CRYSTALLINE SILICON SURFACE PASSIVATION BY THE NEGATIVE-CHARGE-DIELECTRIC Al_2O_3

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ABSTRACT

In this contribution it will demonstrated that Al_2O_3 films synthesized by plasma-assisted atomic layer deposition are a very interesting low temperature solution for the passivation of highly and lowly doped *p*-type c-Si and lightly doped *n*-type c-Si. From experiments it will be shown that the excellent surface passivation by Al_2O_3 can for a large part be attributed to a high fixed negative charge density in the film on the film-substrate interface. The implications of this high fixed negative charge density on the surface passivation of both *n*- and *p*-type c-Si will be addressed.

INTRODUCTION

Surface passivation of crystalline silicon (c-Si) is becoming increasingly important for the performance of c-Si solar cells. Surface passivation is not only requisite for high efficiency solar cells. Surface passivation is, moreover, becoming vital for all solar cells based on c-Si as the cost-driven reduction of the solar cell thickness is increasing the surface-to-volume ratio.

Thin films (typically 20-80 nm) of thermal silicon dioxide (SiO_2), silicon nitride (a-SiN_x:H) and amorphous silicon (a-Si:H) are currently used for surface passivation of c-Si solar cells in industry. A material that has recently regained interest for the passivation of c-Si is aluminum oxide (Al_2O_3). In the late eighties Al_2O_3 was already applied for c-Si surface passivation in a metal-insulator-semiconductor (MIS) solar cell by Hezel and Jaeger.[1] They demonstrated that Al_2O_3 could provide a reasonable level of surface passivation with an effective surface recombination velocity of ~200 cm/s on 2 Ω cm *p*-type c-Si. More recently Agostinelli et al. demonstrated that Al_2O_3 grown by atomic layer deposition (ALD) could provide an excellent level of surface passivation on *p*-type c-Si.[2]

In this contribution we will demonstrate that Al_2O_3 deposited by plasma-assisted ALD[3,4] yields a state-of-the-art level of surface passivation on various c-Si surfaces. Moreover, we will address the c-Si surface passivation mechanism of Al_2O_3 and show that this underlying mechanism makes Al_2O_3 a particularly interesting candidate for the passivation of *p*-type c-Si with an arbitrary doping level. This also includes the passivation of *p*-type emitters which has been found challenging so far.

EXPERIMENTAL

Al_2O_3 films with a thickness of 7-30 nm were grown in a commercial (Oxford Instruments, FlexAL) and home-built PA-ALD reactor (ALD-I) at a substrate temperature of 200 ^oC. The films were prepared by alternating trimethylaluminium (TMA) exposure and a remote O_2 plasma. The film growth was monitored by means of *in situ* spectroscopic ellipsometry (250-1000 nm range) and revealed a growth rate in the 1.2 Å range per cycle. The surface passivation was tested by depositing identical Al_2O_3 films on both sides of low resistivity c-Si substrates with various doping concentrations and dopant types. The substrates received a standard RCA clean with final HF dip prior to deposition to remove the native oxide. After deposition, the lifetime samples were annealed in a N_2 environment for 30 minutes at 425 ^oC in a rapid thermal anneal furnace. The effective lifetime τ_{eff} was measured using a lifetime tester (Sinton WCT-100) in both the quasi steady state and transient mode.[5] The level of surface passivation is quantified by the effective surface recombination velocity. Assuming an infinite bulk lifetime, the upper limit of the effective surface recombination velocity Seff can be calculated by:

$$S_{eff} \leq \frac{W}{2 \cdot \tau_{eff}} \quad (1)$$

with W the substrate thickness.

c-SI SURFACE PASSIVATION BY Al_2O_3

In Fig. 1 the effective lifetime is shown for low resistivity *n*-type c-Si passivated by Al_2O_3 films with a thickness of 7-30 nm as determined from photoconductance measurements.[5] Effective lifetimes in excess of 6 ms were measured indicating a surface recombination velocity $S_{eff,max}$ of 2 cm/s assuming an infinite bulk lifetime. These values are comparable to the best values published for *alnealed* thermal SiO_2.[6] A 7 nm thick Al_2O_3 still yields a $S_{eff,max}$ of 5 cm/s.

