Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 38 (2013) 843 – 848

Energy Procedia

SiliconPV: March 25-27, 2013, Hamelin, Germany

Role of annealing conditions on surface passivation properties of ALD Al_2O_3 films

Friederike Kersten[a,b]*, Alexander Schmid[b], Stefan Bordihn[a], Jörg W. Müller[a] and Johannes Heitmann[b]

[a]Hanwha Q CELLS GmbH, OT Thalheim, Sonnenallee 17-21, D-06766 Bitterfeld-Wolfen, Germany
[b]TU Bergakademie Freiberg, Institute of Applied Physics, Leipziger Straße 23, D-09596 Freiberg, Germany

Abstract

The surface passivation performance of Al_2O_3 films attracted attention in the field of solar cells and semiconductor devices and depends on the conditions of the applied post-deposition annealing step. The effect of annealing temperature and different annealing atmospheres on the surface passivation quality of atomic layer deposited Al_2O_3 films was investigated on *n*-type float-zone Si wafers. Photoconductance decay measurements were carried out to characterize recombination velocities and carrier lifetimes. The chemical and field-effect passivation mechanism, i.e. the interface trap density and the fixed charge density, respectively, were studied by capacitance-voltage experiments. Low surface recombination velocities of $S_{eff,max}$ ~1 cm/s corresponding to a carrier lifetime of 9.0 ms were achieved for samples annealed in O_2 atmosphere whereas annealing in H_2 and N_2 led to slightly higher $S_{eff,max}$-values ~2 cm/s. The annealing temperature was found to affect both the fixed charge density and the interface trap density whereas in contrast the annealing atmosphere affected only the interface trap density, i.e. the chemical passivation. According to the expectations the highest surface passivation quality is based on a high fixed charge density and a low interface trap density.

Keywords: Surface Passivation; ALD Al_2O_3 ; *C-V*-characteristics

1. Introduction

Future generations of high-efficiency solar cells rely on excellent passivation of the silicon (Si) surface [1]. The advantage of thin aluminium oxide (Al_2O_3) films in the field of photovoltaics was firstly shown

* Corresponding author. Tel.: +49 (3494) 6699 - 52134; fax: +49 (3494) 6699 - 51012.
E-mail address: f.kersten@q-cells.com.

doi:10.1016/j.egypro.2013.07.354

in 1989 by Hezel *et al.* and later on in 2006 Agostinelli *et al.* and Hoex *et al.* reported on field-effect passivation based on negative fixed charge and high level of chemical passivation due to a low interface defect density [2-6]. The surface passivation performance of Al_2O_3 films was found to depend on several conditions, i.e. the used oxidant [7,8], the deposition temperature [9] and the post-deposition annealing temperature [10-14]. In particular the temperature of the post-deposition anneal was found to influence the field-effect passivation of the Al_2O_3 films [15].

In this study the surface passivation quality of Al_2O_3 films grown by atomic layer deposition (ALD) was investigated after annealing under various conditions, i.e. annealing at temperatures ranging from 300 to 600°C and annealing in atmospheres such as oxygen (O_2), nitrogen (N_2) and hydrogen (H_2). The impact of the annealing atmosphere on the surface passivation of Al_2O_3 films has not been investigated in detail yet. The experiments included the analysis of the contributions of the field-effect and chemical passivation on the overall quality of the surface passivation. The surface passivation performance was found to depend on both annealing temperature and atmosphere.

2. Experimental

For the experiments float zone (FZ) *n*-type Si substrates with a thickness (W) of 200 µm and an edge length of 6 cm were used. The samples had a resistivity of 2-3 Ω·cm. Prior to the Al_2O_3 deposition the wafers were cleaned using a standard Radio Corporation of America (RCA) process to assure a hydrophobic surface [16] followed by a diluted HF treatment. The Al_2O_3 films were deposited symmetrically on both sample sides and trimethylaluminium ($Al(CH_3)_3$) and ozone (O_3) were used as reactants. The layer had a thickness of 30 nm as determined by spectroscopic ellipsometry. After the Al_2O_3 deposition sample set A was annealed for 10 min at different temperatures in a muffle furnace between 300 and 600°C. The muffle furnace was flooded by N_2 before and during the annealing process. Sample set B were annealed at different pure atmospheres: O_2, N_2 and H_2 at 470°C for 10 min. For the samples that were used for capacitance-voltage (*C-V*) measurements Al contacts with a thickness of 100 nm and an area of 0.04 mm^2 were evaporated by vacuum deposition on one sample side through a shadow mask.

