Erschienen in: Energy Procedia ; 8 (2011). - S. 660-665

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 8 (2011) 660–665

Energy Procedia

SiliconPV: 17-20 April 2011, Freiburg, Germany

Passivation of Si Wafers by ALD-Al_2O_3 Films with Different Surface Conditioning

Thomas Lüder*, Giso Hahn, Barbara Terheiden

University of Konstanz, Department of Physics, P.O. Box X916, 78457 Konstanz, Germany

---

Abstract

We investigate the passivation quality of Al_2O_3 thin films grown by atomic laver deposition on differently etched surfaces of ~500 μm thick, 2.13 Ωcm p-type float zone silicon wafers with an (100) crystal orientation. The applied CP- and KOH-etches lead to differently shaped surface morphologies but almost equal root-mean-squared (rms) roughnesses of ~0.95 nm (CP) and ~1.07 nm (KOH) measured within an area of 1×1 μm^2 on the Si surface. The lowest surface recombination velocities after passivation resulting in effective carrier lifetimes up to 10 ms are achieved for samples treated with CP-etching. The lifetime is determined using a WCT-120 in the transient mode. It is shown that these lifetimes slightly exceed the theoretical limit given by a parameterization of the Auger recombination. Furthermore, scanning electron microscope images show that Al_2O_3 thin films with a thickness of ~29 nm and ~58 nm fully cover random pyramid textured Si surfaces of (111) orientation leading to high effective lifetimes up to 6 ms. The temperature of the wafer surface during the deposition is determined by *in situ* spectroscopic ellipsometry to be ~180°C.

Selection and/or peer-review under responsibility of SiliconPV 2011

Keyords: Passivation; Al_2O_3; ALD; wet chemical treatments

---

1. Introduction

Aiming at cost reduction, the industrial fabrication processes of silicon solar cells point to the application of thinner silicon wafers. With the reduction of wafer thickness the influence of recombination at the surfaces becomes more and more relevant for the cell efficiency. In order to reduce the recombination losses at the surfaces several passivation techniques were developed. Al_2O_3 thin films

---

[*] Corresponding author. Tel.: +49-7531-882260; fax: +49-7531-883895.
E-mail address: Thomas.Lueder@uni-konstanz.de.

1876–6102 © 2011 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of SiliconPV 2011.
Open access under CC BY-NC-ND license. doi:10.1016/j.egypro.2011.06.198

grown by atomic layer deposition (ALD) provide excellent surface passivation quality on crystalline silicon [1] due to both chemical and field effect passivation mechanisms [2]. However, in solar cell fabrication processes the Si surfaces are prepared using different etching procedures (saw damage etching, texturization). The passivation potential of Al_2O_3 deposited on differently etched (100)-oriented Si surfaces is investigated in this work.

2. Experimental

Starting with shiny etched 2.13 Ωcm p-type float zone Si wafers (area: ~5×5 cm², thickness: 525 µm) we immerse them either in a CP-solution at room temperature [3] or in an aqueous solution of KOH (28%) at ~80°C or in an aqueous solution of KOH (2%) combined with a high boiling alcohol at ~100°C [4]. While the first and second etching solutions are used for isotropic silicon removal from the surface the third one is used for texturization leading to pyramid formation with (111) oriented surfaces. The wafers are coated on both sides by Al_2O_3 thin films deposited in a commercial FlexAL ALD reactor from Oxford Instruments equipped with a Woollam M-2000 ellipsometer for *in situ* measurements.

Prior to the deposition of Al_2O_3 the wafers receive a RCA clean. After deposition the wafers are annealed at a temperature of ~400°C for 30 min in nitrogen atmosphere (10 mbar). The passivation quality of the films is studied by the determination of the effective minority carrier lifetime from photoconductance decay (PCD) measurements with a Sinton lifetime tester WCT-120 operated in the transient mode without bias light. The morphology of the surfaces is studied using atomic force and electron microscopy.

