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TIME-RESOLVED SPECTROSCOPY OF PLASMA RESONANCES IN HIGHLY EXCITED SILICON AND GERMANIUM

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ABSTRACT

The dynamics of the electron-hole plasma in silicon and germanium samples irradiated by 20 ps, 532 nm laser pulses has been investigated in the near infrared by time-resolved picosecond optical spectroscopy. The experimental reflectivities and transmissions are compared with the predictions of the thermal model for degenerate carrier distributions through the Drude formalism. Above a certain fluence, a significant deviation between measured and calculated values indicates a strong increase of the recombination rate as soon as the plasma resonances become comparable with the band gaps. These new plasmon-aided recombination channels are particularly pronounced in germanium.

1. INTRODUCTION

The interaction of picosecond laser pulses with semiconductor surfaces has been extensively studied in recent times in view of assessing the temporal evolution of the carrier density and lattice heating prior to the melting of the semiconducting surface¹. For these investigations, time-resolved spectroscopic techniques are a unique tool for the determination of the ratio N/m^* of the carrier concentration to the optical reduced mass. By a proper selection of the probing wavelength, the complex index of refraction is more sensitive to the lattice temperature² or to the carrier density³. The optimum conditions to probe the latter occur near the plasma resonance where the real part of the dielectric constant approaches the zero value. A sharp rise of the reflectivity of the material occurs, which determines the carrier density.

The interpretation of the optical reflectivity and transmission measurements is usually carried on the basis of the Drude formalism which allows a direct determination of the ratio N/m^* . This model has been successfully used in the past for the simulation of the optical response of laser irradiated semiconductors. Its validity in systems driven far out of the equilibrium has been more successful than anticipated. The main parameters which are critical in the interpretation of the experimental data are the optical reduced mass, the momentum relaxation time and their functional dependence on the carrier density and temperature. Experiments in the past have shown little or no dependence of the optical reduced mass on temperature in silicon⁴. Also, different experiments^{5,6} have suggested extremely small momentum relaxation times during picosecond irradiation. The damping of the optical response, as described by the Drude model, occurs via carrier-phonon or carrier-carrier scattering. The short momentum relaxation times, however, point toward a predominance of intervalley scattering mechanisms.

The onset of a plasma resonance can be easily observed⁷ by monitoring the reflectivity at a fixed delay after the excitation pulse as a function of the laser fluence (see e.g. fig. 4 in ref. 1). As soon as the surface carrier density exceeds the critical value $N = N_c(1 - 1/\epsilon'_{\infty})$ with $N_c \approx m^*\omega \epsilon'_{\infty}/(4\pi e^2)$ the reflectivity rises sharply. The extent of its variation depends on the plasmon damping mechanism. For higher plasma densities the reflectivity remains at the

same high level. Information on the further growth of the ratio N/m^* is therefore not accessible. Using this technique with $2.8 \mu\text{m}$ probing it has been found⁸ that the plasma density exceeds $N_C/m^* \approx 4 \cdot 10^{18} \text{ cm}^{-3} \text{ g}^{-1}$ in silicon and $\approx 3 \cdot 10^{18} \text{ cm}^{-3} \text{ g}^{-1}$ in germanium. These experimental values, however, refer to excitation fluences much below the critical value for surface melting. The plasma can in principle reach higher densities which can be monitored by using shorter probing wavelengths. At $1.9 \mu\text{m}$, for example, the plasma resonance is reached at $N/m^* = 4.3 \cdot 10^{18}$ and $4.8 \cdot 10^{18} \text{ cm}^{-3} \text{ g}^{-1}$ for silicon and germanium, respectively.

This paper reports on experimental investigations specifically aimed to the study of the extreme excitation conditions that are reached in silicon and germanium just prior to the onset of the melting of the surface of the sample. A further motivation for investigations in this high excitation regime is the recent proposal of new plasmon-aided recombination channels in silicon⁹ when the plasmon frequency becomes comparable with the energy gap. The case of germanium, with a relatively low band gap, is particularly favourable for such investigations, although different routes for plasmon-aided recombinations become possible in this case^{9,10}. A careful comparison of numerical simulations with the time-resolved reflectivity and transmission data, taken at $1.06 \mu\text{m}$, $1.55 \mu\text{m}$ and $1.9 \mu\text{m}$ under $532 \mu\text{m}$, 20 ps laser irradiation, has been carried out.

