Available online at www.sciencedirect.com

SciVerse ScienceDirect

Physics Procedia 41 (2013) 640 – 649

Physics Procedia

Lasers in Manufacturing Conference 2013

Thermodynamic investigations on the laser ablation rate of silicon over five fluence decades

V. Schütz* , U. Stute, and A. Horn

Laser Zentrum Hannover e.V. Hollerithallee 8, D-30419 Hannover, Germany

Abstract

Laser ablation of silicon is investigated with a large set of laser parameters to determine the ablation rate over five laser fluence decades. A thermodynamic model approach for the ablation of silicon has been derived. This simplified model determines the achievable ablation depth per pulse as a function of the applied laser fluence ranging from femtosecond to microsecond laser pulse duration. Furthermore different laser wavelengths from near-infrared to ultra-violet are investigated to determine the dependence on the optical penetration depth and on the ablation efficiency. The measured ablation depth per pulse is in agreement to the models predictions with the restrictions made.

Keywords: laser ablation; silicon, thermodynamics

1. Introduction

Laser ablation of silicon, either mono- or polycrystalline silicon has been already studied, exemplary by Chichkov et al., 1996, Coyne et al., 2003, Haupt et al., 2009, and Engelhart, 2007 in terms of ablation depth per pulse as a function of laser fluence. These studies focus on a certain laser system, to a specific pulse duration or to a specific laser wavelength. Further, laser processing has been investigated due to different applications, e.g. drilling and structuring, or thin layer ablation. Preferably larger pulse durations ($t_p \sim$ ns - µs) and pulse energies ($E_p =$ µJ - mJ) are used by Ostendorf and Schoonderbeek, 2008 and Karnakis, 2005 for laser drilling of thick silicon wafers. Grooves for structuring are induced by Haupt et al., 2009, Ostendorf and

---

* Corresponding author. Tel.: +49 511 2788 329
E-mail address: v.schuetz@lzh.de

doi:10.1016/j.phpro.2013.03.128

Schoonderbeek, 2008, and Schütz et al., 2010 with smaller pulse durations (t_p = ps-ns) and accordingly smaller pulse energies ($E_\mathrm{p} \sim \mu$J). Thin layers are removed on top of silicon by a lift-off process. Therefore even smaller pulse durations and energies are used by Schoonderbeek et al., 2010 and Hermann et al., 2008 to ablate very small volumes of silicon beneath the thin layer. However, the material removal is induced by ablating a volume fraction of silicon. Therefore a specific thermodynamic enthalpy is required to describe the material removal.

In this work a simple energy balance approach is used to merge and quantify the laser ablation of silicon over five fluence decades. This description results from a thermodynamic approach of using the balance of the state variables intrinsic energy and enthalpy, but ignoring fundamental processes parameters which are not state variables, like

- different absorption processes
- particle dynamics due to enthalpy changes
- energy conduction in phase and through phase changes
- disequilibrium of electrons and phonons
- ...

2. Experimental

In this study mc-silicon is investigated for ablation. The general optical setup is equipped with a laser source and the focused laser radiation is deflected by a galvo scanner. The ablation parameters have been varied in a wide range to induce laser ablated grooves, see Tab. 1 for a set of 21 laser systems, and see Appendix A. All investigations have been made in ambient atmosphere at room temperature. In order to achieve measurable groove depths a by optical microscopy the number of pulses per point

$$N_\mathrm{ppp} = \frac{d_\mathrm{fok} \cdot f_\mathrm{rep}}{\mathrm{v_s}} \tag{1}$$

as well as the laser fluence Φ have been varied with the focal diameter d_fok at 1/e², the repetition rate f_rep, the scanning velocity $\mathrm{v_s}$, and the laser pulse energy E_p.

