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LETTER TO THE EDITOR

Nanosecond laser pulses inducing melting of Si⁺-implanted SiO₂

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Abstract. We analyse the physical processes involved in laser irradiating Si⁺-implanted SiO₂. In particular we discuss the laser light absorption phenomena and we estimate an upper limit for the value of the delay time in energy transfer from Si-implanted impurities to the SiO₂ lattice. The role of a delay time in the thermal behaviour of the SiO₂ lattice is quantitatively analysed.

Recently, Shimizu *et al* [1, 2] reported new experimental results on nanosecond laser pulses (308 nm wavelength) irradiating Si⁺-implanted SiO₂: a shift is observed in the as-implanted Si profile in SiO₂ and also Si re-emission occurs for the higher laser energies. These results have been explained [1, 2] in terms of solid state rate processes where Si impurities (in the form of Si clusters in the SiO₂) are first energised by the absorbed laser light and then migrate interstitially towards the surface because of the Soret effect which is superimposed on the ordinary diffusion. In order to explain the distances covered by the Si species in the solid SiO₂ in time intervals of the order of 10⁻⁶ s, the authors of [1, 2] suggested that the Si diffusion coefficient must be written in the temperature independent form νa^2 where ν is a typical lattice frequency and a is an interatomic distance.

In contrast to this explanation, the present author [3] suggested the occurrence of a melted SiO₂ phase under laser irradiation. Indeed by solving the heat transport equation, with the Stefan boundary condition allowing melting and resolidification, it has been proved that all features of the experimental Si profiles, after laser irradiation, may be consistently interpreted in terms of normal diffusion and Soret drift of Si impurities in the liquid SiO₂ phase [3]. Indeed the obtained diffusion coefficient of Si impurities is consistent with the liquid atomic diffusivity data reported in the current literature. Notice that in solving the heat transport equation we formulated the hypothesis that the optical energy absorbed by the implanted Si impurities is instantaneously converted into SiO₂ lattice heat. The authors of [1, 2] in contrast suggest that only a minor portion of the optically absorbed energy is converted into lattice heat after a delay time. Indeed they estimated [1], without considering the thermal diffusivity of the SiO₂ lattice, a maximum lattice temperature of $T \approx 1300$ K (the energy of the laser pulse is $E_p \approx 1.2$ J cm⁻² and 5×10^{17} cm⁻² Si⁺ ions are implanted). Notice that no melting of the lattice is expected [1, 2]. The present author [3], on the contrary, suggests that not only melting of SiO₂ but also a relevant thermodynamical evaporation must occur at this laser pulse energy density.

In [2] the ESR (electron spin resonance) spectra of the E_1 centres, which are present in the SiO_2 after Si^+ implantation, are reported both after furnace annealing (annealing time $t_f = 30$ min) at different temperatures, and also after laser irradiation ($E_p = 1.2 \text{ J cm}^{-2}$). Furnace annealing induces a decrease in the density of the E_1 centres while after laser irradiation the density remains the same. Just from these experimental results the authors of [2] concluded that no melting of the lattice can occur. Given these initial figures it is quite evident that the problem of the possible Si^+ -implanted SiO_2 lattice melting during laser irradiation must be analysed in a more substantial way, in particular in connection with the possible delay time τ occurring between laser light absorption (by Si impurities) and lattice heating.

The problem of the thermalisation time of the hot carriers produced during ultrashort laser pulse irradiation of solids has been questioned for a long time in the literature in the case of metals and in particular in the case of Si. In the actual case of nanosecond laser irradiation of impurity-implanted dielectric solids where the optical energy is absorbed by the impurities and then transferred to the lattice, the thermalisation process is a relevant new problem which has not previously been considered in the literature [1–3].