For both elemental semiconductors the excitation at 532 nm ensures a linear generation rate of electron-hole pairs as long as picosecond laser pulses are used. In the case of germanium this high photon energy specifically avoids possible competing excitation processes such as intravalence band transitions between light and heavy holes. Also, the eventual filling of the central valley, where the primary excitation occurs, does not reduce the absorption coefficient at the highest excitation levels. These nonlinearities are detrimental for an exact analysis of the carrier dynamics when the excitation energy becomes comparable with the band-gap energy.

2. MODELING OF THE PLASMA DENSITY AND TEMPERATURE

The interaction of picosecond laser pulses with semiconductors can be modeled within the framework of the thermal model^{11,12}. It is assumed that the photogenerated carriers and the lattice reach a common temperature T in times much shorter than the laser pulse duration. Ample experimental evidence that this is the case in the picosecond excitation regime has been provided by many independent tests on various semiconductors. The temporal evolution of the carrier density $N(x,t)$ across the depth x of the material is described in a one-dimensional approach by a diffusion equation where the laser driven source term is balanced by ambipolar diffusion and Auger recombination. This equation is coupled to a similar one for the evolution of the temperature profile $T(x,t)$ in terms of a thermal diffusion and a source terms $S(x,t)$. The latter has two contributions¹³:

$$S(x,t) = G(x,t)(h\nu - E_g(T) - HkT) + \alpha N^3(x,t)(E_g(T) + HkT) \quad (1)$$

where $h\nu$ is the exciting photon energy and k the Boltzmann constant. The first term describes the rate of direct heating provided to the phonons by the light absorption process. This quantity depends on the excess energy available to the carriers. The second term represents the heating rate of the lattice due to the Auger recombination process. The energy transferred to the lattice per single event is the sum of the band gap energy $E_g(T)$ and the thermal content of the carriers, which is described through the degeneracy parameter H . The latter is evaluated through the charge neutrality condition

$$N(x,t) = 2 \left[\frac{2\pi m_e kT}{h^2} \right]^{1/2} F_{1/2}(\eta_e) = 2 \left[\frac{2\pi m_h kT}{h^2} \right]^{1/2} F_{1/2}(\eta_h) \quad (2)$$

h being the Plank constant, $m_{e,h}$ the density-of-states reduced masses and $F_{1/2}(\eta)$ the Fermi integrals of order 1/2 which depend on the reduced quasi-Fermi levels for electrons and holes, respectively, $\eta_{e,h} = E_{e,h}^F/kT$. The degeneracy parameter H is then evaluated through

$$H = F_{3/2}(\eta_e)/F_{1/2}(\eta_e) + F_{3/2}(\eta_h)/F_{1/2}(\eta_h) \quad (3)$$

The presence of the parameter H in eq. (3) accounts for the energy transfer modifications due to the smaller number of states available for scattering in degenerate systems. The effect is to increase the amount of Auger heating at expenses of the direct heating. It has been recently recognized¹³ that the former contribution can substantially delay the heating of the lattice, the rate becoming comparable to the Auger time constant $(\alpha N^2)^{-1}$. At the expected high carrier densities, however, Coulomb screening should provide a saturation to the Auger rate constant¹⁴. It has also been predicted that, when the plasmon energy becomes comparable to the band gap energy, strong carrier recombination can occur by plasmon emission^{9,10}. These two effects, which are not included in the present calculation, give opposite contributions to the carrier density. Thus it is in principle possible to discriminate among them with suitable experiments.

