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Citation for published version (APA):

DOI:
10.1063/1.3497014

Document status and date:
Published: 01/01/2010

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Download date: 02. Oct. 2023
Hydrogen induced passivation of Si interfaces by Al2O3 films and SiO2/Al2O3 stacks

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(Received 11 August 2010; accepted 14 September 2010; published online 12 October 2010)  

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_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/SiOx interface which is formed when Al2O3 is applied on an H-terminated Si surface.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) SiOx, 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^{13} cm^{-3} ([D]=~2.4 at. %, similar to [H] in the Al2O3:H films normally employed),10 and contained only a small density of H of ~1.5 × 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 photocurrent 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_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 ~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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SiO₂ was significantly enhanced by the use of an Al₂O₃ capping film. Figure 1 compares the thermal stability of the passivation afforded by a SiO₂/Al₂O₃ stack (after annealing at 400 °C) with that of (hydrogenated) SiO₂ only. The latter sample underwent the same treatment as the SiO₂/Al₂O₃ stack but the Al₂O₃ capping film was removed after annealing by etching in HF. This SiO₂ sample (prepared with “sacrificial” Al₂O₃) and the SiO₂/Al₂O₃ 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 SiO₂, 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 °C for a number of seconds), which resulted in low D<sub>0</sub><sub>eff</sub> < 9 cm/s. Such increased stability compared to single layer SiO₂, has also been reported for SiO₂/a-SiNₓ:H stacks.

To investigate the mechanism underlying the effective chemical passivation induced by Al₂O₃ and the enhanced thermal stability of the SiO₂/Al₂O₃ stacks, SIMS measurements were performed on three similarly-prepared SiO₂/Al₂O₃: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 Al₂O₃ film, as expected for films prepared by ALD. D atoms were also detected in the SiO₂ film, with significant accumulation near the SiO₂/Si interface, prior to annealing of the stack. It is likely that the D atoms were incorporated into the SiO₂ during the oxidation step in the Al₂O₃ ALD cycle, when atomic deuterium originating from the metal precursor is present in the plasma, as we have corroborated by optical emission spectroscopy. The activation of the surface passivation during annealing at 400 °C, led to a significant drop of the total [D] by ~3.3 × 10<sup>20</sup> cm<sup>-3</sup> in the Al₂O₃ films, which is approximately ~15% of the initial concentration. The D content in the SiO₂ layer increased by ~9 × 10<sup>19</sup> cm<sup>-3</sup> (~100% increase), demonstrating that effective transport of D from the Al₂O₃ film into the underlying SiO₂ takes place during annealing. It is observed that the D content at the Si/SiO₂ interface also increased dramatically (also by ~100%). Hydrogen accumulation in the near surface region has been observed before during forming gas annealing studies. This is consistent with the high mobility of molecular hydrogen in SiO₂ in combination with the Si substrate acting as a diffusion barrier, which promotes the diffusion of hydrogen along the interface and significantly increases its interaction with electronically active recombination centers, and other defects present in this interfacial region. Overall, the data indicate that approximately 4% of the D present in the Al₂O₃ films initially, diffused into the SiO₂ layer during annealing, which is approximately a quarter of the total amount of D that was removed from the Al₂O₃ film. After a subsequent high temperature step (800 °C, 30 s), a strong reduction in [D] in both the Al₂O₃ and SiO₂ layers was observed. Interestingly, the decrease in [D] at Si/SiO₂ interface was significantly lower than that in the SiO₂ bulk. To summarize, these SIMS results clearly demonstrate the release, and subsequent diffusion, of hydrogen from the Al₂O₃ toward the interface region during annealing.

To study the influence of the annealing treatment on the release of hydrogen from the Al₂O₃ films in more detail, effusion experiments were carried out in an ultrahigh vacuum quartz tube with a constant heating rate of 20 °C/min. The effusion measurements on a Al₂O₃: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: D₂O (mass over charge ratio m/z=20), HD (m/z=19), D₂ (m/z=4), and HD (m/z=3). The maxima in the effusion transients were detected at temperatures of T<sub>m</sub> ~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 Al₂O₃ films over a relatively broad temperature range, which is consistent with the improved thermal stability of the
of hydrogen from the Al2O3 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 SiO2/Al2O3 stacks can be related to a supply of hydrogen from the Al2O3 film that balances the depassivation of defects at the SiO2/Si interface at elevated temperatures. The Al2O3 capping may simultaneously serve as a diffusion barrier and impede the rapid effusion of hydrogen from the SiO2. As the interface of Al2O3 applied directly on c-Si is essentially Si/SiO2-like,23 it is likely that a similar hydrogen-induced passivation mechanism can also explain the low interface defect density for single-layer Al2O3 after annealing. Moreover, the important role of hydrogen can be linked to reported trends concerning, for example, the Al2O3 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 Al2O3 for industrial-type solar cells.

We thank Dr. P. Engelhart, Dr. R. Seguin and S. Bordihn (Q-CELLS), N. Terlinden and Dr. M. Mandoc (TU/e), and D. Lennartz (IFW-5) for experimental support and fruitful discussions. The deuterated TMA was kindly provided by Air Liquide. This work is supported by the German Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) under Contract No. 0325150 (“ALADIN”).

SiO2/Al2O3 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 D2O signal. Because [H]/[D], this suggests an effusion process with a surface-enhanced desorption component in which diffusion in the Al2O3 film and the subsequent isotope exchange at the surface (with H2O 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/SiO2 interface defects,19 thermal effusion experiments were carried out on a deuterated SiO2 sample. The deuterium was incorporated into the SiO2 using a sacrificial Al2O3:D layer during annealing as described earlier. The effusion signals of HDO and HD originating from this “SiO2:D” film, which were not detected for a reference SiO2 sample, corroborate the SIMS results by confirming the presence of D in the SiO2 film [Fig. 3(a)]. H2O and H2 were also detected [Fig. 3(d)], with comparable transients for a SiO2 film which received forming gas annealing (not shown). Maxima in the effusion signals were detected at TM1 ~425 °C, TM2 ~520 °C, and TM3 ~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 (TM1) features may be explained by surface desorption of (hydrogen-bonded) H2O 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 TM2 is indicative of the depassivation of interface defects, coinciding with a strong decrease in surface passivation performance for single layer SiO2. It is likely that the reverse process, the interface hydrogenation, also involves the diffusion of H2 in SiO2. A possible role of atomic hydrogen, as has been reported for dense a-SiNₓ: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 Al2O3 capping layer on SiO2 is related to effective transport

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8T.-T. A. Li and A. Cuevas, Prog. Photovoltaics (2010).