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Investigation of depth of laser damage to silicon as function of wavelength and pulse duration

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Abstract

When quantifying laser damage in silicon, two key parameters are of importance, namely the depth of the laser damaged region and the minority carrier lifetime in the laser processed region. In this paper, we investigate the depth of the electrically active laser damage as function of laser wavelength and laser pulse duration. By etch-back experiments, we find that the laser damage from picosecond laser pulses is confined to a considerably shallower region than what is the case for nanosecond pulses. This is as expected due to the longer available times for heat conduction experienced in the latter case. However, the depth of damage is also much shallower than what the linear optical absorption coefficient would suggest, pointing towards non-linear optical confinement. We also develop an analytical expression for the effective minority carrier lifetime measured on a wafer with a laser damaged region, and from this expression, we are able to give an estimate on the lifetime in the laser damaged region. Based on these findings, we develop an optimized laser process.

Using a wavelength of 515 nm and a pulse duration of 3 ps, an effective lifetime of 1.8 ms is completely recovered after removal of just 240 nm of silicon from the wafer surface. The lifetime in the laser damaged region is in this case estimated to be on the order of 1 ns.

Keywords: Laser ablation; laser damage; lifetime

1. Introduction

In laser processing for silicon solar cells, the laser induced damage is a crucial factor. Both the electrical activity of the damage, in the form of reduction in minority carrier lifetime (from here: lifetime),

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and the distribution of the damage are of importance. While it is often stated that the depth of the laser induced damage or heat affected zone is reduced when using ultrashort lasers, this depth is rarely measured. In this paper, we present a comparison of the depth of laser induced damage encountered when using nanosecond and picosecond pulses. We ablate silicon nitride (SiN_x) from a silicon substrate, etch away a controlled silicon thickness, and measure the effective lifetime of the wafer as function of removed silicon thickness. Furthermore, we develop an analytical model for the effective lifetime measured on a wafer with a laser damaged region at one surface. From the model and the measured depth of the laser damage, an estimate on the lifetime in the laser damaged area is given.

2. Theory

2.1. Depth of laser damage

The penetration depth of the laser energy, l_{pen}, is often assumed to be [1]

$$l_{pen} \approx l_{opt} + l_{diff} = 1/\alpha + \sqrt{\tau D_{th}}, \tag{1}$$

where $l_{opt} = 1/\alpha$ is the optical penetration depth, α is the optical absorption coefficient, τ is the pulse duration and D_{th} is the thermal diffusion coefficient. l_{opt} describes the depth at which the laser energy is actually deposited, while l_{diff} is the diffusion term, describing how far the energy may diffuse during the pulse.

Some comments must be made to this model. Firstly, α is very often temperature dependent, and the temperature of the substrate increases during laser processing. As such, an effective optical penetration depth, $l_{opt,eff}$ should be applied. In order to correspond with the definition of l_{opt}, $l_{opt,eff}$ should be defined as the depth after which 1/e of the incoming laser energy remains. As α normally increases with increasing temperature, $l_{opt,eff}$ is normally smaller than l_{opt}. Furthermore, the expression $l_{diff} = \sqrt{\tau D_{th}}$ assumes that the heated material is removed within the duration of the pulse. While this may hold true for laser processing with long pulses, where much of the heated (molten) material is expelled during the laser pulse, it may not be true when applying ultrashort pulses. In this case, the material may be removed some time after the pulse [2], giving a larger diffusion depth than expected from the expression above. Furthermore, the value for D_{th} may deviate from its steady-state value, as the electron gas is strongly heated when applying ultrashort laser pulses. As such, the value for the penetration depth, l_{pen} should be treated with caution, and the link between l_{pen} and the depth of laser induced damage likewise.

Engelhart *et al.* [3] have performed an experiment similar to ours, and report laser damage at 2, 3 and 25 µm, for 30 nanosecond pulses at 355, 532 and 1064 nm, respectively. With l_{opt} of 10 nm, 0.7 µm and ~300 µm for the three wavelengths, and l_{diff} of about 1.5 µm, this result shows that the laser damage in this case is situated deeper than l_{diff}, but may be situated shallower or deeper than both l_{pen} and l_{opt}, depending on which of the above mentioned processes are most dominant. At 355 nm, the depth of damage must be dominated by diffusion, as the optical penetration depth is very small. Hence, $l_{diff} \simeq 2$ µm for this pulse duration (eq. (1) gives $l_{diff} = 1.5$ µm using D_{th} from [4]). At 1064 nm, the depth of damage must be dominated by the optical penetration depth $l_{opt,eff}$. With $l_{opt} \sim 300$ µm at this wavelength, we see that $l_{opt,eff}$ is much smaller than l_{opt} at this wavelength as discussed above.