$$\Phi = \frac{4 \cdot E_\mathrm{p}}{\pi \cdot d_\mathrm{fok}^{\;2}} \tag{2}$$

Table 1. Parameter range for the investigations on the laser ablation of silicon

Laser parameters	Min. value	Max. value
Laser fluence (Φ)	26 mJ/cm²	1552 J/cm²
Pulse duration (t_p)	320 fs	1.6 µs
Repetition rate (f_rep)	100 Hz	3.5 MHz
Wavelength (λ)	193 nm	1064 nm
Number of pulse per point (N_ppp)	1.11	8000

3. Theory

The ablation of silicon can be described by an averaged process. Using pulsed laser radiation an averaging of the single physical processes takes at large repetition rates f_rep and large number of laser pulses per point

N_{ppp} place. The degree of averaging is a matter of the used material with its own thermodynamic properties and the applied laser parameters. As a first statement, even working with laser radiation inducing primary different path ways for ablation, due to the averaging and to the heat accumulation, a general, for all pulse durations valid description can be set-up simply evaluating state variables, like the thermodynamic enthalpy and intrinsic energy. Secondary aspects of ablation such as pulse duration or laser wavelength influence the ablation in detail. The ablation representing an irreversible process can be described by an energy balance equation with enthalpy H and intrinsic energy U

$$H = U + p \cdot V\,, \tag{3}$$

where the total differential of the enthalpy dH is written to

$$dH = dU + p \cdot dV + V \cdot dp\,, \tag{4}$$

with the differential of intrinsic energy dU given by

$$dU = \delta Q + \delta W + \delta W_{\mathrm{rest}}\,. \tag{5}$$

Both, enthalpy H and intrinsic energy U are state variables being only dependent on the initial and the final state. Contrary, the heat Q and the work terms W and W_{rest} are not state variables and therefore dependent on the work path. A simple equation results by neglecting all fundamental processes which correspond to $p \cdot V$ and W, like particle dynamics as well as the volume and pressure changes besides heat capacity and phase changing enthalpies for a specified volume V and is given by

$$\frac{dH}{dV} = \frac{\delta Q}{\delta V}\,. \tag{6}$$

The right hand side of Eq. 6 represents the energy density which is required for a temperature rise from T_0 to T_1 for a material with a constant density ρ. Further a temperature dependent heat capacity $c_{\mathrm{p}}(T)$ and the sum enthalpy for all taken place phase changes $\Sigma H^{\mathrm{V}}{}_{\mathrm{ph}}$ is used and is written to

$$\frac{\delta Q}{\delta V} = \rho \cdot \int_{T_0}^{T_1} c_{\mathrm{p}}(T)\,dT + \sum_{i=0}^{n} H^{\mathrm{V}}{}_{\mathrm{ph}} = H^{\mathrm{V}}{}_{\Delta}\,. \tag{7}$$

The left hand side of Eq. 6 represents the applied heat source which is a function of laser fluence Φ and energy penetration depth $d+a_{\mathrm{p}}$ with the ablation depth per pulse a_{p} and d as a measure of enthalpy losses due to e.g. heat conduction or plasma shielding. For square energy absorption in material, a simple equation can be evolved representing the applied laser energy per unit cube, see Fig. 1 and is given by

$$\frac{dH}{dV} = \frac{\Phi}{a_{\mathrm{p}} + d}\,. \tag{8}$$

The ablation, respectively penetration depth per pulse a_{p} as a function of laser parameters and the material properties (Eq. 6, 7 and 8) results in accordance to Bäuerle, 2000 to

$$a_{\mathrm{p}} = \frac{\Phi}{H^{\mathrm{V}}{}_{\Delta}} - d \tag{9}$$

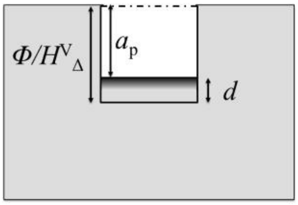

Fig.1. Ablation depth per pulse a_p as a function of the ratio $\Phi/H^V{}_\Delta$ which determines the maximum ablation depth and d which summarizes all enthalpy losses, Eq. 9