The temperature of the substrate table within the FlexAL system is set to 200°C. By *in situ* spectroscopic ellipsometry we determine the actual wafer temperature during the Al_2O_3 deposition. Measuring the optical response every 15 s during the sample heat up and fitting a temperature dependent model to the pseudo dielectric functions, the wafer temperature at each measurement point is determined. The used model is a SiO_x layer [5] on a Si substrate. The model of the substrate which is temperature dependent and developed at J. A. Woollam Co., is valid between 193 and 1700 nm as well as in a temperature range between 25 and 300°C [6]. The fitting is performed in a spectroscopic range between 250 and 700 nm. Thus, reflections from the backside of the ~500 µm thick wafers can be excluded. Little changes in the pseudo dielectric functions have a strong influence in the extracted temperature. In order to minimize errors, the temperature is supposed to be the only fitting parameter. That means all other parameters are kept constant during the measurement. This means for example to exclude an uncontrollable growth of silicon oxide during heat up. Therefore before entering the ALD deposition chamber the sample is exposed intentionally to air for 7 h after an HF dip. Additionally the chamber is flooded by argon gas during the heat up.

3. Results

Fig. 1 shows the temperature profile and the root mean square error (*MSE*). The *MSE* measures the match of the fit to the experimental data and is defined in Appendix A. During the first minute of the heat up process the orientation of the ellipsometer light beam is adjusted to hit the detector.

Fig. 1 demonstrates that the wafer temperature is saturating at ~180°C after ~6 min. Note that the temperature is the *only* free parameter during the applied fitting procedure.

The calculated *MSE* values of ~3 indicate a good fit of the model to the measured data. Since the *MSE* is constant within the heat up process, the change in the pseudo dielectric functions of the sample during heating can be *fully* explained by the determined increase of the sample temperature. We conclude that the wafer temperature during deposition, is ~180°C.

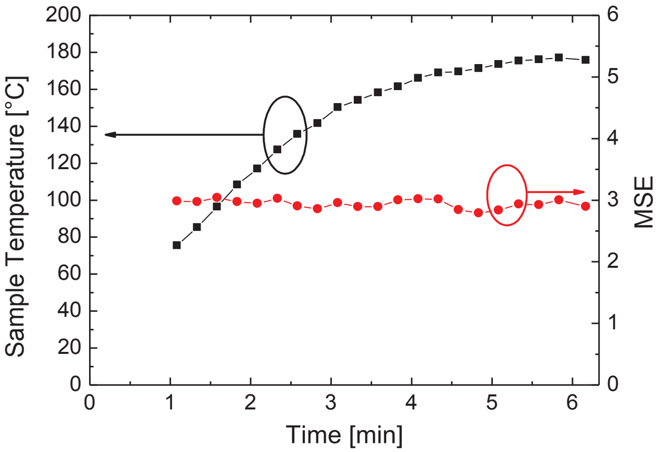

Fig. 1. Temperature profile of the sample during the heat up process.

Fig. 2(a) shows the effective minority carrier lifetimes at an injection level of 1×10^{15} cm^{-3} of the silicon wafers coated with ~29 nm and ~58 nm Al_2O_3 after surface conditioning. As it can be seen the Al_2O_3 thin films passivate all the studied surfaces including the (111) oriented pyramids which is demonstrated by effective carrier lifetimes of above 4 ms. Furthermore, the passivation quality of the Al_2O_3 films in particular on the textured surface is independent of the layer thickness leading to the conclusion that the textured surface is fully covered with Al_2O_3 already at a film thickness of 29 nm as expected from the self limiting ALD deposition process. To support this conclusion, focused ion beam (FIB) cuts are taken into the pyramid structure and the resulting cross sections are analyzed using a scanning electron microscope (SEM). To prevent parasitic charging of the insulating Al_2O_3 film during SEM measurements, a film of ~600 nm aluminum is evaporated on top of the layer.