In this letter we analyse this problem for the case of Si^+ -implanted SiO_2 , looking at some published experimental results in order to estimate the order of magnitude of τ and then showing, through the numerical integration of the macroscopic heat transport equation, the role of τ in the thermal behaviour of the SiO_2 lattice. On the basis of the solution of this new ‘relaxation’ problem alone, we will safely conclude that the observed changes of the Si profiles [1] after laser irradiation are connected to the melting of the SiO_2 lattice and not to the solid state rate processes envisaged in [1, 2]. As to the macroscopic heat transport equation (second Fourier law) used here, notice that any calculation of the temperature T of a laser irradiated sample, when thermodynamical parameters such as the thermal conductivity K or the specific heat c are involved, assumes that the lengths over which we study a given heat phenomenon are longer than the typical length over which it is meaningful to talk in terms of macroscopic parameters such as K or c . As Harrington’s paper [4] shows such a length is about five times the mean free path, l_p , of the hot carriers (mainly phonons in the actual case). As a consequence the heat transport equation assumes the usual form (equation (1) of [3]) only if we are interested in variation of T over lengths greater than $\approx 5 l_p$.

Notice that in the actual case of high Si^+ doses implanted into SiO_2 the lattice impurities or defect densities are quite high and so the phonon mean free path is also related to the scattering of phonons by the introduced lattice imperfections; this means that in any case the phonon mean free path cannot exceed a few Å. On the other hand we are interested in lattice temperature evolution over lengths greater than the Si^+ -implanted range (larger than 80 nm); see also figure 1. In conclusion, since the macroscopic lattice length scales of interest as regards temperature undergoes change, the calculation approach used here, based on a continuum model, is justified.

Before looking at the main topic of this letter (the relaxation time τ) let us discuss simply some aspects of the laser absorption processes in Si^+ -implanted SiO_2 . The photon energy of the laser employed in the experiments under discussion [1, 2] is ≈ 4 eV while the band gap for undamaged SiO_2 is ≈ 9 eV; thus, for undamaged SiO_2 , any absorption phenomena are avoided. However, it is certain that a finite number of defects (less than $\approx 10^{16} \text{ cm}^{-3}$) [5] exist intrinsically in SiO_2 due to the growth process and so light absorption centres may exist. Moreover in the SiO_2 under discussion 2×10^{17} – $5 \times 10^{17} \text{ Si}^+ \text{ cm}^{-2}$ are implanted; this means that a large amount and many kinds of

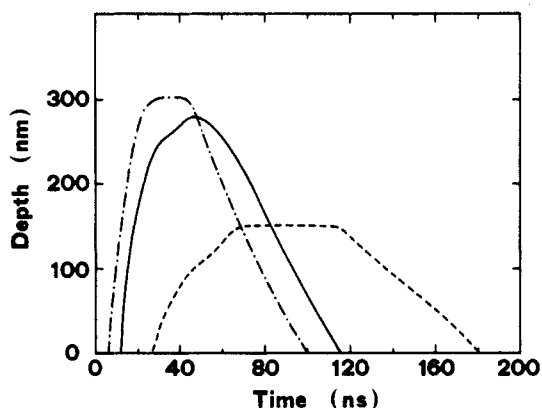


Figure 1. Time evolution of the solid-liquid interface in laser-irradiated Si^+ -implanted SiO_2 . The energy of the laser pulse is 200 mJ cm^{-2} (50 keV ion implantation [1]). Chain curve: $\tau = 1 \text{ ns}$; full curve: $\tau = 10 \text{ ns}$; broken curve: $\tau = 50 \text{ ns}$. For details of the calculations see [3].