Numerical calculations based on the above description have been performed for silicon and germanium excited by 20 ps, 532 nm radiation. The material parameters¹⁵ used in the two cases are summarized in table 1. Silicon has a higher melting temperature and has a thermal diffusivity almost four times bigger than germanium. The two materials also differ greatly in the absorption coefficient α . In silicon it increases with temperature by almost two order of magnitude at the melting point, reaching however a value only a fraction of the one of germanium. These different properties are mirrored in the resulting critical fluences for surface melting F_{th} , which agree well with the experimental results.

Figure 1 illustrates the temporal evolution of the calculated carrier density for silicon and germanium at half the critical fluence value F_{th} . The buildup of the carriers is driven by the laser pulse and the maximum density value is reached within few picoseconds of the maximum irradiation. The density decay is mainly determined by the Auger recombination in silicon. The higher ambipolar diffusivity in germanium also contributes to the process. The reduction in carrier density slows down the Auger recombination process and the smoothing of the spatial gradients decreases the carrier transport to the interior of the sample. Therefore at times longer than ≈ 70 ps the surface density exhibits a much slower decay. The excess energy available to the lattice per absorbed photon is much higher in germanium than in silicon, due to the differences in band-gap energies. Moreover, the energy required to melt the silicon surface is higher than the corresponding quantity in germanium. Therefore, the comparison at $F = F_{th}/2$ of the maximum calculated carrier densities shows that a higher value is reached for silicon.

The calculated behavior of the temperature at the surface, illustrated for the same excitation pulses in Fig. 2, shows a more pronounced material dependence. In the case of silicon, which exhibits a longer absorption depth, relatively low thermal gradients are generated which fully compensate for the higher thermal diffusivity. This results in an almost constant temperature profile after the laser irradiation. Germanium, instead, has an extremely short absorption depth. Correspondingly steeper thermal gradients are present which override the poor thermal diffusivity of the material. Therefore the surface

TABLE I

Material parameters for silicon and germanium used in the numerical calculations

		Silicon	Germanium
<u>a) Thermodynamical parameters:</u>			
melting temperature, $T_m(^{\circ}\text{K})$		1680	1214
latent heat of fusion $L_H (\text{J}/\text{cm}^3)$		4000	2644
density $\rho (\text{g}/\text{cm}^3)$			
	300 $^{\circ}\text{K}$	2.33	5.32
	T_m	2.37	5.2
specific heat $c_p (\text{J}/\text{g } ^{\circ}\text{K})$			
	300 $^{\circ}\text{K}$	.71	.32
	T_m	1.044	.377
thermal diffusivity (cm^2/s)			
	300 $^{\circ}\text{K}$	1.35	.35
	T_m	.196	.075
<u>b) electronic properties:</u>			
ambipolar diffusivity D_a	300 $^{\circ}\text{K}$	20	65
	(cm^2/s)		
	T_m	3.5	7.98
Auger coefficient $\chi (\text{cm}^6/\text{s})$		$2 - 4 \cdot 10^{-31}$	$2 \cdot 10^{-31}$
density of states mass (m_0)			
	e^-	.32 x 6	.22 x 4 (L)
			.32 x 6 (X)
	h	.59	.35
<u>c) optical properties at .53 μm:</u>			
absorption coefficient		$\alpha = \alpha_0 \exp(-T/\Theta) (\text{cm}^{-1})$	
	300 $^{\circ}\text{K}$	$4.5 \cdot 10^3$	$5 \cdot 10^5$
	T_m	$2.2 \cdot 10^5$	$7 \cdot 10^5$
reflectivity R			
	300 $^{\circ}\text{K}$	.37	.5
	T_m	.43	.5
critical fluence for melting $F^{\text{th}} (\text{mJ}/\text{cm}^2)$		200	35

temperature decays more rapidly with time. In both materials the maximum surface temperature is reached after the corresponding maximum surface carrier density. This delayed heating is a direct consequence of the plasma degeneracy, as explained earlier.