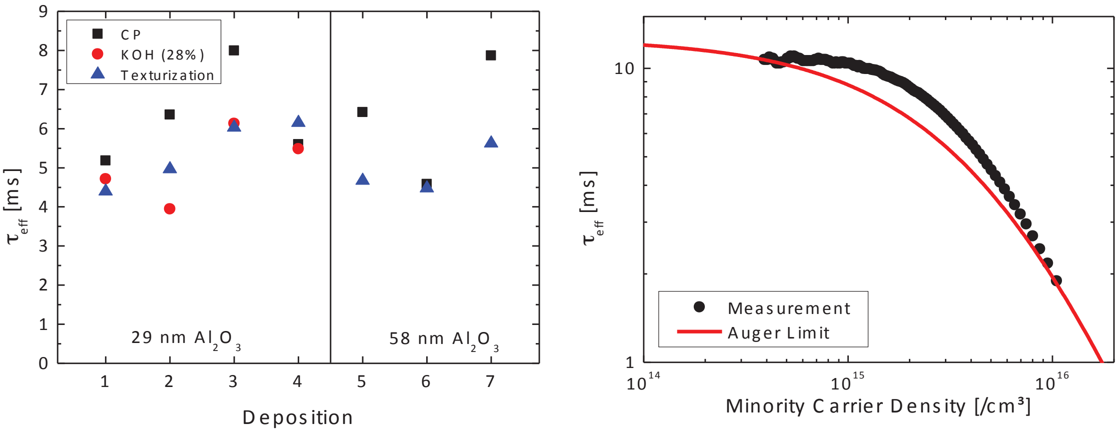

Fig. 2. (a) Effective carrier lifetimes of the wafers coated with 29 nm Al_2O_3 (left) and 58 nm Al_2O_3 (right); (b) Measured and modeled injection level dependent lifetime. The thickness of the p-type Si wafers is ~500 µm and the resistivity is measured to be 2.13 Ωcm.

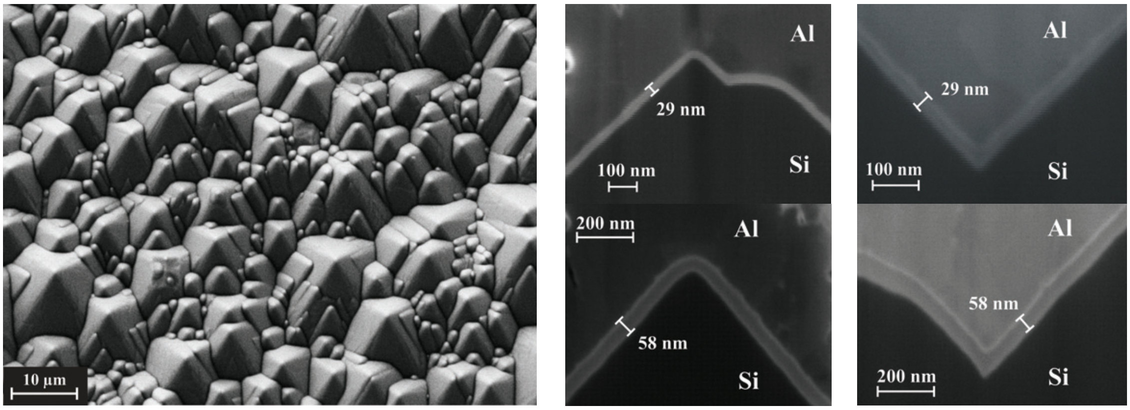

Fig. 3. (a) SEM images of the pyramid structure; (b), (c), (d), (e) SEM images of the cross sections at the tip of a pyramid and a valley between two pyramids covered with either 29 nm or 58 nm Al_2O_3.

Fig. 3 shows the SEM images of the textured Si surface and the cross sections of pyramids covered by both 29 and 58 nm Al_2O_3. The tips, flanks and valleys are fully covered with Al_2O_3. The potential of Al_2O_3 for the passivation of textured p-type Si surfaces has also been reported in [7].

Focusing on the CP- and KOH-etched surfaces which are flat compared to the pyramid structure on the textured samples, Fig. 2(a) clearly shows that the effective minority carrier lifetimes of the CP-etched wafers are higher compared to the KOH-etched ones indicating a higher passivation quality of the Al_2O_3 thin films deposited on a CP-etched surface. Fig. 4 shows the atomic force microscopy (AFM) images of both surfaces within a surface area of 100×100 and 1×1 μm^2. The root-mean-squared (rms) roughnesses are calculated to be 36.0 and 37.2 nm (area: 100×100 μm^2) as well as 0.95 and 1.07 nm (area: 1×1 μm^2) for the CP- and KOH-etch, respectively. The differences in height of the lowest to the highest measured point are also nearly identical as it can be seen in Fig. 4. The AFM-results and the conformal growth of the Al_2O_3 layer on textured surfaces suggest that different surface morphologies are not the reason for the different passivation quality. The difference in the effective lifetimes is therefore probably caused by the different etching chemicals themselves.