defects are introduced [5]. These may be: (i) an oxygen vacancy (E'_1 centres), (ii) non-bridging oxygen-hole centres or (iii) a trapped hole peroxy radical. The energy levels pertinent to the states associated with these defects in the SiO_2 band gap are respectively: (i) $\approx 4.6 \text{ eV}$, (ii) $\approx 2.1 \text{ eV}$ and (iii) $\approx 3.0 \text{ eV}$. Notice that the authors of [2] experimentally detected in Si^+ -implanted SiO_2 substoichiometric SiO_2 (SiO_x) which falls into the class of UV (248 nm) photographable materials [5] since the band gap is $\approx 3 \text{ eV}$. Bearing in mind this new energy level diagram for the high dose Si^+ -implanted SiO_2 it is evident that the laser light of [1] is absorbed not only by the Si^+ -implanted species (most probably in the form of a cluster since a-centres are present [2]) but also from other absorption centres strongly bound to the SiO_2 lattice. In particular the optical absorption cross section reported in figure 4 of [1] must be considered as an 'effective' optical absorption cross section associated with the Si impurities including the absorption effects caused by the defects generated by the Si^+ implant. This means, in conclusion, that a portion of the laser pulse is absorbed directly by the defect structure of the SiO_2 lattice and so the proposal of the authors of [1, 2] that the Si-implanted species are first energised and then, after some delay time, a portion of the absorbed energy is transferred to the lattice, must be drastically altered.

Now let us discuss the possible delay time τ in the energy transfer between energised Si impurities and the SiO_2 lattice. In [6] the $\text{Si}^{16}\text{O}_2/\text{Si}^{18}\text{O}_2/\text{Si}$ system is irradiated with 20 ns single pulses from a Q-switched ruby laser in different atmospheric conditions in order to study, amongst other things, the laser induced vaporisation (or boiling) of SiO_2 . The laser light in this layered system is absorbed in Si near the SiO_2/Si region and the SiO_2 is heated through the thermal contact with the Si bulk [6]. Notice that here the Si surface over which the SiO_2 is deposited plays the same role as the Si atomic clusters of the Si^+ -implanted SiO_2 system [1, 2]. The experimentally detected losses of ^{18}O are explained [6] in terms of thermodynamical surface evaporation in which the evaporation rate is simply governed by the SiO_2 surface temperature. This process occurs at any temperature above melting and it may be the only one existing under conditions that prevent boiling of the molten pool. The only practical limit to the maximum temperature attainable is then the liquid critical temperature [7]. The near surface temperature of

the laser irradiated SiO₂/Si system [6] for laser energy density $E_p = 3.5 \text{ J cm}^{-2}$ is reported in figure 8 of [6]. From this figure we may conclude that the delay time τ occurring between laser light absorption by the Si substrate and heating of the SiO₂ up to temperatures exceeding the SiO₂ melting temperature must be less than $\approx 30 \text{ ns}$. Indeed if τ exceeds 30 ns then the absorbed energy in the Si lattice near the SiO₂ layer would be effectively removed through the Si bulk thermal diffusivity and so the primary cause of ¹⁸O loss (SiO₂ heating through Si thermal contact) disappears.

Having made this initial estimate of an upper limit for τ , let us take into account possible delay effects in the thermal behaviour of laser-irradiated Si⁺-implanted SiO₂ [1, 2]. For this purpose we numerically integrated the previously reported heat transport equations [3] considering a delay time τ in the energy transfer from Si impurities to the SiO₂ lattice. In particular, the energy transfer from Si impurities to the SiO₂ lattice in an interval time dt is now controlled by the well known (in processes governed by a relaxation time) relation:

