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New approach for the ablation of dielectrics from silicon using long wavelength lasers

Jostein Thorstensen*,[a,b] and Sean Erik Foss[a]

[a]Institute for Energy Technology, P.O. Box 40, 2027 Kjeller, Norway
[b]University of Oslo, Department of Physics, P.O. Box 1048 Blindern, 0316 Oslo, Norway

Abstract

Laser ablation of dielectrics from silicon substrates represents a useful technique for e.g. the creation of local contacts. However, these dielectrics are transparent at the laser wavelengths normally employed for silicon solar cell processing, i.e. the first, second and third harmonics of solid state lasers (1064, 532 and 355 nm). As a result of this, the ablation is indirect, and follows from energy deposition in the silicon rather than in the dielectric. This mechanism introduces defects in the silicon substrate, an effect which is detrimental to solar cell performance. Attempts have been made to limit the extent of the laser damage, by going to shorter wavelengths and shorter pulse durations.
In this work, we suggest an alternative route to low-damage ablation of dielectrics by application of long wavelength laser pulses from e.g. CO_2-lasers. At wavelengths above approx. 8 µm, we find absorption bands in many of the dielectrics applied in solar cells. Simulations show that it may be possible to keep the silicon temperature below melting temperature, while reaching vaporization temperature in the dielectric. Experiments using laser pulses at 9.3 µm with a duration of approx. 100 ns show, however, that the silicon substrate experiences melting. We conclude that even shorter pulses must be applied for the method to be successful.

Keywords: Laser ablation; long laser wavelengths

1. Introduction

In processing of silicon solar cells, the local removal of dielectric layers is beneficial for several processes [1–3]. Lasers have been suggested as a possible tool for this local removal, as lithography and masking processes may be incompatible with industrial scale processing. However, laser damage is often

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* Corresponding author. Tel.: +47 63806445; fax: +47 63812905.
E-mail address: Jostein.thorstensen@gmail.com.

observed as a reduction of lifetime in lowly doped silicon, or it can be observed as an increase in the dark saturation current density if processing in emitters [1,4]. This laser damage is a result of laser energy deposition in the silicon. The approach up until now has been to go to shorter pulse durations and wavelengths, in order to either confine the laser energy and damage to a shallow layer in the silicon, or to obtain (non-linear) absorption in the dielectric layers, which normally are transparent at visible and near-infra-red wavelengths due to their high band-gap energy. The problem with going to short laser wavelengths and ultrashort laser pulses is that the silicon will also be highly absorbing in this situation, meaning that there will always be an inherent mechanism present for energy deposition into the silicon. In this article, we propose a new approach for obtaining low damage ablation of dielectric layers from silicon.

We seek a situation where we not only get energy deposition in the dielectric, as will be the case in the situation described above, but where the silicon in addition is transparent to the laser light. In such a situation, once the dielectric is removed, we will get no more laser energy deposition, and one could potentially obtain a much more stable process. Our approach is based on the application of short-pulsed, long wavelength lasers, operating at wavelengths above 8 μm. At these wavelengths, intrinsic silicon is nearly transparent at room temperature, while many dielectrics have absorption bands at these wavelengths. This behaviour opens for the possibility of directly depositing the laser energy into the dielectric, while keeping the silicon at a much lower temperature. We simulate the temperature evolution during such a laser pulse, and compare the results with experiments performed using a CO_2-laser at 9.3 μm and a pulse duration of 100 ns.

2. Simulations

We apply a partial differential equation solver with one spatial dimension in order to solve the heat equation for our system. Using only one spatial dimension in our simulations implies that we expect the lateral dimensions to be much larger than the depth of the deposition of the laser energy. Using long laser wavelengths, the laser spot will tend to be larger than when using shorter wavelengths, as a result of diffraction effects. As such, a focus diameter of around 100 μm would be reasonable. While this is not large compared to the optical absorption depth for silicon at room temperature and a laser wavelength of 9.3 μm, the one-dimensional approximation will be reasonable for the situation with a dielectric covering the silicon. In this case, the strongest energy deposition will take place in the dielectric and in the heated silicon close to the dielectric. We assume that the heated silicon volume lies within one thermal diffusion length from the dielectric-silicon interface, which with a laser pulse duration of 100 ns would correspond to approx. 3 μm [2].

