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Carrier diffusion in semiconductors subject to large gradients of excited carrier density

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Under conditions of intense optical pumping or electrical injection it is possible to excite such a dense plasma of electrons and holes that these carriers interact among themselves much more rapidly than they interact with the lattice phonons. In this circumstance there will be established a temperature of excited carriers, T_e, much larger than the temperature of the lattice, T_L, for periods of time sufficient for many effects to be observed. In the accompanying paper it is shown that the temperature dependence of the forbidden band gap is then described by $\Delta E_{cv}(T_e,T_L)=\Delta H_{cv}(T_L)-T_e\Delta S_{cv}(T_L)$. With $T_e >> T_L$, this means that anomalously large changes in the band gap will occur and, if also there are large gradients of T_L present in the sample, there will be very large gradients in the band gap. This means there will be very large gradients in the chemical potentials of the excited electrons and holes. As the band gap tends to be least where the carriers are most dense and T_L the greatest, these chemical potential gradients oppose the normal outward diffusion of the excited carriers. We find that, under certain conditions, this effect may be sufficient to produce "negative diffusivity" or carrier self-confinement.

I. INTRODUCTION

The forbidden band gap, ΔE_{cv}, of a semiconductor is identically the standard chemical potential for the formation of unbound electron-hole pairs.[1,2] (The standard chemical potential is that part of the total chemical potential which does not depend explicitly on the concentration of the species.) It is also well known to be a function of temperature.[2,3] Under "hot electron" conditions of intense optical pumping, irradiation, or electrical injection, the temperature, T_L, which characterizes the lattice phonons, will not be equal to the temperatures which characterize the distribution of carriers excited within the valence and conduction bands, $T_{e,v}$ and $T_{e,c}$, and the temperature which characterizes the excitation of carriers across the gap, T_e. Carrier-carrier interaction is generally so strong that we may assume

$$T_{e,c}=T_{e,v} \quad . \tag{1}$$

When the excited carrier density is sufficiently high that the rates of Auger recombination and impact ionization are rapid on the scale of the experiment of interest, while carrier lattice interaction is slow on that scale, we reach an interesting regime in which the carrier system may be considered to be in quasiequilibrium with itself and weakly coupled to the lattice. Thus,

$$T_e=T_{e,c}=T_{e,v}>>T_L \quad , \tag{2}$$

for times relevant to the experiment under consideration.

It has been argued[4–8] for some time that pulsed laser annealing[4–14] is a nonthermal phenomenon. More recently it has been argued[7,8] that it primarily involves a plasma of excited electrons and holes at a density of order $10^{21}/\text{cm}^3$ and $T_e >> T_L \approx 300\,^\circ\text{C}$. The argument regarding the thermal or nonthermal nature of pulsed laser annealing was finally settled, when Lo and Compaan showed[14] by direct Raman measure of surface lattice temperature that T_L does not rise more than 300 °C for at least 50 ns after the end of a laser pulse of intensity just below the threshold for damage and more than twice the threshold for normal annealing. Therefore, the electron-hole plasma created by the absorption of this light must retain the energy of this pulse and is heated to several thousand degrees centigrade. Indeed, Lo and Compaan observed a background scattering characteristic of Raman scattering from carriers with $T_e >> 2000$ K. Yoffa's calculations[13] show that when an excited plasma is this dense, the condition of Eq. (2) should be expected to prevail. What is most remarkable about Lo and Compaan's experimental result,[14] and indeed the whole pulsed laser annealing phenomena, is that it prevails for such a long time.[7,8]

When this is the case, we have shown in the accompanying paper[15] that the band gap is described by the simple formula,

$$\Delta E_{cv}(T_e,T_L)=\Delta H_{cv}(T_L)-T_e\Delta S_{cv}(T_L) \quad , \tag{3}$$

where ΔH_{cv} and ΔS_{cv} are the enthalpy and standard

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entropy of the excitation of the carrier across the gap.[1,2] These thermodynamic parameters are functions of T_L and should be affected only moderately by T_e until the carrier density becomes so high that nonlinearities become important. They have been measured under normal furnace conditions, $T_e = T_L = T$, from $T = 0$ K to temperatures near the melting points of several semiconductors. These data have been reviewed and tabulated by Thurmond in Ref. 2. Experimental values for Si to its melting point are shown in Fig. 1, which is borrowed from Ref. 2.

At the very high carrier densities relevant to pulsed laser annealing, the concentration of excited electrons, $[e_c^-] = [h_v^+] \equiv n$, the concentration of excited holes. Therefore, we may consider only the ambipolar diffusion of the neutral plasma rather than the diffusion of electrons and of holes separately. Gradients of T_e and of T_L will produce a gradient of ΔE_{cv}, which is equivalent to an internal field tending to drive the plasma toward the regions where ΔE_{cv} is minimal. As T_e and T_L are greatest where n is greatest and ΔE_{cv} is least, the effect of the internal field is to oppose the normal outward diffusion of the plasma from the region where it was created.

We will here show that under the extreme conditions of pulsed laser annealing this internal field due to ∇T_L and ∇T_e may be sufficient to completely overcome the outward diffusion and cause it to contract. Although we have not solved the problem of the variation of the plasma density with time, it appears that this confinement phenomenon will persist about as long as ∇T_L remains large. That would be comparable to the time required for an equivalent amount of heat to diffuse away, i.e., for times of order 100 ns.