The minority carrier lifetime (τ_{eff}) was characterized by using the transient decay photoconductance technique and a Sinton Instruments WCT-120 system [17]. The measured τ_{eff}-values were used to calculate the maximum surface recombination velocities $S_{eff,max} = W/(2\cdot\tau_{eff})$ by assuming an infinitive bulk lifetime.

In addition *C-V* and conductance measurements were carried out and a metal-oxide semiconductor (MOS) model was used to determine the density of fixed charges Q_f [18] and the density of interface traps D_{it} at the Al_2O_3/Si interface [19,20]. An impedance analyzer Agilent Technologies E4980A Precision LCR Meter was used for the measurements.

3. Results

In Fig. 1 the effective carrier lifetimes obtained for Al_2O_3 films is shown after annealing at various temperatures (sample set A). After annealing at 300°C the lowest τ_{eff}-values of 0.2-0.3 ms were obtained. Annealing between 400 and 600°C led to τ_{eff}-values of ~2 ms at $\Delta n > 7\cdot10^{15}$ cm^{-3} which corresponds to $S_{eff,max} < 5$ cm/s. However, the obtained τ_{eff}-values were slightly different for lower Δn-values $< 5\cdot10^{15}$ cm^{-3}. Therefore the optimum annealing temperature was ~470°C because at low injection levels of $\Delta n < 10^{14}$ cm^{-3} the achieved τ_{eff}-values of 2.3 ms were higher than for the other annealing temperatures. The low injection level is of interest as the range between 10^{13} to 10^{15} cm^{-3} corresponds to the operation conditions of an industrial solar cell as revealed by PC1D simulations [19]. In Fig. 1b the influence of

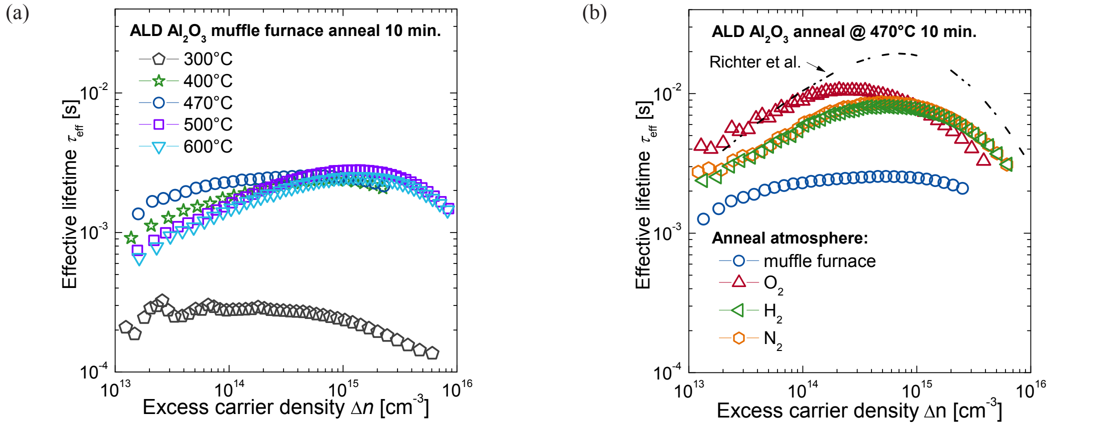

Fig. 1. Injection dependent minority carrier lifetime $\tau_{eff}(\Delta n)$ of 30 nm thick ALD Al_2O_3 films (a) Sample set A: annealed in muffle furnace at indicated temperatures and (b) Sample set B: annealed at 470°C in indicated atmospheres. As a reference the intrinsic lifetime limit, including also the recombination in the surface depletion region, for an Al_2O_3-passivated *n*-type Si wafer is shown [22].