In figures 3 and 4 the calculated carrier surface density and temperature are plotted as a function of the laser fluence, normalized to the critical value for surface melting F^{th} , for three different time delays. These plots allow direct comparison with the experimental data, which are obtained at fixed delay times. Moreover, information of the interplay of the effects considered in the calculations can be obtained. At 0 ps delay time, i.e. at the maximum of the laser pulse, the buildup of the carriers in germanium is almost linear with laser fluence since the absorption coefficient α has a weak temperature dependence. This is further confirmed by the linear slope of the surface temperature in fig. 4. At the same time delay, the bending of the carrier density in silicon shows that the Auger recombination ($\chi = 4 \times 10^{-31} \text{ cm}^6/\text{s}$) is the main limiting mechanism. At 20 ps the surface carrier density in

Fig. 1. calculated carrier density versus time for silicon and germanium under ps green illumination at the fluence levels indicated. The zero of the time scale is the maximum of the pulse.

Fig. 2. calculated temperature versus time for silicon and germanium. The same parameters as in Fig 1 are used.

Fig. 3. Carrier density for silicon and germanium versus normalized laser fluence at the delay times shown.

Fig. 4. Normalized temperature for silicon and germanium versus normalized fluences at the times shown.

germanium is reduced by diffusion of the plasma into the bulk. In silicon, the Auger recombination dominates at low fluences. At $F/F_{th} > 0.5$ the generation rate of electron-hole pairs starts to become nonlinear due to thermal band-gap shrinkage during the picosecond excitation pulse. The simultaneous increase of the indirect absorption gives rise to a further increase of the plasma density at higher fluences. At long time delays between the pump and the probe pulses, the carrier density is reduced by the combined effects of ambipolar diffusion and Auger recombination to an asymptotic value which is independent from the laser fluence.

To illustrate the differences in thermal response between silicon and germanium, the temperature axis in fig. 4 is normalized to the difference between melting (T_m) and room temperature. The positive second derivative of the silicon curves indicates the nonlinear heating of the surface due to the strong temperature dependence of the absorption. The relatively low thermal gradients in silicon prevent a fast cooling of the surface at high irradiation levels. Little difference between the curves for 20 and 200 ps is therefore observed. In germanium a more linear dependence of the temperature versus laser fluence is calculated at all times. The weak temperature dependence of

the light absorption is the primary cause for this behavior. The melting temperature is reached earlier in germanium than in silicon. The ratio F^*/F_{th} of the fluence necessary for reaching the melting temperature to the fluence for melting the surface can be estimated, in absence of thermal diffusion effects, as

$$F^*/F_{th} \approx \{1 + L_H \alpha^* / [\rho C_p \alpha(T_m) \Delta T]\}^{-1} \quad (4)$$

with $\Delta T = T_m - 300^\circ K$ and α^* a suitable average value for the absorption coefficient between the extreme temperatures. This expression gives $F^*/F_{th} = 0.87$ for silicon and 0.45 for germanium, in fair agreement with the numerical results.

The calculated values of carrier density and temperature are used to predict the reflectivity and transmission changes induced by a 532 nm picosecond pulse striking the semiconductor surface, which are determined by the optical dielectric functions ϵ' and ϵ'' :

$$n^2 - k^2 = \epsilon' = \epsilon'_\infty - 4\pi N e^2 \left[\frac{1}{m^*_e} \frac{\tau_e^2}{1 + \omega^2 \tau_e^2} + \frac{1}{m^*_h} \frac{\tau_h^2}{1 + \omega^2 \tau_h^2} \right] \quad (5)$$

$$2nk = \epsilon'' = \epsilon''_\infty + \frac{4\pi N e^2}{\omega} \left[\frac{1}{m^*_e} \frac{\tau_e}{1 + \omega^2 \tau_e^2} + \frac{1}{m^*_h} \frac{\tau_h}{1 + \omega^2 \tau_h^2} \right] \quad (6)$$

the first term in each expression represents the lattice contribution. n and k are the real and imaginary parts of the index of refraction, N the carrier density, e the electron charge and ω the frequency of the probing light beam. The Drude terms in eq. (5) and (6) are dependent on the values of the optical reduced masses m^*_e, m^*_h and of the momentum relaxation times τ_e, τ_h .