Some general trends can be expected when going to shorter pulses. With very short laser pulses, heat transport is strongly reduced. In addition, α increases with increasing optical intensity, as a result of non-linear processes. These two factors both contribute to stronger confinement of the laser energy when applying ultrashort laser pulses.

2.2. Lifetime in laser damaged region

We are also interested in estimating the lifetime encountered in the laser damaged region, and need an expression for the effective lifetime measured in a wafer with laser damage near one surface. Applying the geometry shown in Fig. 1, we investigate the minority carrier distribution in the laser damaged region. We assume that photogeneration occurs only in the undamaged bulk of the wafer, and assume that S_2 is small compared to the recombination taking place in the laser damaged region. We use the continuity equation

$$\frac{\partial n}{\partial t} = -U - \frac{\partial J}{\partial x} = \frac{n}{\tau} - D_n \frac{\partial^2 n}{\partial x^2}\,. \tag{2}$$

where U is the recombination, J is the electron current, D_n is the electron diffusion coefficient, n is the electron density and τ is the electron lifetime. The stationary solution gives

$$\frac{n}{\tau} = D_n \frac{\partial^2 n}{\partial x^2}. \tag{3}$$

We apply the boundary condition of zero recombination current across S_2. The carrier density in the laser damaged region becomes

$$n(x) = A\cosh\left(\frac{x-(d+w)}{\sqrt{D_n\tau_{laser}}}\right), \tag{4}$$

with S_2 at $x = d + w$ where $d + w$ is the total wafer thickness, and w is the width of the laser damaged region, assumed to be constant over the wafer. The total recombination in the laser damaged region can be found by integrating over the laser damaged region, $x \in [d, d + w]$:

$$U_{tot} = \int_d^{d+w} \frac{n(x)}{\tau_{laser}}\,dx = A\sqrt{\frac{D_n}{\tau_{laser}}}\sinh\left(\frac{w}{\sqrt{D_n\tau_{laser}}}\right). \tag{5}$$

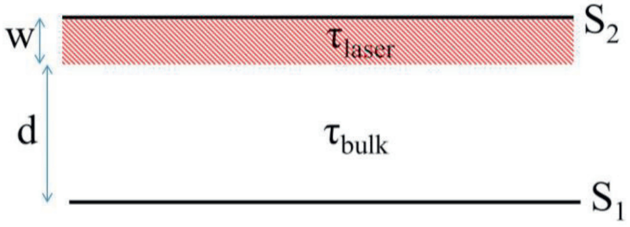

Fig. 1. Wafer with laser damaged region. Thicknesses, lifetimes and surface recombination velocities are indicated.

Inserting a virtual boundary between bulk and laser damaged region ($x = d$), a surface recombination velocity (SRV) can be defined as

$$S_{laser} \equiv \frac{U_{tot}}{n(x=d)} = \sqrt{\frac{D_{el}}{\tau_{laser}}}\tanh\left(\frac{w}{\sqrt{D_n\,\tau_{laser}}}\right) \tag{6}$$

where $n(x = d)$ is the electron concentration at $x = d$. We see that the effective SRV from the laser damage depends on both w and τ_{laser}. For $w \gg \sqrt{D_n\tau_{laser}}$, i.e. laser damage much deeper than the diffusion length, the recombination saturates, and $S_{laser} \approx \sqrt{D_n/\tau_{laser}}$ is independent of w. For a powerful analysis tool, the expression in eq. (6) can be combined with expressions by Sproul [5] for the effective lifetime and the surface lifetime:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s} = \frac{1}{\tau_{bulk}} + \alpha_0^2 D_n \, , \qquad (7)$$

where α_0 is the smallest eigenvalue solution of the equation

$$\tan(\alpha_0 w) = (S_{laser} + S_2)/(\alpha_0 D_n - \frac{S_{laser}S_2}{\alpha_0 D_{el}}) \, . \qquad (8)$$

Here, we apply eq. (6) for S_{laser}, in order to obtain the effective lifetime of the laser damaged structure.

3. Experimental

We deposit a 75 nm thick a-SiN$_x$:H (SiN$_x$) film by plasma-enhanced chemical vapor deposition (PECVD) on polished silicon wafers. The SiN$_x$ has a refractive index of around 2.05 at a wavelength of 633 nm. We ablate the SiN$_x$ by applying non-overlapping laser pulses at 1030, 515 and 343 nm and a pulse duration of 3 ps using a peak fluence of 0.86, 1.2 and 2.1 J/cm^2 at 1030, 515 and 343 nm, respectively, and at 532 nm and 100 ns pulse duration using a peak fluence of around 20 J/cm^2. The remaining SiN$_x$ is removed in an HF dip, and the samples are etched in a concentrated (47 %) KOH solution at 85 °C, showing an etch rate of approx. 1 µm/min. The etch depth is measured by gravimetry, assuming uniform material removal over the wafer. The accuracy of the measurement is +/- 0.2 mg, corresponding to approx. 20 nm etch depth. The samples are then passivated by amorphous silicon (a-Si), ensuring very low SRV, and the effective lifetime of the samples is measured by photoluminescence imaging (PL) using a LIS-R1 setup from BTimaging. The lifetime measured in the laser processed areas is normalized to the effective lifetime measured in damage-free areas.