different pure annealing atmospheres on the τ_{eff}-values is shown. Compared to annealing at 470°C in the muffle furnace a further increase of τ_{eff} is obtained for samples of sample set B. The highest τ_{eff} of 9.0 ms, which corresponds to a $S_{eff,max}$ of about 1 cm/s, was obtained for annealing in O_2 atmosphere, whereas annealing in H_2 and N_2 led to slightly higher values of $S_{eff,max}$ of about 2 cm/s. At injection densities $\Delta n <$ 10^{14} cm^{-3} the obtained τ_{eff}-values of Al_2O_3 films annealed in O_2 atmosphere were near to the intrinsic lifetime according to the model proposed by Richter *et al.* [22]. The τ_{eff}-values achieved after annealing at various temperatures and in different annealing atmospheres are listed in Tab. 1.

By *C-V* measurements the surface passivation mechanism of the Al_2O_3 films, i.e. the contributions of chemical and field-effect passivation, was investigated. The field-effect passivation is represented by the fixed charge density Q_f [18] and the chemical passivation is reflected by the interface trap density D_{it}

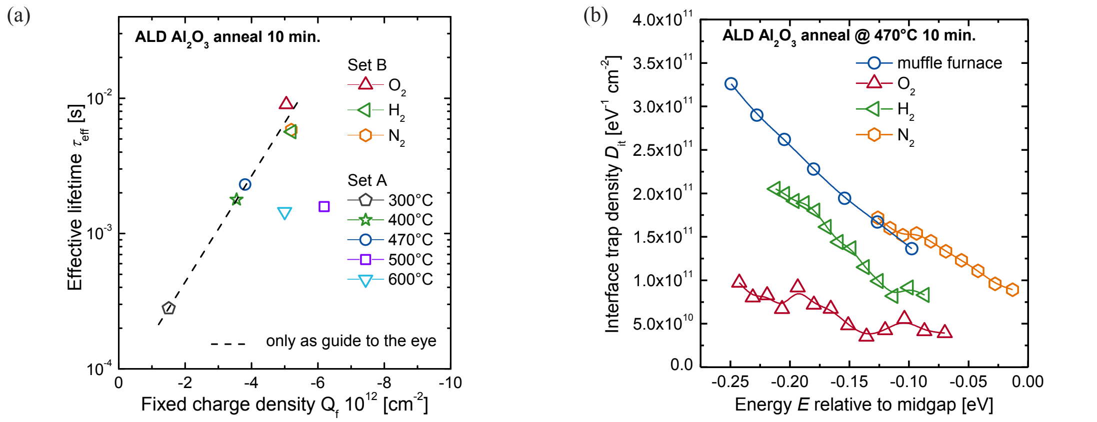

Fig. 2. (a) Maximum τ_{eff}-values as function of the fixed charge density Q_f and (b) interface trap density D_{it} as function of the energy E relative to the midgap energy E.

[19,20]. The τ_{eff}-values increased exponential with higher Q_f, except for the samples annealed at 500 and 600°C in the muffle furnace. The highest level for Q_f of about -6.2·10^{12} cm^{-2} is determined for samples annealed at 500°C. Only slightly lower Q_f-values of about -4 to -5·10^{12} cm^{-2} are obtained for the samples annealed at 400 and 470°C, including the samples of sample set B. In Fig. 2b the obtained D_{it}-values are shown as a function of the energy E relative to the midgap energy. The obtained $D_{it}(E)$ function of the samples annealed in the muffle furnace and in pure N_2 atmosphere resulted in similar values as the same annealing ambient was used. In comparison the D_{it}-values decreased for annealing in atmospheres H_2 and O_2 with the lowest average D_{it}-value of about 0.6·10^{11} eV^{-1} cm^{-2} obtained for annealing in O_2 atmosphere. These D_{it}-values were similar or even slightly lower compared to interface trap densities reported in literature [6,23]. The reduction of the interface trap density lead to an increase in τ_{eff} by a factor of 1.5 compared to the N_2 treated samples which showed an average D_{it} of 1.3·10^{11} eV^{-1} cm^{-2}. In the Tab. 1 all obtained values for τ_{eff}, V_{FB}, Q_f and average D_{it} are summarized.