The fitting of the experimental data is critically dependent on the values of the optical reduced mass $m^* = (1/m^*_e + 1/m^*_h)^{-1}$, the Auger coefficient γ and the momentum relaxation time τ . A particularly useful relation can be derived for long delay times $t \gg (2\gamma N^2)^{-1}$. In this case the Auger effect has depressed the carrier density to a common value independent from the excitation laser fluence, $N \approx (2\gamma t)^{-1/2}$. The corresponding Drude terms in (5) and (6) then become proportional to $(m^* \sqrt{\gamma})^{-1}$. The same optical response is obtained at long delay times whenever the product of the reduced optical mass m^* and of the square root of the Auger coefficient γ is constant.

The use of the Drude formalism for the description of the dielectric functions suffers from the lack of reliable data of the optical reduced mass at high carrier densities. Thus, from the reflectivity and transmission changes, only the ratio N/m^* can be evaluated. By an extensive parametric study of the reflectivity and transmission changes as a function of time delays and laser fluences, however, the temperature dependence of the optical reduced mass can be estimated and the range of variation with the carrier density narrowed.

The final step for a meaningful comparison with the experimental data is the convolution of the actual reflectivity and transmission changes with the temporal profile of the probing pulse.

3. TIME RESOLVED OPTICAL REFLECTIVITY AND TRANSMISSION

The experiments were carried out by exciting the sample with 20 ps, 532 nm laser pulses from the frequency-doubled output of an active-passive mode locked Nd:YAG laser. The probe pulses, at 1.55 and 1.9 μm , were obtained by

Raman shifting the fundamental frequency at $1.06 \mu\text{m}$ in high pressure H_2 and CH_4 gas cells, respectively. The output was spatially filtered and imaged in the center of the irradiated area of the sample. The ratio of the pump and probe spot diameters was larger than 10. Crystalline silicon wafers, polished on the front surface were used. In the case of germanium, the surfaces were also chemically etched. This procedure drastically reduces the plasma recombination on the surface. Indeed, experimental runs on unetched samples showed little or no plasma effects.

In the following figures 5 - 8, we present the measured and calculated reflectivity and transmission for both elemental semiconductors. From the full parametric time resolved study only two time delays between the pump and the probe are selected. At a time delay of 20 ps a high density regime is expected, while the temperature is not fully developed due to the delayed heating mechanism discussed in the preceding section. The reflectivity of silicon first decreases to a broad minimum located at $F \approx 80 \text{ mJ/cm}^2$ and rises again at higher fluences. The high reflectivity phase associated with the transition to metallic, liquid, silicon is reached above the well known threshold value for surface melting, $F^{\text{th}} = 200 \text{ mJ/cm}^2$ observed at long time delays. The energy absorbed from the laser pulse is not completely transferred to the phonon subsystem in 20 ps. The thermal energy stored at this time in the lattice for a 200 mJ/cm^2 laser pulse is not sufficient to melt the surface.

The lines in fig. 5 represent the result of numerical calculations using different optical reduced masses m^* and Auger recombination coefficients. Below 100 mJ/cm^2 a fair agreement between measured and calculated data confirm the validity of the model employed. The value of the reflectivity minimum and the transmission changes associated with free carrier absorption are consistent with a strong damping of the electron-hole plasma oscillations. Extremely short momentum relaxation times $\tau = 8 \times 10^{-15} (300/T)$, being $T(^{\circ}\text{K})$

Fig. 5. Reflectivity and transmission at $1.9 \mu\text{m}$ of silicon samples versus incident $0.53 \mu\text{m}$ fluence for 20 ps delay. Lines: calculated values (see text).

the lattice temperature, have to be introduced to fit the measured transmission changes. The reflectivity data rule out the possibility for a low value of the Auger coefficient ($\gamma = 2 \times 10^{-31} \text{ cm}^6/\text{s}$, dotted lines). In this case the calculations show the reflectivity rising to a plasma resonance which is not observed. The agreement with the data can be extended somewhat above $100 \text{ mJ}/\text{cm}^2$ by using a constant Auger coefficient $\gamma = 4 \times 10^{-31} \text{ cm}^6/\text{s}$. However, even using the high density reduced optical mass $m^* = 0.165 m_0$ (fig. 5, dashed lines) or a strong density dependent value $m^* = 0.123 m_0 (1 - \beta N)^{-1}$, $\beta = 5 \times 10^{-22} \text{ cm}^3$, (solid lines), a substantial discrepancy is noted in the high fluence regime which can be reconciled only if the ratio N/m^* is simulated to decrease.