The laser ablation depth per pulse a_p as a function of laser fluence Φ is decreased by various material depended parameters. Further, it is a matter of the optical d_{opt} as well as the thermal penetration depth d_{therm}, but also a matter of transferred photon energy to the electron system of the bulk. These all ablation efficiency decreasing processes and parameters are summarized by the parameter d. A thermodynamic efficiency η_a (enthalpy change from room temperature $T_R = 300$ K to vaporization temperature $T_{vap} = 2628$ K for silicon with phase change enthalpies for melting and vaporization $\Sigma H^V{}_{ph}$) can be derived based on Eq. 6, 7 and 8 to benchmark the laser parameters for ablation, see Eq. 10.

$$\eta_a = \frac{\Phi / a_p}{\rho \cdot \int_{T_R}^{T\text{vap}} c_p(T)dT + \sum_{i=1}^{2} H^V{}_{ph}} \cdot 100 \qquad (10)$$

For modeling the removal of material due to laser processing occurs if at minimum one phase change, from solid to liquid, takes place. In general the phase changes are melting, vaporization, first order ionization (1st I), and higher orders of ionization. Each phase change corresponds to a specific enthalpy and in case of melting and vaporization to a transition temperature, see Tab. 2. The required enthalpies $H^V{}_\Delta$ achieving larger ionization degrees are determined for instantaneous ionization for temperatures above the evaporating point. In addition to the phase change enthalpies, a constant enthalpy increase is given with the heat capacity as a function of the temperature $c_p(T)$ up to the vaporization temperature T_{vap} by Soma and Kagaya, 1988 and von Allmen, 1982, see Fig. 2. A constant heat capacity $c_p = 1000$ J·kg-1·K-1 is assumed from melting temperature $T_{melt} = 1683$ K up to the vaporization temperature $T_{vap} = 2628$ K.

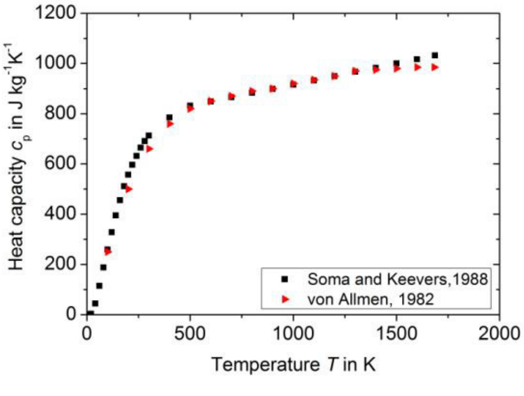

Fig.2. Heat capacity as a function of temperature $c_p(T)$ for silicon by Soma and Kagaya, 1988 and von Allmen, 1982, melt temperature $T_{melt} = 1683$ K

Table 2. Phase change enthalpies H^V_{ph} for silicon, data taken from David, 2010; required enthalpy H^V_Δ to induce a phase change from $T_R = 300$ K; the density is kept constant at $\rho = 2330$ kg·m^{-3}

phase change	H^V_{ph} in GJ·m^{-3}	H^V_Δ in GJ·m^{-3}
Melting	4.2	7.1
Vaporization	31.9	41.1
1st Ionization	65.2	(106.4)
2nd Ionization	130.9	(237.2)
3rd Ionization	268.2	(505.3)

4. Results and Discussion

The measured ablation depth per pulse a_p as a function of laser fluence Φ (ablation rate) for the different sets of laser parameters, like pulse duration t_p or laser wavelength λ features a linear dependence as indicated with $a_p \propto \Phi$. The phase change enthalpies in terms of ablation depth per pulse a_p as a function of the laser fluence Φ are determined for melting, vaporizing, ionization, and higher orders of ionization with Eq. 7 and with all losses set to $d = 0$, see colored lines in Fig. 3.