Table 1. Minority carrier lifetime τ_{eff} at an injection level of $\Delta n = 1\cdot10^{14}$ cm^{-3}, flatband voltage shift V_{FB}, density of fixed charges Q_f and average interface trap density D_{it} obtained of annealed Al_2O_3 films at indicated annealing temperatures and atmospheres.

Annealing temperature	Annealing atmosphere	Annealing time	τ_{eff} (ms)	V_{FB} (V)	Q_f 10^{12} (cm^{-2})	D_{it} 10^{11} (eV^{-1} cm^{-2})
300°C	N_2	10 min	0.3	0.1	-1.5	—
400°C	N_2	10 min	1.8	3.4	-3.6	—
470°C	N_2	10 min	2.3	3.8	-3.8	2.3
500°C	N_2	10 min	1.6	5.7	-6.2	1.8
600°C	N_2	10 min	1.5	4.7	-5.0	1.2
470°C	O_2	10 min	9.0	5.1	-5.1	0.6
470°C	H_2	10 min	5.6	4.6	-5.2	1.4
470°C	N_2	10 min	5.8	4.7	-5.2	1.3

— = not applicable

4. Summary

The Al_2O_3 surface passivation was found to depend strongly on the annealing temperature and the annealing atmosphere. The measured lifetime values increased with higher annealing temperatures in muffle furnace. Under low injection conditions the maximum value was obtained at ~470°C whereas at higher injection conditions annealing at $T > 400$°C served a similar passivation quality. This is important for solar cells, since simulations in PC1D have shown that they often operate at relatively low illumination levels. It was shown that an annealing at 470°C in a pure atmosphere leads to an improved surface passivation. The best result of $\tau_{eff} = 9.0$ ms at an injection density of $\Delta n = 10^{14}$ cm^{-3} was achieved for annealing in pure oxygen atmosphere. This effect was attributed to an increased chemical passivation, whereas there is no significant influence of the annealing atmosphere on the fixed charge density, hence on the field-effect passivation.

Acknowledgements

The authors would like to thank Barbara Abendroth, Ronald Otto, Uwe Sczech, the entire team of the central clean room laboratory at TU Bergakademie Freiberg, Ina Förster, Jens Reinhold, Gerd Kesser for their contribution to that work and the Hanwha Q CELLS Technology team for perfect and friendly support.

References

[1] S.W. Glunz. High-Efficiency Crystalline Silicon Solar Cells. *Advances in Opto Electronics, 2007*;**97370**.

[2] R. Hezel and K. Jäger. Low Temperature Surface Passivation of Silicon for Solar Cells. *J. Electrochem. Soc. 1989*;**136** (2):518.

[3] G. Agostinelli, A. Delebie, P. Vitanov, Z. Alexieva, H. F. W. Dekkers, S. De Wolf and G. Beaucarne. Very low surface recombination velocities on *p*-type silicon wafers passivated with a dielectric with fixed negative charge. *Sol. Energy Mater. Sol. Cells 2006*;**90**:3438-34443.

[4] B. Hoex, S.B. Heil, E. Langereis, M.C.M. van de Sanden and W.M.M. Kessels. Ultralow surface recombination of c-Si substrates passivated by plasmaassisted atomic layer deposited Al_2O_3. *Appl. Phys. Lett. 2006*;**89**:042112.

[5] J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M.C.M. van de Sanden and W.M.M. Kessels. Surface passivation of high-efficiency silicon solar cells by atomic-layer-deposited Al_2O_3. *Prog. Photovolt: Res. Appl. 2008*;**16**:461.

[6] J. Benick, A. Richter, M. Hermle and S.W. Glunz. Thermal stability of the Al_2O_3 passivation on *p*-type silicon surfaces for solar cell application. *Phys. Status Solidi RRL 2009*;**3**:233.