$$(1 - e^{-dt/\tau}). \quad (1)$$

In figure 1 we report the time evolution of the solid-liquid interface for three representative values of τ , namely: $\tau = 1 \text{ ns}$, $\tau = 10 \text{ ns}$ and $\tau = 50 \text{ ns}$. The energy of the laser pulse is 200 mJ cm^{-2} (the lower one employed in [1] for 50 keV Si⁺-implanted SiO₂). The delay effect in the heat transfer from Si impurities to the SiO₂ lattice is quite evident on comparing the three reported solid-liquid interface curves. In particular, while there is no appreciable difference in the SiO₂ thermal behaviour for τ less than $\approx 1 \text{ ns}$ (compare the chain curve of figure 1 ($\tau = 1 \text{ ns}$) and the full curve of figure 2 in [3] ($\tau = 0 \text{ ns}$) where the optical and thermodynamical parameters are the same), some relevant changes appear when τ becomes of the order of the laser pulse duration. In particular the threshold time for the appearance of the liquid phase increases with increasing τ while the maximum molten thickness decreases with increasing τ . These results are also intuitive if we consider that the delay time τ allows for a more effective heat transport into the SiO₂ bulk thus preventing an excessive temperature rise in the first surface layers where laser light absorption actually occurs. However, the more important result of figure 1 is connected to the presence of a molten layer extending up to 275 nm for $\tau = 10 \text{ ns}$ and up to 150 nm for $\tau = 50 \text{ ns}$. This means that for the lower laser energy employed in [1] melting occurs for any possible choice (on a physical basis) of the delay time τ (τ less than $\approx 50 \text{ ns}$) [8]. Our conclusions about the order of magnitude of τ (which implies melting of Si⁺-implanted SiO₂) may seem contrary to the qualitative analysis of the results of [2] where isochronal annealing for 30 min at various temperatures of the Si⁺-implanted SiO₂ shows that the density of the E₁ centres is reduced while, in contrast, laser pulses inducing re-emission of Si do not modify the E₁ density. However, a quantitative analysis of such results shows that there is no inconsistency. Indeed, if as discussed by the authors of [1, 2] during laser irradiation the Si migration occurs in the SiO₂ solid phase (since the SiO₂ temperatures may also be of the order of 1300 K for time intervals of the order of 10^{-6} s [1]), then the observable effects in the density of E₁-centre annealing must also be observed after laser annealing (see figure 2 of [2], the $5 \times 10^{17} \text{ cm}^{-2}$ Si⁺ implants). Indeed the ratio of the annealing rates of the E₁ centres and the ratio of the annealing times in a furnace (f stands for furnace) and in laser experiments (l stands for laser) are quite similar:

$$\exp(-E/k_B T_f)/\exp(-E/k_B T_l) \approx t_l/t_f \quad (2)$$

when $T_f = 473 \text{ K}$, $T_l = 1300 \text{ K}$ [1], $t_l \sim 10^{-6} \text{ s}$, $t_f \approx 30 \text{ min}$ and the activation energy E is

1.35 eV [2]. However, no annealing effects of the E_1 centres are observed after laser irradiation but in contrast their density remains constant.

This result may be explained in the context of a melting phase induced in the SiO_2 as follows: if the density of the E_1 centres after high dose Si^+ implants (greater than 10^{17} cm^{-2}) is at a saturation value, we may also safely argue that in resolidified SiO_2 , when the resolidification velocity is of the order (see figure 1) of $\approx 5 \text{ ms}^{-1}$ (an extreme non-equilibrium resolidification process) a saturation value for the E_1 -centre density should be easily attained [5].

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- [8] The estimated value of τ is most probably an upper limit. Indeed Liu *et al* (Liu J M, Lompre L A, Kurz H, Bloembergen N 1984 *Appl. Phys. A* **34** 25), performing picosecond time-resolved reflectivity measurements (during 20 ps laser pulses at 532 nm wavelength) on bare silicon surfaces and silicon surfaces with oxide layers and revealing material evaporation on subnanosecond time scales, concluded that heating of the SiO_2 layer through heat diffusion from the overheated molten silicon surface (SiO_2 does not absorb light at 532 nm wavelength) may raise the temperature to the softening point (1853 K) or even to the melting point (1983 K) of the SiO_2 . The softened or molten SiO_2 may react with the molten silicon to form SiO which then evaporates. From these results we may argue that the delay time τ occurring between laser light absorption in Si and heat transfer to the SiO_2 lattice cannot exceed $\approx 1 \text{ ns}$ since, as in the case reported above concerning the laser pulse in the nanosecond regime, if $\tau > 1 \text{ ns}$ then the heat would be effectively removed by the Si bulk and the primary cause of the SiO_2 evaporation disappears. However, in order to be more precise on this point it is necessary to calculate the degree of overheating of the molten Si: this cannot be done with confidence since the Si thermodynamical parameters in an overheated liquid phase are not known.