Fig. 2(b) compares the injection level dependence of the measured effective minority carrier lifetime with the parameterization of Kerr and Cuevas [8] of a CP-etched sample from a subsequent experiment. An effective carrier lifetime close to 10 ms (wafer resistivity ~2.13 Ωcm) is achieved corresponding to a maximum surface recombination velocity of 2.5 cm/s.

The parameterization [8] takes only Auger recombination into account. As it can be seen in Fig. 2(b) the measured lifetimes slightly exceed the theoretical Auger lifetime values between 1×10^{15} and 1×10^{16} cm^{-3}. In [8] the authors proposed an Auger parameterization that fitted quite well the measured minority carrier lifetime data for Si wafers passivated by high quality SiN_x and alnealed SiO_x films. However, surface recombination was not taken into account which results in the parameterization as a lower limit for the actual Auger lifetime. Due to the ultralow surface recombination velocity caused by the ALD-Al_2O_3 films this limit could be exceeded.

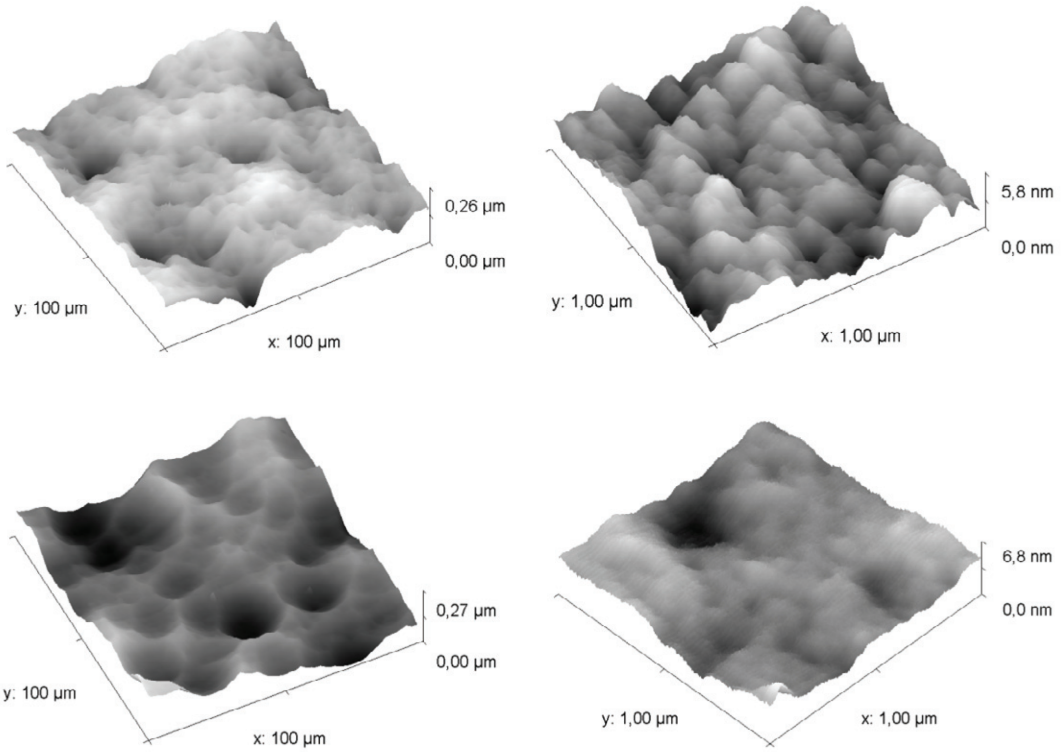

Fig. 4. Surface morphologies of the differently etched Si surfaces: (a), (b) AFM measurement of the CP-etched surface; (c), (d) AFM measurement of the KOH-etched surface.

