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FUNDAMENTALS OF PULSED LASER IRRADIATION OF SILICON

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Abstract - Most of the experimental work on pulsed laser processing of semiconductors is consistent with an optical heating model. Thermal equilibrium between the dense electron-hole plasma and the lattice of amorphous or crystalline silicon is established on a time scale of 2 ps or less, during the laser pulse. Nevertheless, a series of speculations on the nonthermal nature of laser annealing of ion-implanted silicon surfaces has persisted. These invoke a hot, dense carrier plasma, inducing a phase transformation in a much cooler silicon lattice. According to the thermal model the observed phase changes involve melting. Picosecond irradiation experiments provide a stringent test of the time scale on which the thermal model remains valid. In this paper we present our recent time-resolved measurements of refractive index changes of silicon on a picosecond time scale. During and after the irradiation with a single picosecond laser pulse, the reflectivity and transmission of thin silicon films exhibit characteristic transients, which allow a detailed insight into the plasma kinetics, energy transfer to the lattice and lattice heating, and subsequent melting of the surface. In agreement with recently-published results, obtained with subpicosecond resolution, the energy stored in the electron-hole plasma is found to be transferred to the lattice in a few picoseconds.

1 - INTRODUCTION

The coupling mechanism between lasers and semiconductors has been of great interest during the development of a new field of material science generally described as laser processing. Ultrafast optical heating and melting of semiconductor surfaces are key processes for the development of new structures and technologies [1-5].

The discovery of pulse laser annealing (PLA) of ion implanted semiconductors stimulated an enormous amount of experimental work seriously dedicated to exploring the technological prospects for device fabrication. Fast recrystallization of ion-bombarded semiconductor surfaces preserving the intended dopant distribution has been the most attractive promise for high speed circuits and high integration. The impact of PLA on material processing has been quite impressive, and a large variety of novel techniques has emerged [6].

During the exploratory phase of PLA the question arose of whether the observed liquid phase epitaxy phenomena of structural phase changes, dopant redistribution and quenching from the melt can be entirely explained by heating, melting and rapid resolidication. A series of nanosecond pulse experiments have been performed on amorphous and crystalline silicon to clarify the thermal nature of PLA. Most of the experimental results devoted to this question, which were obtained with nanosecond pulses, can be interpreted within the framework of a simple thermal model [7-10]. The transformation of electronic excitation into heat occurs nearly instantaneously during the laser pulse. The time-resolved reflectivity measurements by D. Auston clearly demonstrated the formation of a liquid layer at a certain laser fluence [11]. Remarkably late, the melting picture has been confirmed in transmission experiments [12]. A classical time-of-flight measurement of silicon atoms evaporated from ruby-irradiated surfaces indicates a lattice temperature of 2000 K at the phase transition
Synchrotron X-ray studies, designed to measure the temporal temperature distribution and to prove the occurrence of structural changes at the surface, clearly show that the phase transition is thermally induced [14]. Thermal melting is further confirmed by photoemission studies on laser-irradiated Si surfaces, as well as by transient conductance measurements [15,16]. At least the explanation of postannealing morphologies, redistribution of dopants and the solubility limits achieved in PLA require the formation of a liquid layer on the surface of silicon [17].

However, Raman experiments designed to measure the lattice temperature deliver data which are inconsistent with the thermal model [18,19]. This puzzling discrepancy with the majority of experiments has stimulated a wave of speculations about the nonthermal nature of ns PLA. The presence of a dense electron-hole plasma should weaken the covalent bonds in silicon enough to initiate the phase transition far below the melting point. Van Vechten and his associates ascribe the experimentally observed reflectivity and transmission changes to the formation of a long-lived, confined plasma, requiring an unexplained decrease of the well-known electron-phonon interaction strength by many orders of magnitude [20].

The first space-time resolved reflectivity measurements of ps irradiated silicon by R. Yen et al. show clearly that subnanosecond time resolution is required to study the phase transition, e.g., to clarify the question of whether the lattice becomes unstable by electronic or vibronic excitation [21]. The discovery of the reverse reaction of PLA, the photoinduced amorphization of single crystal silicon by picosecond irradiation opened the way to a series of picosecond experiments where details of the behavior of the electron-hole plasma and the solid-to-liquid transition have been studied [22-26]. The time resolution of picosecond and femtosecond excite and probe techniques appears particularly attractive for the investigation of temporal sequences of the physical processes involved.

The intention of this paper is to review briefly the fundamental aspects and open questions concerning the energy transfer route in intensively photoexcited single crystal silicon. The experimental approach to these questions is discussed, followed by the presentation of the most important results in the picosecond regime. In the final chapter the experimental results are summarized and compared with the theoretical descriptions of the PLA process. The validity of alternative proposals is discussed.