In order to obtain more experimental information on the optical reduced mass m^* we consider in figure 6 the data at long time delays (200 ps). At this time, the density has dropped to the asymptotic value $N \approx (2\gamma t)^{-1/2}$ independent of the laser fluence, while the temperature is strongly increasing with F as illustrated in fig. 4. The incremental change of the real part of the dielectric constant is proportional to $(m^* \sqrt{2\gamma t})^{-1}$. Excellent agreement between measured and calculated values is found if a $m^* \sqrt{\gamma}$ product of $7.5 \times 10^{-15} \text{ g cm}^3 \text{ s}^{-1/2}$ is used in the calculations (solid lines of fig. 6). We know from figs 1 - 4 that at long time delays the density remains constant, while the lattice temperature increases strongly with fluence. This agreement certainly indicates that the $m^* \sqrt{\gamma}$ product is completely insensitive towards the drastic increase of the lattice temperature. Thus the optical reduced mass itself cannot exhibit a noticeable temperature dependence. The fitting value of the $m^* \sqrt{\gamma}$ product can be separated in a constant high density mass of $m^* = 0.165 m_0$ and $\gamma = 2 \times 10^{-31} \text{ cm}^6/\text{s}$ or $m^* = 0.123 m_0$ and $\gamma = 4 \times 10^{-31} \text{ cm}^6/\text{s}$, respectively. At the highest fluences before melting, the transmission data are in better agreement with $m^* \sqrt{\gamma} = 1 \times 10^{-16} \text{ g cm}^3 \text{ s}^{-1/2}$ (dashed lines of fig. 6), corresponding to $m^* = 0.165 m_0$ and $\gamma = 4 \times 10^{-31} \text{ cm}^6/\text{s}$. Consistently with

Fig. 6. Reflectivity and transmission at $1.9 \mu\text{m}$ of silicon samples versus incident $0.53 \mu\text{m}$ fluence for 200 ps delay. Lines: calculated values (see text).

Fig. 7. Reflectivity and transmission at 1.9 μ m of germanium samples versus incident 0.53 μ m fluence for 20 ps delay. Lines: calculated values (see text).

Fig. 8. Reflectivity and transmission at 1.9 μ m of germanium samples versus incident 0.53 μ m fluence for 200 ps delay. Lines: calculated values (see text).

the observations at earlier times, the transmission indicates a lower density profile across the sample at the highest fluences.

From the comparison of the data obtained at 20 and 200 ps on silicon we can therefore deduce the following: 1) The insensitivity of the optical reduced mass towards temperature indicates degenerate carrier distributions, where the optical relevant parameters are only depending on the band structure and scattering process at the Fermi level. 2) Contrary to the expected drop of the Auger recombination by screening of the Coulomb interaction, the results indicate rather an increase of the recombination rate at high densities.

Thus, in silicon, the experimentally observed decrease of the N/m^* ratio is most likely due to the saturation of the obtainable density by the occurrence of new recombination channels as soon as the plasma resonance approaches the energy of the indirect band gap.

To prove this possibility of plasmon aided recombination in highly excited semiconductors, we have performed the same experiments in germanium, which has a lower band gap than silicon. Also, the maximum attainable carrier density is higher, as long as only Auger recombination is assumed to be the main density limiting process. The measurements on germanium at 20 and 200 ps delay times are shown in figures 7 and 8, respectively.