4. Conclusion

In conclusion, we have shown high, but different passivation qualities of the Al_2O_3 thin films on differently etched surfaces of p-type float zone Si wafers with a thickness of ~500 µm and a resistivity of 2.13 Ωcm. The applied CP- and KOH-etches lead to different surface morphologies but almost equal rms roughnesses of ~0.95 nm (CP) and ~1.07 nm (KOH) measured within an area of 1×1 μm^2 on the Si surface. A CP-etch leads to the highest effective minority carrier lifetime up to 10 ms exceeding the theoretical Auger limit as defined by Kerr and Cuevas [8]. The differences of passivation quality on the CP- and KOH-etched surfaces are not found to be a result of different surface roughness as those are measured to be almost equal. Al_2O_3 thin films with a thickness of ~29 nm grown by atomic layer deposition are well suited to passivate random pyramid textured Si surfaces of (111) orientation fully covering the surface. The wafer temperature during the applied ALD process as determined by *in situ* ellipsometry is ~180°C.

Acknowledgements

The authors thank A. Zuschlag and T. Hanke for the SEM and AFM measurements, respectively. The financial support from the BMU projects 0325168 and 0325079 is gratefully acknowledged in particular for the processing equipment. The content of this publication is the responsibility of the authors.

References

[1] Hoex B, Heil SBS, Langereis E, van de Sanden MCM, Kessels WMM. Ultralow surface recombination of *c*-Si substrates passivated by plasma-assisted atomic layer deposited Al_2O_3. *Appl Phys Lett* 2006;**89**:042112.

[2] Dingemans G, Terlinden NM, Pierreux D, Profijt HB, van de Sanden MCM, Kessels WMM. Influence of the Oxidant on the Chemical and Field-Effect Passivation of Si by ALD Al_2O_3. *Electrochem Solid-State Lett* 2011;**14**:H1-H4.

[3] Bogenschütz AF. *Ätzpraxis für Halbleiter*, München:Carl Hauser Verlag; 1967.

[4] Ximello N, Dastgheib-Shirazi A, Scholz S, Hahn G. Influence of Pyramid Size of Chemically Textured Silicon Wafers on the Characteristics of Industrial Solar Cells. *Proc 25th EU PVSEC* 2010;1761-64.

[5] Herzinger CM, Johs B, McGahan WA, Woollam JA, Paulson W. Ellipsometric determination of optical constants for silicon and thermally grown silicon dioxide via a multi-sample, multi-wavelength, multi-angle investigation. *J Appl Phys* 2002;**83**:3323-36.

[6] Personal communication with Dr. Thomas Wagner, LOT Oriel GmbH.

[7] Dastgheib-Shirazi A, Steyer M, Junge J, Gindner S, Hahn G. A Study of the Surface Morphology of Silicon: Effect of Parasitic Emitter Etching on the Rear-Side Performance of Silicon Solar Cells. *Proc 25th EU PVSEC* 2010;2107-13.

[8] Kerr MJ, Cuevas A. General parameterization of Auger recombination in crystalline silicon. *J Appl Phys* 2002;**91**:2473-80.

Appendix A. Definition of the MSE

The *MSE* is a measure of the quality of the fit and is here defined as:

$$MSE := \sqrt{\frac{1}{3n-m}\sum_{i=1}^{n}\left[\left(N_{\mathrm{E}_i}-N_{\mathrm{G}_i}\right)^2+\left(C_{\mathrm{E}_i}-C_{\mathrm{G}_i}\right)^2+\left(S_{\mathrm{E}_i}-S_{\mathrm{G}_i}\right)^2\right]}\times 1000$$

with

$$\begin{aligned} N_{\mathrm{E;G}_i} &= \cos(\,2\Psi_{\mathrm{E;G}_i}) \\ C_{\mathrm{E;G}_i} &= \sin(2\Psi_{\mathrm{E;G}_i})\cos(\Delta_{\mathrm{E;G}_i}) \\ S_{\mathrm{E;G}_i} &= \sin(2\Psi_{\mathrm{E;G}_i})\sin(\Delta_{\mathrm{E;G}_i}) \end{aligned}$$

where Ψ and Δ are the ellipsometric parameters and E,G refer to the measured and model generated data, respectively. Furthermore *n* denotes the number of wavelengths and *m* the number of free fitting parameters.