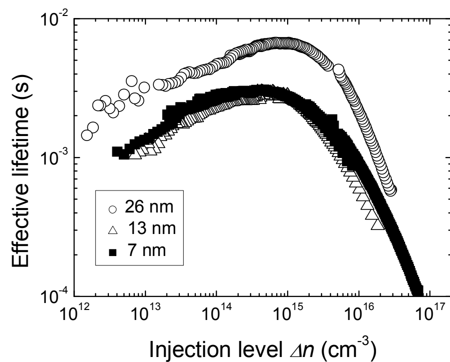

Figure 1: Effective lifetime as a function of the excess carrier density for low resistivity *n*-type (275 μm, <100>, 1.9 Ω cm) float zone c-Si substrate passivated with a 30, 15 and 7 nm thick Al_2O_3 film.[7]

In Fig. 2 the effective lifetime is shown for a 2 Ω cm *p*-type wafer passivated by a 10 and 30 nm Al_2O_3 film. Effective lifetimes in excess of 3 ms were measured, corresponding to a $S_{eff,max}$ of 5 cm/s. In Fig. 3 the combined $S_{eff,\ max}$ values are shown for *p*-type c-Si with various doping concentrations passivated by Al_2O_3. Literature values obtained by thermal SiO_2 (either forming gas annealed or *alnealed*), *as deposited* a-SiN_x:H and a-Si:H are included for comparison. The values for a B-doping concentration > 10^{18} cm^{-3} were extracted from the measured emitter saturation current density on B-doped *p*-type emitters as discussed in detail in a separate publication.[8] The effective surface recombination values for lightly B-doped c-Si were calculated assuming an infinite bulk lifetime and using the best values published in the studies of Kerr et al. [6,9,10] and Dauwe et al.[9]

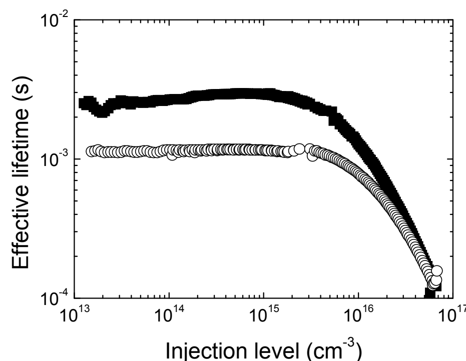

Figure 2: Effective lifetime as a function of the excess carrier density for low resistivity *p*-type (300 μm, <111>, 2 Ω cm) float zone c-Si substrate passivated with a 30 and 10 nm thick Al_2O_3 film.

Figure 3 clearly demonstrates that Al_2O_3 provides a state-the-art level of surface passivation on *p*-type c-Si with an arbitrary doping level.

The excellent level of surface passivation by Al_2O_3 was also confirmed by solar cell device performance. Al_2O_3 applied at the rear of *p*-type c-Si solar cells yielded a maximum efficiency of 20.6 %. This work was done in collaboration with the solar cell institute ISFH in Germany and will be presented in a separate contribution at this conference.[11,12] The performance of the Al_2O_3 passivated solar cells was at least equal to the solar cells with an *alnealed* thermal SiO_2 rear surface passivation.[11,12]

c-Si SURFACE PASSIVATION MECHANISM OF Al_2O_3

In Fig. 4 field-effect passivation is simulated for a moderately doped *n*-type c-Si wafer for both a negative and positive charge density $Q_{effective}$ at the surface. It can clearly be seen that a high *positive* or *negative* $Q_{effective}$ results in a significant reduction of S_{eff}. For a sufficiently high $Q_{effective}$ the minority surface carrier density scales with $1/Q^2$ at the c-Si surface; hence the field-effect passivation scales with Q^2, irrespective of the polarity of the $Q_{effective}$.