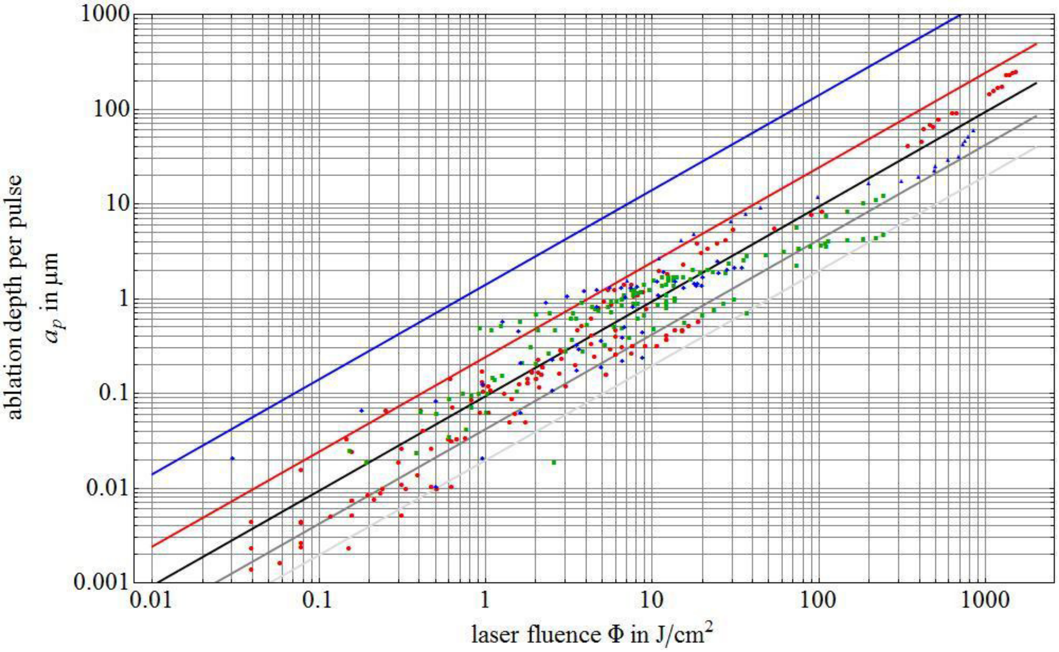

Fig.3. Comparison of theoretical penetration depth per pulse and measured ablation depth per pulse; red dots correspond to ablation depths for the laser wavelength $\lambda = 1064/1047/1030/1025$ nm; green dots correspond to ablation depths for the laser wavelength $\lambda = 532/515$ nm; blue dots correspond to ablation depths for the laser wavelength $\lambda = 355/193$ nm; colored lines represent the penetration depths beginning with blue for melting, red for vaporization and black, grey, and light-grey represent the three presented ionization degrees; laser pulse durations range from $t_p = 320$ fs to $t_p = 1.6$ µs; material properties of silicon taken from David, 2010, Soma and Kagaya, 1988, von Allmen, 1982, and Green and Keevers, 1995; additional data for the ablation depth per pulse for silicon taken from Ostendorf et al., 2008 and Karnakis, 2005; all losses are set to $d = 0$ µm

Considerable ablation starts for temperatures above evaporation temperature, e.g. for silicon $T_{\mathrm{vap}} > 2628$ K, which corresponds to an enthalpy $H^{V}_{\Delta,\mathrm{vap}} \geq 41.1$ GJ/m^3. In the most cases larger enthalpies are required to remove the material by laser radiation due to energy losses, like heat conduction, different absorption mechanisms in the material and particle kinetics in the plasma plume. The comparison of the measured and the models predicted ablation rate, respectively the ablation efficiency η_a summarizes all physical processes which reduce or subduct the energy input into or out of the absorption volume during laser processing. In result, an effective thermodynamic ablation is characterized by e.g. a large vapor pressure which effectively removes the melt out of the ablation groove or by a coulomb explosion of ionized atoms in the bulk (exemplary results in Fig. 4 and 5).