The system consists of a stack structure with a dielectric on top of a silicon slab. The silicon substrate is 100 μm thick, and the dielectric is 100 nm thick. We assume that ablation of the dielectric is obtained when the dielectric reaches vaporization temperature, and we shall abort the simulations if the silicon reaches melting temperature, as the recrystallization is assumed to introduce defects in the silicon, being an undesired situation. The heat equation is given by [5]:

$$C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\kappa \frac{\partial T}{\partial x}\right) + \alpha I(1-R) . \tag{1}$$

Here, C_p is the heat capacity, modified to include the enthalpy of phase change, κ is the heat conductivity, α is the optical absorption coefficient. I is the optical fluence, R is the reflectivity and $\alpha I(1-R)$ is the energy input from the laser. At the boundary between dielectric and silicon, we apply extra thermal interface resistance, R_{int}, as reported by Huang *et al.* [6] and Kuo *et al.* [7]. This resistance is related to the mismatch between phonon modes in different materials, and will delay heat transfer.

Material parameters are taken from the literature and are shown in table 1 and table 2. T_v indicates the vaporization temperature.

Table 1. Material parameters for SiO$_x$ and SiN$_x$.

Parameter	SiO$_x$	SiN$_x$	Unit	Ref
R_{int}	2.4×10^{-4}	3.7×10^{-4}	cm^{2}K/W	[6]
T_v	3223	2100	K	[8,9]
C_p	3	1.80	J/cm^3 K	[10,11]
κ	0.0123	0.0107	W / cm K	[6]

Table 2. Material parameters for Si.

Parameter	Value	Unit	Ref
$C_{Si,solid}$	2.24	J/cm^3 K	[12]
$C_{Si,liquid}$	2.33	J/cm^3 K	[13]
$\kappa_{Si,solid}$	$1.521 \times 10^3 T^{-1.226}$ ($300 < T < 1200$) $8.96 \times T^{-0.502}$ ($1200 < T < 1683$)	W / cm K	[12]
$\kappa_{Si,liquid}$	0.62	W / cm K	[13]

The optical absorption coefficient α is of course of outmost importance for the outcome of the simulations, however, this term is not straightforward in these simulations. For energy deposition in the dielectrics, absorption coefficients from FTIR measurements are used, however, we need an expression for α in silicon. As we are applying long wavelength irradiation, band-to-band absorption is prohibited, and we are left with free-carrier absorption (FCA) and absorption by defect states $\alpha = \alpha_{defect} + \alpha_{fca}$. α_{defect} is obtained from FTIR measurements. α_{fca}, on the other hand, is more difficult to quantify. α_{fca} at room temperature is given by the expression $\alpha_{fca} = 2 \times 10^{-18} N_{doping} \lambda^2$ [14], where N_{doping} is the background doping level. More fundamentally, FCA is expected to have an absorption coefficient following the trend [14]:

$$\alpha_{fca} \propto \frac{N}{\mu} \lambda^2, \tag{2}$$

meaning that α_{fca} is dependent on the mobility μ, number density of free electrons N, and wavelength of the laser irradiation, λ. As μ and N are temperature dependent, so is α_{fca}. The temperature dependence of N is given by [15]:

$$N(T) = N_{doping} + N_i(300) \times \frac{N_i(T)}{N_i(300)} = N_{doping} + N_i(300) \times \frac{T^{\frac{3}{2}} \exp\left(-\frac{E_g(T)}{2k_B T}\right)}{300^{\frac{3}{2}} \exp\left(-\frac{E_g(300)}{2k_B \times 300}\right)}, \tag{3}$$

where $N_i(300)$ is the intrinsic carrier concentration in silicon at 300 K, $E_g(T)$ is the temperature dependent band-gap energy and k_B is the Boltzmann constant. $E_g(T)$ is given by [16]:

$$E_g(T) = E_g(0) - \frac{BT^2}{C+T}, \tag{4}$$

in units of eV, where $E_g(0) = 1.155$ eV, $B = 4.73 \times 10^{-4}$ eV/K and $C = 635$ K are fitting parameters. The electron mobility μ is given by [17]:

$$\mu_e(N,T) = 88T_n^{-0.57} + \frac{7.4\times10^8 T^{-2.33}}{1+(N/(1.26\times10^{17}T_n^{2.4}))\times0.88T_n^{-0.146}} \tag{5}$$

where T_n is T/300. Combining these expressions, we can write α_{fca} as

$$\alpha_{fca}(N,T) = \alpha_{fca}(10^{16},300) \times \frac{N(T)}{10^{16}} \times \frac{\mu(10^{16},300)}{\mu(N,T)} \tag{6}$$