2 - THEORETICAL BACKGROUND

The central question of how pulsed laser annealing (PLA) is achieved during and following the absorption of laser energy requires a detailed treatment of the energy relaxation processes illustrated in Fig. 1. The coupling between laser and electronic carriers is determined by the photon absorption rate $g$.

$$g(x,t) = \frac{I(x,t)(1-R)}{E_L} \alpha(x,T,t) \exp\left(-\int_0^x \alpha(x',T,t) \, dx'\right)$$

where $\alpha = \alpha_L + \alpha_{NL}$ measures the sum of linear and nonlinear absorption coefficients. The Gaussian-shaped temporal intensity profile $I(x,t) = I_0 \exp\left(-t/t_0^2\right)$ of a single mode beam is corrected by the reflectivity $R$ of the sample. Due to the strong temperature and carrier density dependence, the spatial dependence of the optical absorption has to be taken into account. If the photon energy $E_L$ exceeds the band gap $E_g$ between an occupied valence band and the empty conduction band, electron-hole pairs are created with a generation rate of $G = q \cdot g$, where $q$ is the quantum efficiency of electron-hole pair generation.

The physics of optical heating for $E_L > E_g$ in the ns range is based on the assumption of thermal equilibrium between photoinjected carriers and phonons. The evolution of a common carrier lattice temperature is described by one-dimensional coupled diffusion equations for electron-hole pair density $N$ and temperature $T$ [25,29,30].
where $D_{th}$ is the thermal diffusivity, $S$ the heating source, $G$ the generation rate of electron-hole pairs, $\gamma(N)$ the Auger recombination and $j_m$ the electron-hole pair current density defined by:

$$j_m = \frac{e D}{a} \left( \frac{\partial N}{\partial x} + \frac{N}{2kt} \frac{\partial E_g}{\partial x} + \frac{N}{T} (p+1) \frac{\partial T}{\partial x} \right)$$

The first term in equation (4) is the diffusion current density; the second term represents the driving force caused by the bending of the band gap $E_g$, the importance of which was first suggested by W. Brown [31]. The third term describes the thermoelectric effect characterized by the kinetic energy dependence $p$ of the carrier scattering.

In a first step towards nonequilibrium considerations, A. Lietoila and J. Gibbons introduced an energy relaxation time $\tau_e$ into the heating process given by [29]

$$S = \frac{3kN(T_e - T_h)}{\rho c \tau_e^2}$$

where $T_e$ is the equilibrium carrier temperature determined by particle statistics, $\rho c$ the specific heat, and $T_h$ the lattice temperature. Both temperatures and the specific heat are definitive parameters of equilibrium conditions. Thus, the relaxation time $\tau_e$ in equation (5) describes the conversion of electronic energy of thermalized carrier distributions in random atomic motion. The oscillations of the atoms are directly related to the heat content of the crystal. The relaxation time $\tau_e$ is introduced as a thermodynamic parameter that covers the whole time span in which the excess electronic energy is shared among the different vibrational modes and thermal equilibrium among them is established. For laser pulses whose duration $\tau_p$ is shorter than $\tau_e$, the optical input energy is stored in the electron-hole plasma. The lattice remains cool and considerable differences between carrier and lattice temperature would occur.

The thermodynamic description of optical heating becomes questionable if the laser pulses become shorter than $\tau_e$. From the point of statistical mechanics, the central problem underlying the whole process is that of trying to understand the manner in which the energy distribution functions of hot carriers and hot phonons influence each other. The correct description requires the solution of coupled Boltzmann equations displaced from equilibrium and the understanding of the microscopic nature of melting. Both problems have not yet been solved. However, in picosecond experiments some assumptions can be made which break the problem logically into several time regimes, illustrated in Fig. 1.

In picosecond PLA experiments the time-averaged generation rate $g$ is on the order of $g = 10^{33}$ cm$^{-3}$s$^{-1}$, if a temperature averaged value of $\alpha = 1 \times 10^{45}$ cm$^{-1}$ is assumed. Electron-hole pair densities between $10^{20}$ and $10^{21}$ cm$^{-3}$ are expected. Thermal equilibrium among electrons and among holes is attained in less than $10^{-14}$ s [30]. The carrier distribution function can be taken as Maxwellian at an elevated carrier temperature $T_e = T_h$, determined by the carrier density $N$ through a set of balance equations [33].

This density-temperature relation has been calculated by E. Yoffa and R. Biswas et al. for the case or time where no energy can be transferred to the lattice. They
assume that Auger recombination is balanced by impact ionization establishing equilibrium between electrons and holes. A common quasi-Fermi level $\mu_0 = \mu_e$ is deduced [30,34]. The electron temperature $T_e$ increases strongly with increasing density of the plasma. At a density above $N_c = 10^{21} \text{cm}^{-3}$, the carrier temperature $T_e$ would be comparable to the band gap. Under this energy condition impact ionization may become important. Before any significant energy can be transferred between electrons and phonons, the plasma becomes extremely hot and dense.