As defects or surface roughness may act as seeds for etching, thereby increasing the local etch rate, we analyze the shape of the laser spots before and after etching by atomic force microscopy (AFM). If the laser spot gets deeper by etching, there would be a preference for etching in the spots, and hence, the depth of damage must be corrected correspondingly.

4. Results

4.1. Depth of laser damage

When etching the wafers, the lifetime in the laser treated areas is gradually restored, at some point reaching the 1.8 ms seen outside of the laser treated areas. AFM analysis shows that the shape of the laser spot remains constant with etching, ruling out the possibility of preferential etching in the spots.

The results of the etch-back experiments are shown in Fig. 2 (left), showing that the depth of the laser damage using ultrashort pulses is in the range of 70 – 130 nm for 343 nm (between the last measurement point showing lifetime degradation and the first measurement point showing complete recovery of the lifetime), 120 – 240 nm using 515 nm and below 210 nm using 1030 nm laser wavelength (we unfortunately don’t have any measurements showing lifetime degradation for this laser wavelength and pulse duration). Using long laser pulses at 532 nm, the damage is situated much deeper, in the range of 1.8 – 2.7 µm. This depth corresponds approximately to l_{diff}.

It should be noted that also on non-laser treated reference samples, surface-near damage was observed as reductions in effective lifetime down to a depth of approx. 70 nm. This is attributed to ion bombardment damage from the PECVD-process. However, this ion bombardment damage is less pronounced than the laser damage, making it easy to extract the contributions from laser induced damage.

It is interesting to note the difference between long and short pulses at wavelengths at 515 nm laser wavelength. The 3 ps, 515 nm pulse results in a much more shallow damage than at the same wavelength using long pulses, confined to within 240 nm of the wafer surface. This is a result of the elimination of thermal diffusion (which at a pulse duration of 3 ps would correspond to around 20 nm). Comparing with measurements by Engelhart *et al.*, the same reduction is also seen in the UV, where the depth of damage using long pulses was dominated by thermal diffusion. Using 3 ps, 343 nm pulses, thermal diffusion is eliminated, and the depth of damage is much smaller. At 1064 nm, the depth of damage using nanosecond-pulses [3] was around 25 μm, and dominated by the optical penetration depth. Using 3 ps, 1030 nm pulses, we see no reduction in lifetime even at 210 nm from the surface, indicating that the optical penetration depth must have been dramatically reduced (by two orders of magnitude!), as a result of non-linear absorption mechanisms using ultrashort pulses. In combination, the comparison between depth of damage using nanosecond and picosecond lasers at three wavelengths shows that both the optical penetration depth and the thermal diffusion depth are decreased using ultrashort laser pulses.

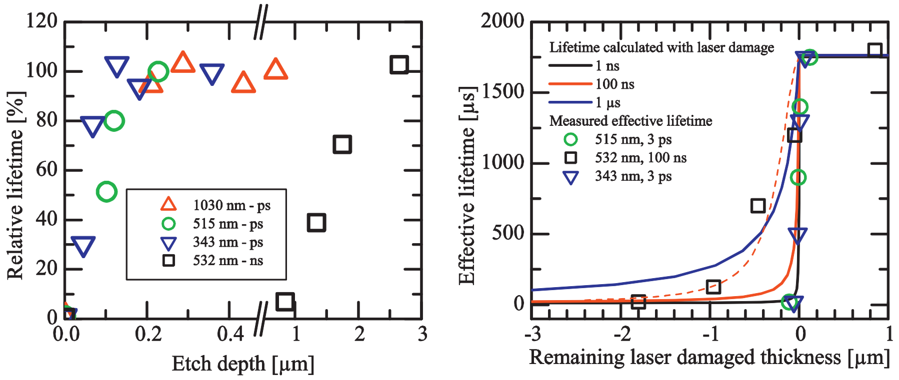

Fig. 2. (Left) Relative lifetime measured as function of etch depth using four different lasers. (Right) Modeled effective lifetime (solid lines) assuming three different values for τ_{laser} and measured effective lifetime (symbols) as function of depth of laser damage. Also shown is a calculation of effective lifetime taking into account the finite area coverage and geometry of the laser damage (dotted line).

