. 2. (Color online) Deuterium depth profiles measured with SIMS for $\text{Al}_2\text{O}_3:\text{D}/\text{SiO}_2$ stacks on Si, (1) as-deposited, (2) after annealing at 400 °C (10 min), and (3) after annealing at 400 °C (10 min) and subsequent annealing at 800 °C (30s). The vertical axis displays the calibrated [D] in the Al_2O_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.

onstrating that effective transport of D from the Al_2O_3 film into the underlying SiO_2 takes place during annealing. It is observed that the D content at the Si/SiO_2 interface also increased dramatically (also by $\sim 100\%$). Hydrogen accumulation in the near surface region has been observed before during forming gas annealing studies.^{13,15} 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.^{13,15–17} Overall, the data indicate that approximately 4% of the D present in the Al_2O_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_2O_3 film. After a subsequent high temperature step (800 °C, 30 s), a strong reduction in [D] in both the Al_2O_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_2O_3 toward the interface region during annealing.

To study the influence of the annealing treatment on the release of hydrogen from the Al_2O_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 $\text{Al}_2\text{O}_3:\text{D}$ film, 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_2O (mass over charge ratio $m/z=20$), HDO ($m/z=19$), D_2 ($m/z=4$), and HD ($m/z=3$). The maxima in the effusion transients were detected at temperatures of $T_M \sim 670\text{--}715 \text{ °C}$. The onset of the signals, however, already occurred at temperatures as low as $\sim 400 \text{ °C}$. These observations indicate that hydrogen is released from the Al_2O_3 films over a relatively broad temperature range, which is consistent with the improved thermal stability of the

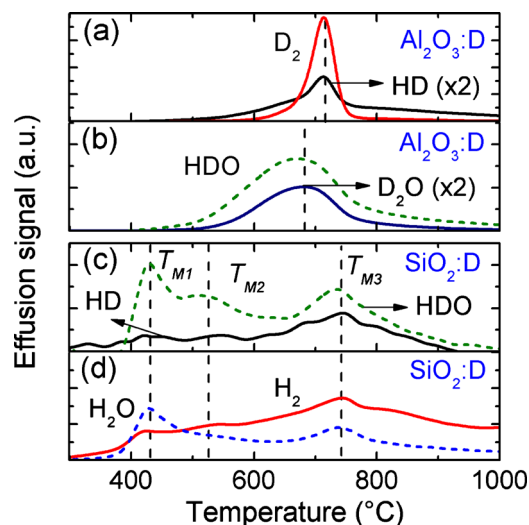


FIG. 3. (Color online) Thermal effusion measurements for an $\text{Al}_2\text{O}_3:\text{D}$ film [(a) and (b)] and for deuterated SiO_2 (“ $\text{SiO}_2:\text{D}$ ”) prepared using a sacrificial $\text{Al}_2\text{O}_3:\text{D}$ film during annealing [(c) and (d)].

$\text{SiO}_2/\text{Al}_2\text{O}_3$ 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_2O signal. Because $[\text{H}] \ll [\text{D}]$, this suggests an effusion process with a surface-enhanced desorption component in which diffusion in the Al_2O_3 film and the subsequent isotope exchange at the surface (with H_2O 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 $\text{Al}_2\text{O}_3:\text{D}$ layer during annealing as described earlier. The effusion signals of HDO and HD originating from this “ $\text{SiO}_2:\text{D}$ ” 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_2O 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_2O and by dehydroxylation 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 $a\text{-SiN}_x:\text{H}$ 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_2O_3 capping layer on SiO_2 is related to effective transport

of hydrogen from the Al_2O_3 toward the Si interface during annealing. The effective hydrogenation is reminiscent of the *alenealing* effect employing an Al capping layer.²² Furthermore, it was shown that the significantly enhanced thermal stability of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ stacks can be related to a supply of hydrogen from the Al_2O_3 film that balances the depassivation of defects at the SiO_2/Si interface at elevated temperatures. The Al_2O_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_2O_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_2O_3 after annealing. Moreover, the important role of hydrogen can be linked to reported trends concerning, for example, the Al_2O_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_2O_3 for industrial-type solar cells.