At high densities Auger processes will dominate recombination [35]. Electrons combine with holes; the energy released is transferred to a third carrier. This hot carrier will rapidly thermalize through intercarrier collisions, and a common quasi-Fermi level $\mu_0 = \mu_e$ will be established. This process rates with $N_0^3$ and does not remove energy from the electronic system as long as the electronic carrier relaxation time $\tau_{e-e}$ is much faster than the electron-phonon collision time $\tau_{e-\text{phonon}}$. The plasma system is completely described by $T_e$, $\mu$ and $N$. Heating of the lattice by Auger recombination can only occur if the density of carriers drops to levels where $\tau_{e-\text{phonon}}$ becomes comparable to the electron-phonon collision time $\tau_{e-\text{phonon}}$. Heat generation via the Auger recombination process [34], in which the recombination energy $(E_e + 3kT_e)$ is given to a third carrier is directly transferred to the lattice, is unlikely during ps excitation.

The influence of carrier diffusion on the energy balance between plasma and phonons has been treated by Yoffa. The energy loss due to diffusion of hot carriers is characterized by a conventional diffusion lengths $L_D = (D_e T_e)^{1/2}$ where $D_e$ means the ambipolar diffusion coefficient of hot carriers, depending on the carrier temperature and lattice temperature through carrier-carrier and carrier phonon scattering [30]. For energy transfer considerations the electron-hole pair current density $j_m$ defined in equation (4) starts to play a role if the energy relaxation time $\tau_e$ is larger than $\tau_e \gg \tau_0 (1 - R)/j_m$ where $\tau_0 (1 - R)$ means the total energy fluence of the laser deposited in the plasma.

During the picosecond laser pulse the equilibrium carrier temperature $T_C$ is determined by equating the rate of energy at which the electron-hole plasma receives energy from the photoexcited carriers to the rate at which the plasma loses energy to the phonons. Energy transfer to the phonon system occurs via deformation potential scattering. Dumke calculated the energy loss rate of hot carriers having 1 eV excess energy by intervalley and intravalley scattering. Most of the energy is transferred on the order of ps [36]. If the mean energy of the carriers exceeds the thermal energy of the lattice vibrations significantly, the energy transfer is even accelerated by a nonlinear scattering mechanism with optical and higher acoustic phonon modes [37].
In general, the initial electron-phonon collisions will not produce a thermal distribution $N_0$ of phonons. Phonon-phonon scattering thermalizes gradually the excitation of particular modes. The energy released from hot carriers to the lattice, described thermodynamically by the source term in equation (2), can be connected to the phonon statistics by [38]:

$$\frac{d\overline{\omega}}{dt} = -\frac{3Nk(T_C - T_L)}{\tau_e} \sum \sum \omega_j \frac{dN_j(t)}{dt}$$  \hspace{1cm} (6)$$

where $N_j(q,r,t)$ is the distribution of the emitted phonons and $j(\beta,q)$ the mode index. As soon as the thermal distribution of phonons is achieved the concept of temperature can be introduced again. Time resolved measurements of the lattice temperature allow direct information about the details of phonon relaxation mechanisms at excitation levels used in PLA. The details of the cooling kinetics of nonequilibrium carrier-phonon systems are unelucidated in the case of extreme photoexcitation. The time-dependent phonon Boltzmann equation for the distribution function $N(q,r,t)$ of each mode has to be solved. Thermal relaxation of the nonequilibrium phonon system towards the final bulk temperature $T_L$ occurs via anharmonic coupling effects at a slower pace. Relaxation times between 1 and 100 ps have to be considered, depending on the phonon decay process and the location in the Brillouin zone. The anharmonicity increases with $T_L$, as the temperature dependence of the thermal conductivity of silicon indicates. Wavevector selection rules may be lifted in the presence of a dense electron-hole plasma.

The single steps in the energy transfer route are further complicated by interrelations between generation rate and lattice temperature, $N(T_e)$ dependence of electron-phonon coupling and phonon-phonon interactions. The last has been demonstrated by Raman linewidth measurements on heavily-doped elemental semiconductors.