The ablation rate can be classified with respect to the optical penetration depth at $T = 300$ K and with the restriction $d_{\mathrm{opt}} > d_{\mathrm{therm}}$ into three domains, see exemplary for $\lambda = 515/532$ nm Tab. 3.

Table 3. Domain specification as a function of the laser fluence for silicon, laser wavelength $\lambda = 515/532$ nm, $d_{\mathrm{opt}} = 0.9\text{-}2$ µm

Domain	Φ in J/cm²
D1 ($d_{\mathrm{opt}} > a_p$)	0-3.7
D2 ($d_{\mathrm{opt}} \approx a_p$)	3.7-8.2
D3 ($d_{\mathrm{opt}} < a_p$)	8.2-...

D1 is characterized by a larger optical penetration depth d_{opt} in comparison to the ablated depth per pulse a_p, see Fig. 4.

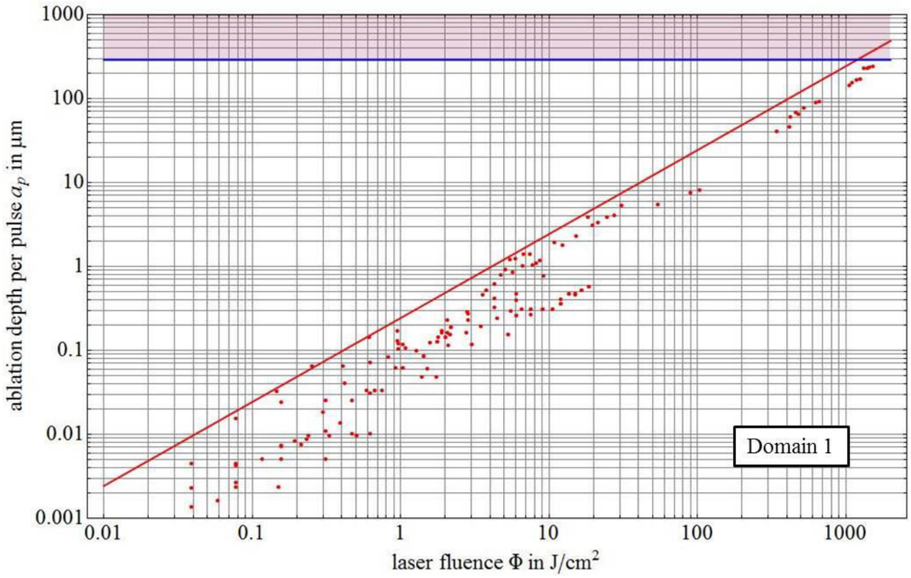

Fig.4. Ablation depths per pulse as a function of the laser fluence; red dots correspond to laser wavelengths λ = 1064/1047/1030/1025 nm, blue-red bar corresponds to the d_{opt} at $T = 300$ K and at the mentioned wavelength spectrum, Green and Keevers, 1995; red line corresponds to the penetration depth per pulse at vaporizing temperature according to Eq. 9 at $d = 0$; additional data for the ablation depth per pulse for silicon taken from Ostendorf et al., 2008; investigated pulse durations 320 fs $\leq t_p \leq$1.6µs

In D2 d_{opt} and a_{p} are more or less equal and in D3 the ablation depth per pulse a_{p} exceeds the optical penetration depth d_{opt}. The ablation efficiency η_{a} decreases in D2 and D3 with increasing laser fluence while in D1 the ablation efficiency can achieve almost values of $\eta_{\mathrm{a}} \leq 100$ %. The reduced ablation efficiency η_{a} in D2 and D3 is due to the reduced energy transport beyond the optical penetration depth d_{opt} by the thermal conductivity λ_{T} in terms of the thermal penetration depth d_{therm} of the material at elevated temperatures. In this cases the restriction $d_{\mathrm{opt}} > d_{\mathrm{therm}}$ is not true and it results in a large thermal overheating of phonons at small optical or thermal penetration depths. This yields a small ablation efficiency (exemplary results in Fig. 5 D2 and D3 and Fig. 6 D3). Therefore, the definition of the domains has to be extended by the thermal penetration depth d_{therm}. Exemplary processing with UV-laser radiation at a laser fluency range of Φ = 8-35 J/cm² and at the pulse duration t_{p} = 20 ns yield a thermal penetration depth $d_{\mathrm{therm}} \approx 2$ µm which is much larger than the optical penetration depth of d_{opt} =5-10 nm, Green and Keevers, 1995. However, the ablation efficiency η_{a} is also reduced by other laser processing parameters, e.g. N_{ppp} at a distinct t_{p} which results in an enhanced heat load to the material.