The surface passivation mechanism of Al_2O_3 is mainly based on field-effect passivation by a high fixed *negative* charge density Q_f in the Al_2O_3 film. In Fig. 5 it is demonstrated that a *positive* corona charge density Q_{corona} of 1.3×10^{13} cm^{-2} at the Al_2O_3 surface is required to cancel the field effect passivation. Q_{corona} is balancing the *negative* fixed charge density in a 26 nm Al_2O_3 film, resulting in a maximum in S_{eff}.

Negative fixed charges are routinely reported for Al_2O_3 films deposited on c-Si, irrespective of the deposition technique. The origin of these negative charges is most probably related to the

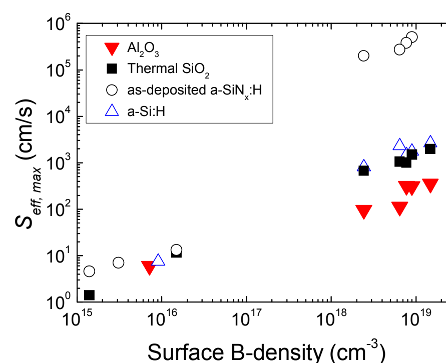

Figure 3: Upper level of the effective surface recombination velocity as a function of the B-concentration for c-Si wafers passivated by plasma-assisted ALD Al_2O_3, thermal SiO_2, a-SiN_x:H, and a-Si:H.[6,9,10]

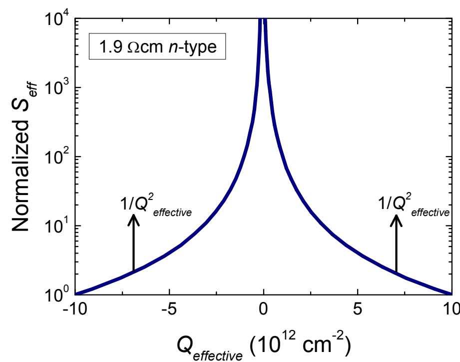

Figure 4: Normalized S_{eff} for a 1.9 Ω cm *n*-type c-Si surface as a function of the fixed charge density $Q_{effective}$ present at the surface. These simulations were performed in PC1D.[13]

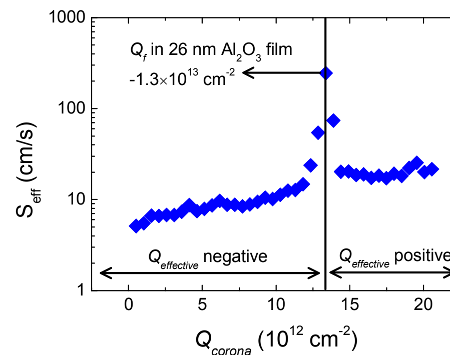

Figure 5: S_{eff} of a *n*-type c-Si (1.9 Ω cm <100> 275 μm) wafer symmetrically passivated by a 26 nm Al_2O_3 film as a function of the positive corona charge density deposited at the surface.

presence of Al vacancies in the Al_2O_3 film.[14] It was shown that these vacancies are predominantly present at the c-Si/Al_2O_3 interface,[15] in excellent agreement with the position of the fixed negative charge density deduced from thickness dependent capacitance voltage measurements by for example Abouaf et al.[16]