A major open question remains: whether the solid-liquid phase transition requires an established thermal equilibrium between the modes, or if not, which particular phonon modes have to be excited to initiate melting. To clarify this point, which is of general importance for the lattice dynamic theory of melting, the Lindemann criterion may be applied. Melting occurs when the mean square root amplitude of the lattice vibration becomes equal to some critical fraction $c_m$ of the mean radius $r_C$ of the unit cell [38,39]. The displacement of an atom is due to the superposition of all normal modes $q_j$:

$$\langle u^2 \rangle = \frac{1}{nq} \sum_j \langle q_j \rangle^2$$  \hspace{1cm} (7)$$

Under equilibrium conditions the Lindemann theory predicts a melting temperature $T_m$ with:

$$T_m = \left( \frac{c_m}{9n^2} \right) \cdot \frac{MkT^2}{\theta_D^2} \cdot r_C^2$$  \hspace{1cm} (8)$$

where $\theta_D$ is the Debye temperature and $c_m \sim 0.2$ for Si. Melting by nonequilibrium phonons can be explained if the Lindemann criterion is applied to the superposition of a few energetic phonon modes only. The vibronic energy necessary to break the bonds is delivered by a limited number of phonons far away from equilibrium. Contrary to the 'vibronic' origin of the phase transition, the supporters of the plasma hypothesis assume that the optical energy remains stored in the plasma and the transfer to the lattice is blocked for unknown reasons. The phase transition to a liquid is caused by a softening of the TA phonons if the number of electron-hole pairs $N$ exceeds a critical value [20]:

$$\omega_{TA} = \frac{\omega_{TA}^0 \left( 1 - \frac{f_{e_h}N}{4N_T} \right)}{1 - \frac{4N_T f_{e_h} N}{4N_T}}$$  \hspace{1cm} (9)$$
where \( f \) is the bond charge reduction factor equal to 0.85 in Si and \( \varepsilon_m \) the high frequency dielectric constant, \( N_a \) the number of atoms/cm\(^3\). At low lattice temperature the material is predicted to undergo a phase transition to a 'plasma-like' liquid. Principally, the often-cited controversy between the thermal or vibronic model and the plasma hypothesis is reduced to a discussion of whether the lattice becomes hot or remains cool during the phase transition.

The hierarchy of relaxation times depicted in Fig. 1 specifies the design of time-resolved experiments, where the temporal evolution of plasma density, lattice heating and the phase transition encountered in PLA are investigated.

3 - EXPERIMENTAL APPROACH

Prima facie evidence for a structural phase transition is provided by the post-annealing morphology [21]. The formation of amorphous and recrystallized layers depends strictly on the absorbed laser energy and is in all cases accompanied by reflectivity changes to the liquid state value of silicon. Thus the appearance of high reflectivity signatures represents a more general criterion, also applicable in ns experiments where the formation of amorphous structures is not observed. In the following sections the investigations are restricted to single crystals of silicon.

In Table I the laser fluences of nano-, pico- and femtosecond pulses are summarized which are required to induce a high reflectivity phase. At 1064 nm pump wavelength the lattice absorption \( \alpha_L \) is low \((10 \text{ cm}^{-1})\), and nonlinear heating is caused mainly by free carrier absorption. With decreasing wavelength the lattice absorption increases rapidly while free carrier absorption decreases. At 532 nm single-photon absorption dominates in ns and ps experiments. For femtosecond pulses at 620 nm significant two-photon absorption contributions are expected. By comparing the absorbed threshold fluence levels \( \phi_{th} \), it becomes obvious that the laser intensity can be varied within several orders of magnitude without affecting the mechanism for phase transition. A two-order-of-magnitude increase of the plasma density and the transition to nonequilibrium conditions barely affects the energy balance of PLA. This strict energy dependence and the time at which the phase transition occurs provide essentially the boundary conditions for the solution of the energy transfer problem outlined in Fig. 1.

The large differences of the refractive index \( n=n+ik \) between solid and liquid silicon are favorable for studying this phase transition with optical probing techniques. In addition, plasma modification and lattice heating can be detected optically. In a first approximation the optical properties of an electron-hole plasma embedded in a solid state lattice may be described by the well-known Drude formula [40]:

\[
\begin{align*}
\frac{n^2 - k^2}{n_L^2 - k_L^2} &= 1 - \frac{4\pi Ne_{th}^2}{\omega^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \\
2nk &= 2n_Lk_L + \frac{4\pi Ne_{th}^2}{\omega^3} \left( \frac{1}{m_e^*} \frac{1}{\omega^2} + \frac{1}{m_h^*} \frac{1}{\omega^2} \right)
\end{align*}
\]

(10)

where \( \omega \) is the frequency of the probing light and \( n_L + ik_L \) is the intrinsic part of the refractive index, depending on the phonon temperature, \( N \) the plasma density, \( m_{e,h}^* \) the electron or hole optical effective mass and \( \tau_{e,h} \) the corresponding scattering times. The angled brackets imply the average over the Boltzmann distribution of hot carriers, required by the energy dependence of the scattering times \( \tau_{e,h}(E_c) \).