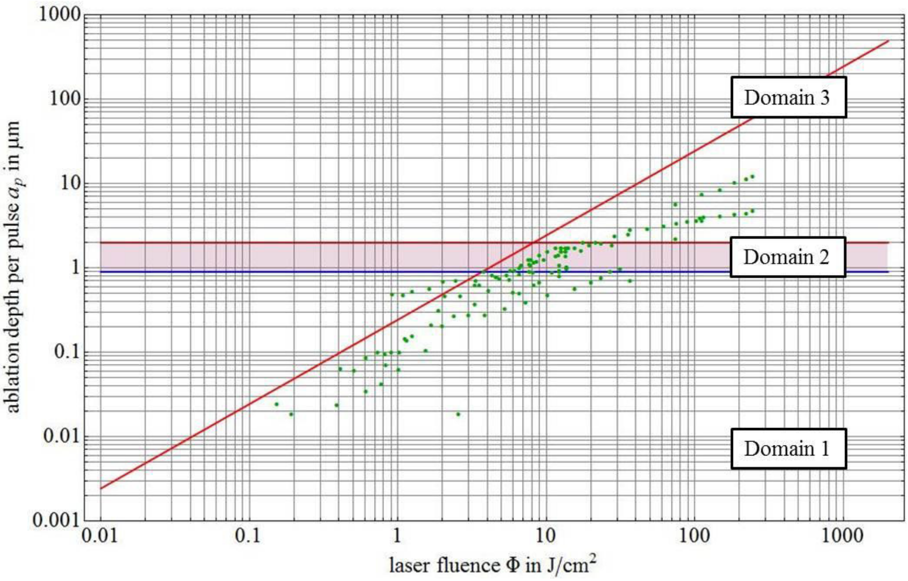

Fig.5. Ablation depths per pulse as a function of the laser fluence; green dots correspond to laser wavelengths λ = 532/515 nm, blue-red bar corresponds to the d_{opt} at $T = 300\ K$ and at a mentioned wavelength spectrum, Green and Keevers, 1995; red line corresponds to the penetration depth per pulse at vaporizing temperature according to Eq. 9 at $d = 0$; additional data for the ablation depth per pulse for silicon taken from Ostendorf et al., 2008