The plasma induced reflectivity drop is considerably less pronounced than in silicon, for comparable laser fluences. At a delay time of 20 ps the reflectivity drops from 30% to $\approx 20\%$. Again, a broad minimum is observed at $\approx F_{th}/2$. Contrary to the expected behavior, the reflectivity rises continuously with increased fluence. A much slower and delayed rise to the value for molten germanium occurs than in silicon. In contrast with the observations in silicon, but in agreement with measurements on GaAs¹⁶, the rise of the reflectivity towards the liquid value is always gradual. The transmission experiences a complementary behavior. Between $F_{th}/2$ and F_{th} a saturation of the absorption takes place. The fitting of the germanium data using $m^*=0.08 m_0$ and $\gamma = 2 \cdot 10^{-31} \text{ cm}^6 \text{ s}^{-1}$, indicates that at low fluences the calculations describe accurately the carriers. At higher fluences, however, the simulations are neglecting a basic mechanism in the evolution of the carrier plasma. Strong plasma resonance conditions, which would drastically increase the reflectivity of the surface, and reduce the transmission accordingly, are predicted above $\approx 10 \text{ mJ/cm}^2$. Instead, a saturation of the transmission is observed and a very slow rise of the reflectivity occurs. These results are strongly indicative of an increased recombination rate, which affects the surface and bulk carrier density.

The reflectivity measured at a delay time of 200 ps is qualitatively similar to the one at 20 ps. The initial decay slope of the transmission is comparable with the one observed at shorter times. The reflectivity minimum is less pronounced, due to the combined effects of Auger recombination and plasma diffusion into the bulk. Again, the slow recovery of the reflectivity versus fluence, when only an increase of the temperature occurs, supports the notion of a very weak temperature dependence of the optical reduced mass. The reflectivity data at 200 ps delay are well described by the calculations, indicating that at this long delay time the plasma evolution at the surface is again determined by the balance of ambipolar diffusion and slow Auger recombination. At $F > F_{th}/2$ the transmission, on the contrary, shows a marked increase with laser fluence which is abruptly interrupted by the melting of the surface. This behavior, which cannot be simulated by the present calculations, indicates a progressive reduction of the bulk carrier density. The trend is suddenly changed by the onset of the melting of the surface.

The data on germanium, therefore, strongly suggest that a new recombination channel opens up at a well-defined laser fluence, as soon as the plasma oscillations become resonant with the band gap. During the excitation laser pulse, these conditions are met at progressively lower density due to the reduction of the band gap energy with temperature. Once these recombination channels open up, the whole subsequent evolution of the plasma is affected. Lower densities occur at the surface of the sample, as the data at

short time delays suggest. This in turns reduces the ambipolar diffusion of the carriers inside the material. At longer times, however, the resonance conditions cannot be sustained by the reduced plasma density and the evolution of the plasma on the surface can be again described in terms of diffusion and Auger recombination. In the bulk of the material, on the contrary, the initial reduced ambipolar diffusion still affects the overall carrier density and a transmitted beam will experience a smaller absorption at later times, as the transmission data at 200 ps show.

4. CONCLUSIONS

The interaction of picosecond laser pulses with silicon and germanium surfaces has been investigated by comparing the results of time-resolved spectroscopic measurements in the infrared region with numerical simulations. This analysis has revealed the importance of the plasma degeneracy in the evaluation of the carrier dynamics, which in turns affects the temporal evolution of the lattice heating even in the picosecond time-scale. The experimental results for both materials indicate extremely small momentum relaxation times, suggesting the dominance of intervalley scattering mechanisms over other competing processes.

Due to the high excess photon energy used for the excitation, the strong discrepancies at high laser fluence between the observed and the calculated optical response are not affected by either nonlinearities in the excitation process or by thermally induced interband transitions of the probing light. The predicted saturation of the Auger effect at high carrier density has not been observed. On the contrary, there are indications in silicon of an increase in the recombination rate of the carriers at the highest laser fluences. In germanium, due to the more favourable ratio $h\nu/E_g$, the experimental data provide strong evidence for a plasmon-assisted recombination which limits the carrier density as soon as the plasmons become resonant with the thermally reduced band gap.

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