Changes of the refractive index are displayed in modifications of the reflectivity and transmission through the classical Fresnel formula or the appropriate thin film optics expressions [41]. The most significant change of the optical properties occurs during the transition from the solid to liquid phase of silicon. The
reflectivity of bulk samples increases roughly by a factor of two, and the transmission drops to zero for a broad range of probing wavelengths, corresponding to the metallic character of liquid silicon [42, 43]. The solid state reflectivity drops when the probing light frequency $\omega$ approaches the plasma resonance $\omega_p$ from the $\omega > \omega_p$ region. The reflectivity minimum is reached if:

$$N_{\min}^{\ast} = \frac{(n_L^2 - k_L^2 + k - 1)\omega^2}{4\pi e^2}.$$  

The absolute measured value of the minimum is determined by the plasmon damping mechanism, the temperature dependence of $n_L$ and $k_L$ and the convolution of pump and probe pulse. Using picosecond excite and probe techniques, changes of the reflectivity and transmission can be measured with a high spatial and temporal resolution.

In infrared reflectivity measurements of highly doped silicon, effective mass changes have been found above a carrier concentration of $5 \times 10^{20}$ cm$^{-3}$ [44]. It has been argued that at this concentration the Fermi level enters a new conduction band valley with heavier effective mass $m^*_0$. Similar phenomena are expected for the effective hole mass $m^*_1$. The concentration dependence of the optical reduced masses prevent a direct evaluation of the plasma density $N(t)$. Rapid changes of the carrier density and carrier statistics will stimulate reflectivity transients via changes in the optical reduced masses. Only the ratio $N(t)/(m^*_0 + m^*_1)$ and the average scattering times $<T_{e, h}>$ can be determined by simultaneous measurements of reflectivity and transmission.

At increasing probing frequencies $\omega$ the plasma sensitivity of the optical constants decreases generally with $\omega^2$, while the temperature dependence of the intrinsic refractive index remains approximately constant. The temperature dependence of the absorption coefficient $k_L$ in the visible spectral range is determined by the temperature dependence of the band gap $E_g$ and the occupation statistics for phonons participating in the indirect transition process [45, 46].

$$k_L = k_0 \exp(T/\Theta),$$

where $k_0 = 2.1 \times 10^{-2}$ and $\Theta = 430 \text{ K}$

$$n_L = n_0 + 6 \times 10^{-4} T(K),$$

where $n_0 = 3.93$ at 532 nm [45]. These data can be used to determine the temperature below the phase transitions. Frequency doubled pulses of a Nd:YAG laser monitor sensitively the temperature of silicon on sapphire samples, if the thickness of silicon matches the wavelength.

The use of thin silicon films on sapphire (SOS) offers several advantages. The sensitivity of reflectivity and transmission towards changes in the optical refractive index are considerably enhanced by multiple reflections between the air/silicon interface and the silicon/sapphire interface. The transmission can be measured for photon energies far above the band gap, allowing access to information about phonon occupations governing the indirect transition in Si. Finally, if the Si film thickness is less than the penetration depth of the excitation pulse $\alpha^{-1}$, the spatial dependences of plasma density and lattice temperature do not severely limit the analysis.

The ps-probing of transmission and reflectivity changes at the fundamental and doubled frequency of a mode-locked Nd:YAG laser allows the in situ investigation of the central question of PLA, the energy transfer between electron-hole plasma and lattice and the nature of the phase transition. Details of the experimental technique can be found in Ref. 23.

The close correlation between the fluence level of picosecond pulses where the formation of amorphous surface layers is observed $F_{\text{th}}^\text{th}$ with the energy necessary to switch the crystal into the high reflectivity state led R. Yen et al. to the
conclusion that a liquid metallic layer is formed temporarily on the surface of silicon. Time-resolved probing with a He-Ne laser beam revealed resolidification kinetics similar to those observed in the ns melting regime [22]. The melt duration, regrowth speeds for amorphization and recrystallization can be entirely explained by a thermal model. The largest temperature gradients are generated between 0.2 and 0.26 J/cm², driving the liquid-solid interface back to the surface with more than 15 m/s. As Turnbull and Spaepen have pointed out, supercooling of the melt may be the reason for the formation of disordered structures at these resolidification speeds [10].

The thickness of the amorphous layer has been estimated by cross-section TEM and optical analysis with several 100 Å. This phase transition occurs within an extremely shallow region indicating that diffusion of hot carriers spreading the energy deeply into bulk cannot play a significant role.

In addition, the critical fluence \( F_{ch} \) coincides with the threshold for the emission of charged particles, as reported by J.M. Liu et al., signaling the onset of surface vaporization [21]. Consequently, it has to be assumed that the lattice is heated up above the melting point during the 25 ps excitation pulse. Heating phenomena during the ps excitation pulse have been postulated by the same group to interpret the significant drop in the transmission of the heating beam passing through thin silicon films on sapphire [26].