[7] G. Dingemans, N.M. Terlinden, D. Pierreux, H.B. Profijt, M.C.M. van de Sanden and W.M.M. Kessels. Influence of the Oxidant on the Chemical and Field-Effect Passivation of Si by ALD Al_2O_3. *Electrochem. Solid-State Lett. 2011*;**14** (1):H1-H4.

[8] G. Dingemans and W.M.M. Kessels. Status and prospects of Al_2O_3-based surface passivation schemes for silicon solar cells. *J. Vac. Sci. Technol. A 2012*;**30**:040802.

[9] G. Dingemans, M.C.M. van de Sanden and W.M.M. Kessels. Influence of the Deposition Temperature on the c-Si Surface Passivation by Al_2O_3 Films Synthesized by ALD and PECVD. *Electrochem. Solid-State Lett. 2010*;**13** (3):H76-H79.

[10] G. Dingemans, R. Seguin, P. Engelhart, M.C.M. van de Sanden and W.M.M. Kessels. Silicon surface passivation by ultrathin Al_2O_3 films synthesized by thermal and plasma atomic layer deposition. *Phys. Status Solidi RRL 2010*;**4** (1):10-12.

[11] J. Benick, A. Richter, T.T.T.A. Li, N.E. Grant, K.R. McIntosh, Y. Ren, K.J. Weber, M. Hermle and S.W. Glunz. Effect of a post-deposition anneal on Al_2O_3/Si interface properties. *Proc. 35th IEEE PVSC 2010*, Honolulu, Hawaii.

[12] A. Richter, J. Benick, M. Hermle and S.W. Glunz. Excellent silicon surface passivation with 5 Å thin ALD Al_2O_3 layers: Influence of different thermal post-deposition treatments. *Phys. Status Solidi RRL 2011*;**5** (5-6):202-204.

[13] J.M. Rafi, M. Zabala, O. Beldarrain, and F. Campabadal. Deposition Temperature and Thermal Annealing Effects on the Electrical Characteristics of Atomic Layer Deposited Al_2O_3 Films on Silicon. *J. Electrochem.* Soc. *2011*;**158** (5):G108-G114.

[14] D. Schuldis, A. Richter, J. Benick and M. Hermle. Influence of Different Post Deposition Treatments on the Passivation Quality and Interface Properties of Thermal ALD Al_2O_3 Capped by PECVD SiNx. *27th EUPVSEC 2012*, Frankfurt, Germany.

[15] S. Bordihn, I. Kiesow, V. Mertens, P. Engelhart, J.W. Müller and W.M.M. Kessels. Impact of the Deposition and Annealing Temperature on the Silicon Surface Passivation of ALD Al_2O_3 Films. *En. Proc. 2012*;**27**:396-401.

[16] W. Kern. Cleaning Solutions Based on Hydrogen Peroxide for Use in Silicon Semiconductor Technology. *RCA Review 1970*;**31**:187-206.

[17] R.A. Sinton, A. Cuevas and M. Stuckings. Quasi-Steady-State Photoconductance, A New Method for Solar Cell Material and Device Characterization. *Proc. 25th IEEE PVSC 1996,* Washington, USA.

[18] S.M. Sze and K.K. Ng. Physics of Semiconductor Devices. 3rd ed. New Jersey: Hoboken; 2007.

[19] E.H. Nicollian and A. Götzberger. The Si-SiO_2 Interface - Electrical Properties as Determined by the Metal-Insulator-Silicon Conductance Technique. *The Bell Syst. Tech. J. 1967*;**46**:1055-1133.

[20] D.K. Schroder. Semiconductor Material and Device Characterisation. 3rd ed. Arizona: Tempe; 2007.

[21] P.A. Basore. Numerical modeling of textured silicon solar cells using PC-1D. *IEEE Trans. Electron Devices 1990*;**7** (2):337-343.

[22] A. Richter, S. Glunz, F. Werner, J. Schmidt and A. Cuevas. Improved quantitative description of Auger recombination in crystalline silicon. *Phys. Rev. B 2012*;**86**:165202.

[23] F. Werner, A. Cosceev and J. Schmidt. Silicon surface passivation by Al_2O_3: Recombination parameters and inversion layer solar cells. *En. Proc 2012*;**27**:319-324.