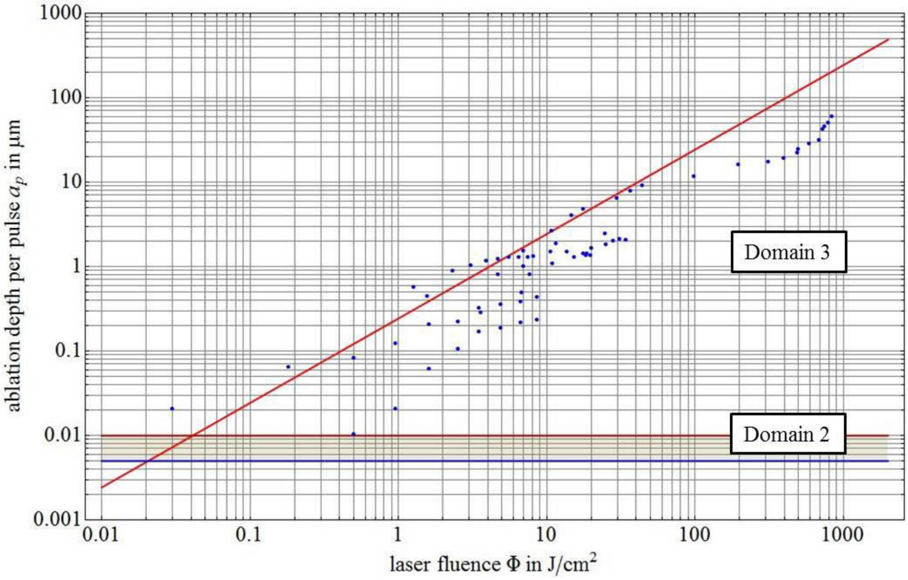

Fig.6. Ablation depths per pulse as a function of the laser fluence; blue dots correspond to laser wavelengths λ = 355/193 nm, blue-red bar corresponds to the d_{opt} at *T = 300 K* and at a mentioned wavelength spectrum, Green and Keevers, 1995; red line corresponds to the penetration depth per pulse at vaporizing temperature according to Eq. 9 at *d = 0;* additional data for the ablation depth per pulse for silicon taken from Ostendorf et al., 2008 and Karnakis, 2005

5. Summary and Outlook

The ablation of silicon has been described as a function of its thermodynamic material properties and laser parameters. A set of 21 laser systems at miscellaneous parameters, e.g. pulse duration variation from $t_p = 320$ fs to $t_p = 1.6$ µs and laser fluence variation from $\Phi = 0.03$ J/cm² to $\Phi = 1550$ J/cm² have been evaluated for laser ablation of silicon in terms of ablation depth per pulse a_p and the applied laser fluence Φ. Considerable ablation of material starts at the evaporation temperature of $T_{vap} = 2628\,K$ at enthalpies larger than $H^V_{\Delta,vap} \geq 41.1$ GJ/m³. The developed simplified energy balance approach describes well both ultra-short as well as short pulsed laser ablation of silicon. The determined enthalpy for ablation with different laser parameters is larger compared to models prediction due to a variety of laser induced processes, e.g. plasma shielding or heat conduction and summarized by the ablation efficiency η_a and characterized with 3 ablation domains. In D1 large ablation efficiencies are achievable due to the larger initial optical penetration depth d_{opt} at $T = 300$ K in comparison to the ablation depth per pulse a_p. A reduced ablation efficiency η_a has been observed if the ablation depth per pulse a_p is in the same range or larger than the optical penetration depth d_{opt}. In conclusion the theoretical ablation depth per pulse a_p is determined by the thermodynamic parameters heat capacity c_p and the sublimation enthalpy for melting and vaporization of the used material. The experimental determined ablation depth per pulse a_p is smaller in comparison to the theoretical a_p due to other material and laser processing parameters. Further investigations have to be made in the theoretical evaluation of each determined ablation curve. This has to include the comparison of the two-temperature model and the developed solution in this work in terms of the ablation depth per pulse a_p as a function of the laser fluence Φ. The ablation efficiency η_a has to be precised by incorporation of the neglected physical processes described in the introduction. These investigations can be easily extended to different materials to verify the ansatz of the developed solution.

Acknowledgements

The authors would like to thank all industrial companies, namely: Amplitude Systemes, Asys Automatisierungssysteme GmbH, Innolight GmbH, Jenoptik Laser GmbH, and Trumpf GmbH + Co. KG for supplying additional laser sources for the determined ablation curves of silicon.