3.1 - Phase Transition and Plasma-Kinetics

Self-transmission data are averages of the spot area and the temporal profile of the excitation pulse. More precise information is provided by pump and probe experiments, where the optical properties are monitored with delayed and highly focused probe pulses at different wavelengths. The sensitivity for plasma detection increases quadratically with the wavelength of the probing beam. Plasma formation and phase transitions to the metallic liquid state of silicon are measured favorably at 1064 nm. With a highly focused probe beam the reflectivity change in the center of the frequency-doubled pump beam is monitored with a temporal resolution of 30 ps [25]. The data in Fig. 2 are plotted versus the energy fluence of the pump beam. At zero delay the probe pulse of 30 ps overlaps the pump pulse of 20 ps entirely. The convoluted reflectivity represents an average of the changes occurring during the pump pulse. At low fluence levels the reflectivity drops slightly below the intrinsic solid state value. At 0.2 J/cm² a positive increase is reported which continues to a maximum of 76 percent at 0.4 J/cm². It is clear that during the picosecond excitation the reflectivity increases rapidly to liquid state values. At 0.2 J/cm² the major part of the interrogating probe pulse experiences only negative plasma contributions, which are compensated by high reflectivity values at the very end of the pulse. With increasing laser energy, the reflectivity jump moves towards the temporal center of the probing beam, enhancing the average reflectivity. Above 0.5 J/cm² the reflectivity drops again, presumably due to further heating of the highly absorbing liquid and the formation of a highly dense vapor cloud. The suppressed reflectivity recovers to the original high reflectivity value after several hundred picoseconds, as the overheated liquid cools off again.

At 100 ps delay the probe pulse is temporally completely separated from the pump pulse and an abrupt rise in the reflectivity at \( F_{ch} = 0.2 \) J/cm² is observed. The reflectivity rises to 76 percent ± 3 percent, characteristic for molten silicon at this probe wavelength. Thermal model calculations, using equations (1-5), predict lattice heating up to the melting point at an incident fluence of 0.2 J/cm², if the relaxation time \( T_e \) in equation (5) is kept below 10 ps [29]. For \( T_e >> 10 \) ps, melting would occur after the picosecond probe and at significantly higher fluence levels. Conclusive support for ultrafast melting during the ps excitation is provided by the temporal behavior of reflectivity and transmission, of SOS-samples, as shown in Fig. 3.

The reflectivity and transmission signatures are anticorrelated, as dictated by the laws of thin film optics. At 0.1 J/cm² the reflectivity drops from 0.55 to 25 percent at a time delay \( A_t = 0 \) and recovers with the same time constant as observed in
BULK SILICON WAFER SOS SAMPLE, \(d = 0.5 \mu m\) 

0.8 0.8 0.2 \(psec\) 13/cm

Fig. 2. Reflectivity changes at the surface of bulk silicon.

Fig. 3. Time-resolved reflectivity and transmission changes of a silicon on sapphire (SOS) sample.

the bulk. At zero time delay changes in the refractive index, time-averaged over the probing pulse at 1064 nm, yields a normalized plasma density of

\[
\left\langle \frac{N}{m_e + m_h} \right\rangle = 3.4 \times 10^{48} \text{ cm}^{-3} \text{ g}^{-1}
\]

and an average scattering time \(\langle \tau \rangle = 7 \times 10^{-15} \text{ sec}\).

Above the phase transition threshold \(F^\text{th}\) at 0.3 \(J/cm^2\), both transmission and reflectivity drop simultaneously, indicating drastic increases in the optical absorption. Therefore, at time delay \(\Delta t = 0\), the multiple reflections are nearly suppressed. The reflectivity rise and coincident transmission drop can barely be temporally resolved by the picosecond probe pulses. The melt front of the metallic layer moves with a speed of more than 1000 m/s into the bulk. Recent time-resolved reflectivity measurements on silicon pumped with femtosecond pulses confirm these data. The time required to form a liquid layer on the surface of silicon has been measured to be a few picoseconds [27]. After the ultrafast phase transition the optical constants remain unchanged for several tens of nanosecond. The postillumination behavior is determined by strictly thermodynamic processes; like cooling and resolidification.