When the silicon is cold, α_{fca} is small, and the substrate is nearly transparent. When the temperature rises, however, α_{fca} increases significantly, meaning that we have a mechanism for thermal runaway in silicon, where heated silicon will absorb stronger, confine the laser energy to a smaller volume and hence grow even hotter. It should be noted that μ and α_{fca} have not been measured at temperatures close to the melting temperature of silicon, where the FCA is strongest. As such, the values for α_{fca} are uncertain, and introduces a significant source of error in the simulations.
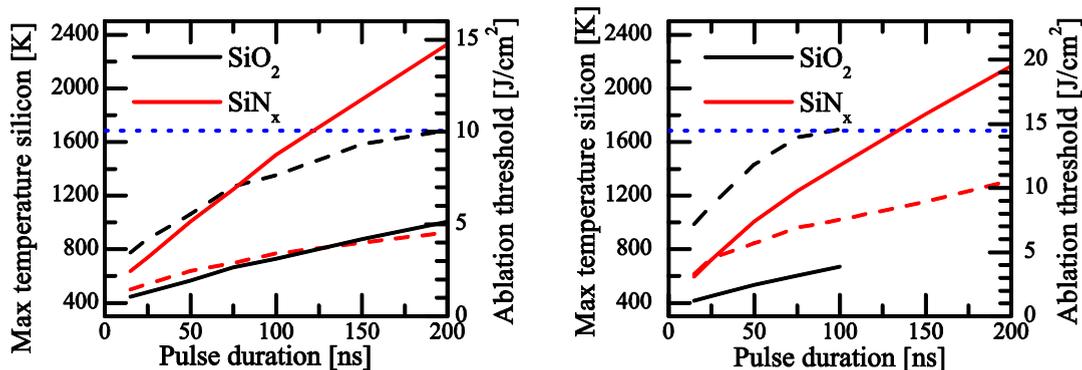

Fig. 1. (Left) Ablation threshold for dielectric from silicon using literature values (Solid lines). Also shown is the maximum temperature reached in the silicon substrate (dashed lines). (Right) The same values, but with higher thermal conductivity in the dielectric, and thermal interface resistance removed. Also shown is the melting temperature of silicon (dotted blue lines).

Fig. 1 (left) shows the simulated ablation threshold (solid lines) and the maximum temperature of the silicon substrate (dashed lines) using literature values. We see that the substrate temperature decreases with decreasing pulse duration, a sign of reduced heat transfer from the dielectric. Reducing the pulse duration is therefore a way to reach ablation with substrate temperatures well below melting temperature. Fig. 1 (right) shows the same simulations, but with the thermal conductivity, κ, in the dielectric increased by a factor 10 and the thermal interface resistance removed, constituting a pessimistic scenario. Here, significantly shorter pulses must be applied in order to keep the silicon from melting.

3. Experimental

We measure the infrared absorption coefficient of several dielectrics commonly used in solar cell processing, by means of Fourier-transform infrared spectroscopy (FTIR). The dielectrics are deposited by plasma-enhanced chemical vapor deposition (PECVD) in an RF direct plasma system. The results are shown in Fig 2. We see that SiO_x, SiN_x and SiO_xN_y show significant absorption at around 9.3 µm, suitable for the CO_2-laser, while AlO_x shows absorption only at longer wavelengths. In addition to the results shown here, we also measured the absorption spectra of two SiN_x films deposited with slightly different deposition parameters. These films showed somewhat different absorption spectra, with different absolute and relative heights of the absorption peaks. The calculated absorption coefficient at 9.3 µm for

these films deviated by as much as 50 % compared to the value shown for the SiN_x film in Fig. 2. The absorption spectrum is built up from the absorption contributions from the various chemical bonds in the film [18], and it would be reasonable to believe that films deposited by other methods would show different absorption characteristics as a result of different chemical and structural composition.