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- ¹B. Hoex, S. B. S. Heil, E. Langereis, M. C. M. van de Sanden, and W. M. M. Kessels, *Appl. Phys. Lett.* **89**, 042112 (2006).
- ²B. Hoex, J. J. H. Gielis, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **104**, 113703 (2008).
- ³G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H. F. W. Dekkers, S. De Wolf, and G. Beaucarne, *Sol. Energy Mater. Sol. Cells* **90**, 3438 (2006).
- ⁴G. Dingemans, R. Seguin, P. Engelhart, M. C. M. van de Sanden, and W. M. M. Kessels, *Phys. Status Solidi (RRL)* **4**, 10 (2010).
- ⁵G. Dingemans, N. M. Terlinden, D. Pierreux, H. B. Profijt, M. C. M. van de Sanden, and W. M. M. Kessels, *Electrochem. Solid-State Lett.* (in press).
- ⁶A. Roy Chowdhuri, C. G. Takoudis, R. F. Klie, and N. D. Browning, *Appl. Phys. Lett.* **80**, 4241 (2002).
- ⁷G. Dingemans, R. Seguin, P. Engelhart, F. Einsele, B. Hoex, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **106**, 114907 (2009).
- ⁸T.-T. A. Li and A. Cuevas, *Prog. Photovoltaics* (2010).
- ⁹W. C. Sun, W. L. Chang, C. H. Chen, C. H. Du, T. Y. Wang, T. Wang, and C. W. Lan, *Electrochem. Solid-State Lett.* **12**, H388 (2009).
- ¹⁰G. Dingemans, M. C. M. van de Sanden, and W. M. M. Kessels, *Electrochem. Solid-State Lett.* **13**, H76 (2010).
- ¹¹J. J. H. Gielis, B. Hoex, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **104**, 073701 (2008).
- ¹²J. Schmidt, M. J. Kerr, and A. Cuevas, *Semicond. Sci. Technol.* **16**, 164 (2001).
- ¹³N. M. Johnson, D. K. Biegelsen, M. D. Moyer, V. R. Deline, and C. A. Evans, Jr., *Appl. Phys. Lett.* **38**, 995 (1981).
- ¹⁴S. B. S. Heil, J. L. van Hemmen, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **103**, 103302 (2008).
- ¹⁵M. Wilde, M. Matsumoto, K. Fukutani, Z. Liu, K. Ando, Y. Kawashima, and S. Fujiede, *J. Appl. Phys.* **92**, 4320 (2002).
- ¹⁶L. Tsetseris and S. T. Pantelides, *Phys. Rev. B* **70**, 245320 (2004).
- ¹⁷A. Stesmans, *J. Appl. Phys.* **88**, 489 (2000).
- ¹⁸W. Beyer, J. Herion, H. Wagner, and U. Zastrow, *Philos. Mag. B* **63**, 269 (1991).
- ¹⁹J. H. Stathis, *J. Appl. Phys.* **77**, 6205 (1995).
- ²⁰Y. Kawashima, Z. Liu, K. Terashima, K. Hamada, K. Fukutani, M. Wilde, S. Aoyagi, and M. Kudo, *Appl. Surf. Sci.* **212–213**, 804 (2003).
- ²¹M. Sheoran, D. S. Kim, A. Rohatgi, H. F. W. Dekkers, G. Beaucarne, M. Young, and S. Asher, *Appl. Phys. Lett.* **92**, 172107 (2008).
- ²²M. L. Reed and J. D. Plummer, *J. Appl. Phys.* **63**, 5776 (1988).
- ²³A. Stesmans and V. V. Afanas'ev, *Appl. Phys. Lett.* **80**, 1957 (2002).