3.2 - Lattice Temperature

The conclusive answer to the question of whether this phase transition is caused by thermal or plasma effects is given by direct time-resolved measurement of the temperature. By changing the probing wavelength to 532 nm, Lompré et al. have been able to measure directly the lattice heating via thermally induced variation of the multiple reflections in SOS samples [25]. As shown in Fig. 4 the time resolved reflectivity signature is still affected by plasma contributions despite the doubling of the frequency and the lowering of the pump fluence to 0.05 \(J/cm^2\). Compared to the lattice absorption the free carrier absorption is negligible at 532 nm. Any change in the transmission is solely due to heating of the lattice. The transmission decrease in Fig. 4 is terminated immediately after the excitation pulse. Thus heating of the lattice is completed, while a considerable fraction of plasma is still
present as displayed by the reflectivity transients after the pulse. However, at this time the plasma is in equilibrium with the lattice. At a time delay of $\Delta t = 200$ ps, plasma induced effects are far below the detection limit, as Fig. 5 shows. Between 200 ps and 1 ns only incipient changes of the induced variations of $n$ and $k$ are observable. The heating process is certainly terminated after 200 ps and thermal equilibrium between phonons can be assumed. Thus the thermal diffusion equation (2) can be applied to calculate the temperature at $\Delta t = 200$ ps. With increasing fluences the transmission drops continuously, displaying termally-enhanced absorption. The reflectivity reaches a plateau value of 40 percent before it rises to the final value of liquid silicon. At the reflectivity plateau the multiple reflections become suppressed and the reflectivity of a hot bulk material is observed. The further increase of reflectivity and drop of transmission signals the formation of a thin layer with optical constants drastically different from hot solid silicon. The rise to the high reflectivity value of 72 percent is caused by the formation of a new interface between hot and liquid silicon, giving rise to multiple reflections within an extremely shallow liquid layer. As soon as the high reflectivity value is observed at 0.2 J/cm$^2$, the thickness of the liquid layer has been increased to several 100 Å. The transmission drops to the detection limit of 1 percent, consistent with the formation of an optically thick metallic layer of silicon within $\Delta t = 200$ ps.

With the measured optical densities $\tilde{n} = \frac{1}{d} \int_0^X n(x) dx$ and $\tilde{k} = \frac{1}{d} \int_0^X k(x) dx$ evaluated from thin film optics expressions and the data of Jellison and Modine, the average temperature $\bar{T} = \frac{1}{d} \int_0^X T(x) dx$ has been calculated. As shown in Fig. 6, the average temperatures increase nonlinearly with the fluence of the pump beam. The slope depends strongly on the film thickness, indicating the development of large temperature gradients. Most of the thermal energy is stored in a layer of 0.1 μm after 200 ps. The heating process is not affected by free carrier and two-photon absorption at 532 nm. The nonlinear heating characteristic has to be attributed to absorption enhancement during the heating process. Within the duration of the 25 ps laser pulse, thermally-induced band-gap shrinking occurs, as predicted by the calculations of Lietoila and Gibbons [29]. Local thermal equilibrium between plasma and lattice, or at least phonons which participate in the indirect absorption process, is established during excitation with the picosecond pump pulse.
The large temperature gradients measured after 200 ps below 0.2 J/cm² and the extremely shallow layer of amorphous material generated at the surface slightly above 0.2 J/cm² leads to the assumption that the energy spreading by hot carrier diffusion must be certainly less than some cm. Diffusion of hot carriers is not important in picosecond experiments. Before hot carriers can diffuse, they lose their energy to the phonons. With this conclusion the transport processes listed in equation (4) may become negligible in the consideration of the energy transfer problem. However, they do play a role after the plasma has been cooled off to an equilibrium with the lattice.

The density dependence of the reduced optical masses \( m_{e-h}^* \), noted in equation (12), do not allow an unambiguous calculation of \( N \) through equation (10). The reduced electron-hole pair mass \( m_{e-h}^* \) measured for densities below \( 10^{19} \) cm\(^{-3} \) differs from the electron mass \( m_0 \) by a factor of 7 (~0.14 \( m_0 \)), leaving a wide range of speculation about \( N \). As a consequence the nature of the plasma density relaxation cannot be explained conclusively. Both Auger recombination and diffusion of the carriers after energy transfer to the lattice may be the responsible processes. In addition, changes in the reduced optical mass during cooling of the plasma may add further complexities.

The time-resolved optical experiments are crucial for the discussion of the validity of nonthermal models proposed in the past. Clearly the original plasma model proposed by J.A. Van Vechten [47], assuming the formation of a long-lived, highly dense plasma embedded in a cold lattice, has no experimental backing. Later modifications and adaptations to the experimental experience, such as plasma condensation and plasma confinement, do not predict any measurable quantity which has been confirmed experimentally [48]. The only remaining point of interest is the hypothesis of Martin that the excitation of electrons from the bonding state of the valence band to the antibonding state of the conduction band will soften the transverse acoustic lattice modes [49]. A 'plasma-like liquid' is formed within a rather cold lattice. Several groups have investigated the possibility for electronically-induced phase transitions based on a lowering of the TA-phonon frequency formulated in equation (9).