We perform experiments on ablation of thermal SiO_2, PECVD - SiO_x, SiN_x and SiO_xN_y using a CO_2-laser at 9.3 µm and pulse duration of 100 ns. The experiments, however, show expulsion of the silicon, shown in fig. 3, and we conclude that the substrate has melted, indicating that the applied pulses are too long for the desired behaviour. This also means that the heat conduction from the dielectric or the absorption in the silicon substrate is significantly higher than what we have simulated. We also perform ablation experiments on bare silicon (without dielectric cover), and we find that in this situation, the ablation threshold is very much higher than that obtained with a dielectric covering the silicon. This is taken as an indication that laser energy deposition in cold silicon is indeed very weak, and that the silicon is heated by heat conduction from the dielectric. The heated silicon will thereafter absorb more strongly, leading to melting of the silicon. The lack of suitable laser sources has prevented us from investigating the ablation behaviour at shorter pulse durations.
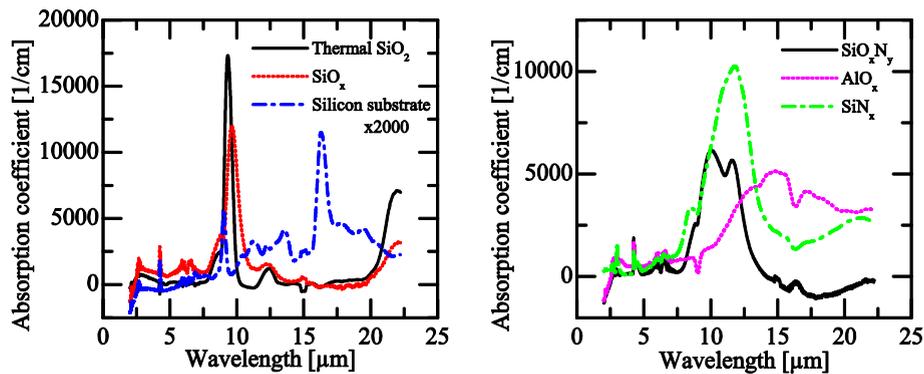

Fig. 2. Absorption coefficient in various dielectrics as measured by FTIR. All are deposited by PECVD, with the exception of the thermal SiO_2. Also shown is the absorption in the silicon substrate (x2000). The absorption bands are seen from around 8 µm.
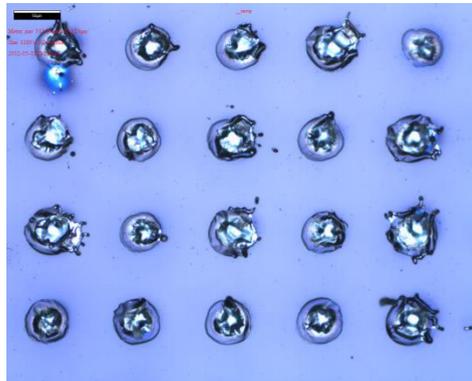

Fig. 3. Process result from the laser ablation of SiO_x using a laser wavelength of 9.3 µm and 100 ns pulse duration. Expulsion of silicon is clearly seen, indicating that the silicon has reached the melting temperature.

4. Discussion

We have shown that the optical characteristics of a thin film may vary with deposition parameters. In addition, it must be expected that the deposition parameters and the resulting structure and composition of the film will also affect other physical properties, such as the thermal properties used in the simulations. This constitutes a source of uncertainty in the simulations.

We have found that the simulations fail to predict the ablation behavior of dielectrics from silicon when applying 100 ns pulses at 9.3 µm wavelength. We have already noted that this means that either the heat transfer from the dielectric is higher than expected, e.g. as a result of temperature dependent R_{int}, or the absorption in silicon is stronger, e.g. if eq. (6) is an inaccurate description at high temperatures. Our simulations are sensitive to both of these quantities, which have not been experimentally determined in literature at high temperatures, making our simulation results uncertain. The discrepancy between experiments and simulations could, however, also mean that some of our assumptions are incorrect. We assume that ablation of the dielectric occurs when the surface of the dielectric reaches vaporization temperature and that the vapor pressure expels the remaining dielectric. This description may not necessarily be correct.

5. Conclusion

We suggest using long wavelength laser irradiation for removal of dielectric layers from silicon wafers, as many dielectrics have absorption bands at wavelengths above 8 µm, and as silicon is transparent at these wavelengths. Simulations show that there is a possibility of reaching vaporization temperatures in the dielectric while keeping the substrate below melting temperatures if using short enough pulses. Experiments, however, show that substrate melting is observed for pulses as short as 100 ns, indicating that the heat transfer from the dielectric or absorption in the substrate is significantly higher than what we have simulated. As such, even shorter pulses must be applied for the method to be successful.

Acknowledgements

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