References

Chichkov B.N., Momma C., Nolte S., 1996, Femtosecond, picosecond and nanosecond laser ablation of solids, Journal of Applied Physics A, 63, p.109-115

Coyne E., Magee J., Mannion P., O´Connor G., 2003, A study of femtosecond laser interaction with wafer grade silicon, Proc. of the SPIE, 4876, p.487-499

Haupt O., Schütz V., Kling R., 2009, Improved laser edge isolation of crystalline silicon solar cells using a high power picosecond laser, Proc. 28th ICALEO, Orlando, USA, paper#M903

Engelhart P., 2007, Lasermaterialbearbeitung als Schlüsseltechnologie zum Herstellen rückseitenkontaktierter Siliciumsolarzellen, PhD-thesis, Leibniz Universität Hannover, Germany

Ostendorf A., Schoonderbeek A., 2008, Lasers in energy device manufacturing, Proc. of SPIE Vol.6880, San Jose, USA

Karnakis D.M., 2006, High Power single-shot laser ablation of silicon with nanosecond 355 nm, Applied Surface Science 252, p.7823-7825

Schütz V., Haupt O., Stute U., et.al., 2010, Laser edge isolation with a focus on damage reduction by the use of ultra-short pulse lasers, Proc. of the 25th EUPVSEC, Valencia Spain

Schoonderbeek A., Schütz V., Haupt O., Stute U., 2010, Laser processing of thin films for photovoltaic applications, Journal of Laser Micro/Nanoengineering, 5, p.248-255

Hermann S., Neubert T., Wolpensinger B., et.al., 2008, Process characterisation of picosecond laser ablation of SiO2 and SiNX layers on planar and textured surfaces, Proc. of the 23rd EUPVSEC, Valencia Spain

Bäuerle D., 2000, Laser Processing and Chemistry, 3th Edition, Springer, Berlin, p.189

David R. Lide, ed., 2010, CRC Handbook of Chemistry and Physics, 90th Edition (Internet Version), CRC Press/Taylor and Francis, Boca Raton, USA

Soma T., Kagaya H.M., 1988, Thermal Expansion Coefficient of Si, in Properties of Silicon, INSPEC, p.35-36

von Allmen, M., 1982, Fundamentals of Energy Deposition, in J.M. Poate & J.W. Mayer (ed.) Laser Annealing of Semiconductors, , Academic Press, p.43-75

Green M.A. and Keevers M., 1995, Optical properties of intrinsic silicon at 300 K, Progress in Photovoltaics, 3, p.189-92

Ostendorf A., Kling R., Richter L, Schoonderbeek A., Siegel F., Haupt O., 2008, Laser Dicing of Silicon: Comparison of ablation mechanisms with a novel technology of thermally induced stress, Proc. of 9th LPM, Quebec City, Canada

Appendix A

Table A1: laser systems with specifications used for this study; * taken from Ostendorf et al., 2008.; ** taken from Karnakis, 2006.

No.	Company	Product	Pulse duration t_p (ns)	Wavelength λ (nm)	Repetition rate f_{rep} (kHz)
1*	Rofin	StarDisc	1600	1030	15
2	Jenoptik	G100	300	515	15
3	IPG	YLP-1-120-50-50	120	1064	50
4*	Trumpf	TL20-FQ	56	1047	15
5**	Lightwave Electronics	UV210	44	355	0.4
6*	Coherent	Avia	40	355	100
7	IPG	YLPM-1-A4-20-20	20	1064	100 / 50
8	Rofin	Powerline	20	532	70
9	Coherent	Avia	20	355	30 / 15
10	Rofin	Powerline	13	532	40
11	Rofin	Powerline	7	532	15
12	Coherent	LPX300	<10	193	0.1
13	Innolight	Helios	2.2	1030	35
14	Innolight	Helios	0.54	1064	20
15*	Lumera	Staccato	0.012	1064	50
16*	Lumera	Rapid	0.012	532	50
17	Trumpf	TruMicro5050	0.007	1030	400 / 200
18	Trumpf	TruMicro5050	0.007	515	400 / 200
19	Trumpf	N.N.	0.0009	515	3500
20	Jenoptik	D2.fs	0.00038	1025	200 / 100 / 50
21	Amplitude	Tangerine	0.00032	1030	2000 / 1000 / 500 / 250