4.2. Lifetime in laser damaged region

We plot the modeled effective lifetime as extracted using eqs. (6-8) as function of the remaining laser damage, shown in Fig. 2 (right) as solid lines. The measured effective lifetime is shifted along the x-axis for best fit, shown as symbols. We see that for the 515 nm, 3 ps sample, a fairly good fit is found if inserting a lifetime in the laser damaged region of 1 ns. However, as we only have a limited number of experimental values, a smaller lifetime in the laser damaged region would give an equally good fit.

For the 532 nm, 100 ns sample, however, the fit is not as good, indicating that other effects are taking place. One effect could be the geometry of the laser damage. We have applied spots in a square pattern, with 30 μm pitch. Using long laser pulses, it is not unreasonable to assume that the molten volume will be deepest in the middle of the laser spot. Assuming that the laser damaged volume has the shape of a paraboloid with depth 1.8 μm (estimated from the etch depth showing recovery of the effective lifetime), the area fraction of laser damage will decrease as we etch into the wafer, decreasing the effective SRV. With a width of the paraboloid at the wafer surface of 30 μm, we can calculate the fill factor of the laser damage as function of etch depth. We can then apply Fischer’s formula for effective SRV [6]

$$S_{eff} = \frac{D_{el}}{W}\left(\frac{p}{2W\sqrt{\pi f}}\arctan\left(\frac{2W}{p}\sqrt{\frac{\pi}{f}}\right) - \exp\left(-\frac{W}{p}\right) + \frac{D_{el}}{fWS_{laser}}\right)^{-1} + \frac{S_{pass}}{1-f}. \tag{9}$$

Here W is the wafer thickness, p is the laser spot pitch, f is the fill factor of laser damage and S_{pass} is the passivated SRV. Using this value for S_{laser}, and using a modeled lifetime in the laser damaged region of 100 ns, the red dashed line in Fig. 2 is obtained. Although still not a perfect fit to experimental data, the fit is now much better. Arguably, the assumption that the laser damaged depth takes on a parabolic shape is somewhat arbitrary. In addition, the shape of the lifetime curve using long pulses may also be a result of other mechanisms, such as varying lifetime throughout the laser damaged region. As such, the dashed line in Fig. 2 is only meant as an indication that the shape of the lifetime curve will vary with assumptions on damage geometry and variations in lifetime throughout the laser damaged region.

5. Conclusion

We have measured the depth of laser-induced damage in silicon using ultrashort and long laser pulses, by etch back experiments. The laser-induced damage in silicon is found to be confined within 70 nm, 240 nm and 210 nm for 3 ps laser pulses at 343, 515 and 1030 nm, respectively. This is a strong reduction in depth of damage compared to what was observed by Engelhart et al. [3] using nanosecond pulses at corresponding wavelengths. We conclude that strong reduction in thermal diffusion and non-linear confinement of the optical energy cause this trend.

With knowledge of the depth of laser damage, the laser source can be more efficiently targeted to a specific process. As an example, in our process for creation of diffractive structures in silicon [7], 300 – 350 nm of silicon is removed by etching after laser processing. As such, laser damage is expected to be removed when applying any of the three picosecond lasers investigated herein, yielding a process where the laser-induced damage is eliminated.

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References

[1] D. Bäuerle, Laser Processing and Chemistry, 3rd ed., Springer, Berlin Heidelberg, 2000.

[2] R. Holenstein, S.E. Kirkwood, R. Fedosejevs and Y.Y. Tsui, Simulation of femtosecond laser ablation of silicon, in: Proc. SPIE 5579, Photonics North 2004: Photonic Applications in Telecommunications, Sensors, Software, and Lasers, Spie, Ottawa, Canada, 2004: pp. 688–695.

[3] P. Engelhart, R. Grischke, S. Eidelloth, R. Meyer, A. Schoonderbeek, U. Stute, et al., Laser Processing for Back-contacted Silicon Solar Cells, in: ICALEO Congress Proceedings, Scottsdale, AZ, 2006: pp. 218–226.

[4] H.R. Shanks, P.D. Maycock, P.H. Sidles and G.C. Danielson, Thermal conductivity of Silicon from 300 to 1400 K, Physical Review. 130 (1963) 1743–148.

[5] A.B. Sproul, Dimensionless solution of the equation describing the effect of surface recombination on carrier decay in semiconductors, Journal of Applied Physics. 76 (1994) 2851–2854.

[6] 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, Progress in Photovoltaics: Research and Applications. 16 (2008) 461–466.

[7] J. Thorstensen, J. Gjessing, E. Haugan and S.E. Foss, 2D periodic gratings by laser processing, Energy Procedia. 27 (2012) 343–348.