A negative Q_f is especially beneficial for the passivation of *p*-type c-Si as the minority carriers, the electrons, are effectively shielded from the c-Si surface. This is clearly apparent from the fact that the negative-charge-dielectric Al_2O_3 provides a state-of-the-art level of surface passivation even on highly B-doped *p*-type c-Si surfaces as shown in Fig. 3. The negative sign of the fixed charge also explains the flat injection level dependence of the surface passivation on low resistivity *p*-type c-Si as shown in Fig. 2 of this proceeding in excellent agreement with the extended Shockley-Read-Hall model.[17] A strong injection level dependence is routinely reported for *p*-type c-Si passivated by thermal SiO_2, a-SiN_x:H and a-Si:H.[6,9,10] As the fixed charge density in Al_2O_3 is typically one order of magnitude higher compared to a-SiN_x:H and two orders of magnitude higher compared to thermal SiO_2 and a-SiC_x this implies that the field-effect passivation by Al_2O_3 is 2 - 4 orders of magnitude stronger compared to these types of surface passivation films. This difference in the level of field-effect passivation significantly relaxes the requirements on the interface defect density at the c-Si/Al_2O_3 interface. However, the relative low S_{eff} at the point where the field-effect passivation is cancelled in Fig. 5 illustrates that the c-Si/Al_2O_3 interface defect density is also relatively low due to the presence of a thin SiO_2-like film between the c-Si and the Al_2O_3 film as generated during the Al_2O_3 deposition process.[7]

CONCLUSIONS

It is demonstrated that Al_2O_3 is an interesting material to obtain a high level of c-Si surface passivation as required for high efficiency solar cells. Al_2O_3 not only yields a state-of-the-art level of surface passivation on low resistivity *n*- and *p*-type c-Si, but its high fixed negative charge density makes it also particularly interesting for the passivation of *p*-type c-Si with an arbitrary doping level such as highly doped *p*-type emitters. The field-effect passivation by Al_2O_3 is orders of magnitude stronger than for passivation layers such as a-SiN_x:H and thermal SiO_2 and this relaxes the demanding requirements on the electrical interface quality. The excellent level of surface passivation has already been demonstrated by *p*-type c-Si solar cell devices.

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REFERENCES

[1] R. Hezel and K. Jaeger, J. Electrochem. Soc. **136**, 518 (1989).

[2] G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H. F. W. Dekkers, S. De Wolf, and G. Beaucarne, Sol. Energ. Mat. Sol. C. **90**, 3438 (2006).

[3] J.L. van Hemmen, S. B. S. Heil, J. Klootwijk, F. Roozeboom, C.J. Hodson, M. C. M. van de Sanden, and W. M. M. Kessels, J. Electrochem. Soc. **154**, G165 (2007).

[4] W. M. M. Kessels, B. Hoex, and M. C. M. van de Sanden, This conference.

[5] R. A. Sinton and A. Cuevas, Appl. Phys. Lett. **69**, 2510 (1996).

[6] M. J. Kerr and A. Cuevas, Semicond. Sci. Tech. **17**, 35 (2002).

[7] B. Hoex, S. B. S. Heil, E. Langereis, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. **89**, 042112 (2006).

[8] B. Hoex, J. Schmidt, R. Bock, P. P. Altermatt, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. **91**, 112107 (2007).

[9] S. Dauwe, J. Schmidt, and R. Hezel, Proc. of the 29th IEEE Photovoltaic Specialist Conference, New Orleans, (IEEE, Piscataway, NJ, 2002), p. 1246.

[10] M. J. Kerr and A. Cuevas, Semicond. Sci. Tech. **17**, 166 (2002).

[11] J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M. C. M. van de Sanden, and W. M. M. Kessels, This conference.

[12] J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M. C. M. van de Sanden, and W. M. M. Kessels, Progr. Photovoltaics, 10.1002/pip.823 (2008).

[13] P. A. Basore, IEEE Trans. Electron. Dev. **37**, 337 (1990).

[14] K. Matsunaga, T. Tanaka, T. Yamamoto, and Y. Ikuhara, Phys. Rev. B **68**, 085110 (2003).

[15] K. Kimoto, Y. Matsui, T. Nabatame, T. Yasuda, T. Mizoguchi, I. Tanaka, and A. Toriumi, Appl. Phys. Lett. **83**, 4306 (2003).

[16] J. A. Aboaf, D. R. Kerr, and E. Bassous, J. Electrochem. Soc. **120**, 1103 (1973).

[17] R. B. M. Girisch, R. P. Mertens, and R. F. Dekeersmaecker, IEEE Trans. Electron Devices **35**, 203 (1988).