Wautelet and Laude studied the effect of laser irradiation on the cohesion of Si and suggested that the melting temperature \( T_m \) and the Debye temperature \( \theta_D = \frac{\hbar \nu_{TA}}{k} \) are
principally reduced in the case of Si being irradiated by a 20 MW/cm² laser pulse at 2 eV photon energy [50]. Taking the same point of view, Bok computed the variation of melting temperature $T_m$ with the density $N$ of electron-hole pairs created using the Lindemann criterion for melting [38,39,52]. He finds: $T_m(N) = T_m(0)(1-aN)^{2}$ with $a^{-1} = 8 \times 10^{21}$ cm$^{-3}$. For $N = a^{-1} = 8 \times 10^{21}$ cm$^{-3}$, the transverse acoustic mode goes to zero and the phase transition becomes of the second order.

In a modified proposal Combescot and Bok derive an instability temperature $T^*$ below the melting point, which depends essentially on two parameters: the electron-hole masses and the electron-phonon coupling [53]. The temperature dependence of these parameters is not included. The instability temperature $T^*$ decreases when the generation rate $G$ increases. For $G \sim 10^{33}$ cm$^{-3}$s$^{-1}$ a sizeable but not quantified decrease of $T^*$ is stated. In any case, the optical response should be changed considerably if the instability temperature is reached at a certain fluence level. However, the optical measurements do not reveal any intermediate values of the optical constants between solid and liquid silicon below the threshold fluence for melting, where the generation rate becomes more than $3 \times 10^{34}$ cm$^{-3}$sec$^{-1}$. This proposal is inconsistent with the experimental results obtained in picosecond and femtosecond experiments [21-27].

Furthermore, plasma-induced lowering of the melting point would lead to a reduction of the critical laser fluence $F_{th}^0$ required for the phase transition. The combined influence of plasma and vibronic excitation should be manifested in significant differences of $F_{th}^0$, depending on the laser intensity. There is no experimental evidence for modifications of $F_{th}^0$, as comparison of the data in Table I shows. Neglecting diffusion in equation (3), the maximum obtainable plasma densities $N_\text{p} = (G/\gamma)^{1/3}$ are changed by two orders of magnitude between femto- and nanosecond irradiations.

<p>| TABLE I. LASER CHARACTERISTICS FOR PHASE-TRANSITIONS OF c-Si |
|---------------------------------|-----------------|----------|----------|----------|----------|</p>
<table>
<thead>
<tr>
<th>LASER</th>
<th>WAVELENGTH (nm)</th>
<th>$t_p$ (s)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$F_{th}$ (J/cm$^2$)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Q-SWITCHED SYSTEM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RUBY</td>
<td>694</td>
<td>$1.5 \times 10^{-8}$</td>
<td>$3 \times 10^3$</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>1064</td>
<td>$4 \times 10^{-8}$</td>
<td>$10 + \alpha_{PCA}$</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>$3 \times 10^{-8}$</td>
<td>$1 \times 10^4$</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>$1.5 \times 10^{-8}$</td>
<td>$2 \times 10^6$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>II MODE-LOCKED SYSTEMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>1064</td>
<td>$3 \times 10^{-11}$</td>
<td>$10 + \alpha_{PCA}$</td>
<td>3</td>
<td>[21]</td>
</tr>
<tr>
<td>+SHG</td>
<td>532</td>
<td>$2 \times 10^{-11}$</td>
<td>$1 \times 10^6$</td>
<td>0.2</td>
<td>[21]</td>
</tr>
<tr>
<td>+QHG</td>
<td>266</td>
<td>$1 \times 10^{-11}$</td>
<td>$2 \times 10^6$</td>
<td>0.08</td>
<td>[21]</td>
</tr>
<tr>
<td>III PCM-DYE SYSTEMS</td>
<td>620</td>
<td>$9 \times 10^{-14}$</td>
<td>$3.3 \times 10^3$</td>
<td>0.1</td>
<td>[27]</td>
</tr>
</tbody>
</table>

In a more elaborate study Biswas and Ambegaokar calculated the conditions for electronically induced phonon instabilities [34]. Conditions for plasma induced lattice destabilizations prior to thermal melting may be achieved during irradiation with femtosecond pulses [27]. Time-resolved measurement of the reflectivity, however, demonstrates clearly that phase transition occurs several picoseconds after the pump pulse. During the 90 femtosecond pulse and prior to melting, only transient plasma-induced modifications of the optical constant are found [27]. The search for plasma-induced phase transitions belongs certainly to one of the most fascinating investigations in the PLA field. Without any confusion brought into the field by the original plasma hypothesis, the limits of the validity of the thermal model and the ultimate time scales of the energy exchange between the electron-hole plasma and phonons should be investigated seriously in experiments on a subpicosecond time scale.

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