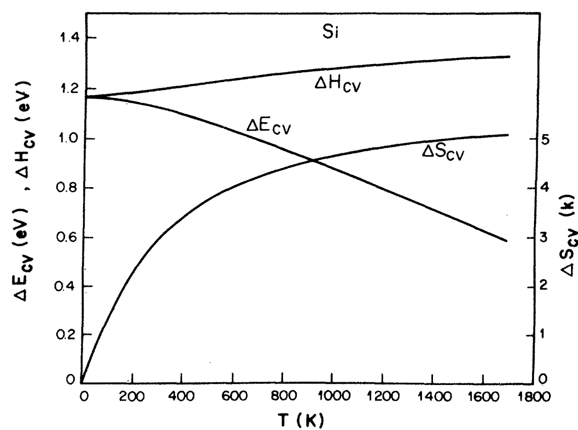

FIG. 1. Variation with temperature of the fundamental band gap, ΔE_{cv} of Si. As ΔE_{cv} is the standard chemical potential for the creation of (unbound) electron-hole pairs, it is equal to a free energy. The corresponding standard enthalpy and standard entropy of this reaction, ΔH_{cv} and ΔS_{cv}, are also shown. This figure is borrowed from Thurmond, Ref. 2.

II. DERIVATION

The effect of gradients of the band gap, whether induced by thermal or by composition gradients, has, of course, been treated previously in the literature.[16-18] It is particularly significant to the operation of double heterostructure lasers, where it causes both electrons and holes to be confined in the active layer.[18]

To simplify the discussion, we shall take the ratio of the laser annealed spot diameter to the depth of penetration of the heat and the carriers to be sufficiently large that the problem may be treated as one dimensional. Thus, we only consider diffusion perpendicular to the surface, which direction we denote z. Following the notation of Stratton,[16] let us denote the current of electron-hole pairs at a point, z, near the surface of the sample in the z direction as J. Further,

$$J = J_F + J_D \quad , \tag{4}$$

where J_F is the contribution due to the gradient of the band gap, which drives pairs up towards the surface where the density is greatest,

$$J_F = n\mu F \quad , \tag{5}$$

and where J_D is the contribution due to normal diffusion, which drives pairs down away from the surface,

$$J_D = -D\frac{dn}{dz} \quad . \tag{6}$$

(We neglect the fact that D may vary with z in this rather qualitative discussion.) Here, F is the field acting on the pairs due to the variation of the band gap,

$$F = \frac{d\Delta E_{cv}}{dz}$$
$$= -\frac{d\Delta H_{cv}}{dT_L}\frac{dT_L}{dz} + \Delta S_{cv}\frac{dT_e}{dz} + T_e\frac{d\Delta S_{cv}}{dT_L}\frac{dT_L}{dz} \quad . \tag{7}$$

D is the ambipolar diffusivity of the pairs, and μ is their mobility. D and μ are connected by the Einstein relation,

$$\mu = \frac{DF_{-1/2}(\eta' - \eta_0)F_{-1/2}(-\eta')}{kT_eF_{1/2}(\eta' - \eta_0)F_{1/2}(-\eta')} \quad , \tag{8}$$

where $F_{-1/2}$ and $F_{1/2}$ are the Fermi-Dirac functions and $\eta_0 = -\Delta E_{cv}/kT_e$ and $\eta' = E_F/kT_e$, with Fermi energy, E_F measured from the valence-band edge. For the present we approximate Eq. (8) with the nonde-

generate formula,

$$\mu = D/kT_e \quad . \tag{9}$$

The error introduced thereby is only a factor of 2.6 even at $\eta_0 = 2.5$.

We use the Varshni equations[19] and the data of Thurmond[2] for $\Delta H_{cv}(T_L)$ and $\Delta S_{cv}(T_L)$. These give

$$\frac{d\Delta H_{cv}}{dT_L} = \frac{2\alpha\beta^2 T_L}{(T_L+\beta)^3} \tag{10}$$

and

$$\frac{d\Delta S_{cv}}{dT_L} = \frac{2\alpha\beta^2}{(T_L+\beta)^3} \quad , \tag{11}$$

with $\alpha = 4.73 \times 10^{-4}$ eV/K $= 5.49k$ and $\beta = 636$ K for Si.

Thus, Eq. (4) becomes

$$\frac{J}{D} = \frac{2n\alpha\beta^2}{k(T_L+\beta)^3}\left(1 - \frac{T_L}{T_e}\right)\frac{dT_L}{dz} + \frac{n\Delta S_{cv}}{kT_e}\frac{dT_e}{dz} - \frac{dn}{dz} \quad . \tag{12}$$

The first term, which vanishes when $T_e = T_L$, comes from combining the contributions from $d\Delta H_{cv}/dT_L$ and $d\Delta S_{cv}/dT_L$. (Positive values of J/D imply the plasma is confined and driven to higher densities.) Note that T_e is a function of n because that is how it is defined.

III. DISCUSSION

Initially after a short laser pulse both dn/dz and dT_e/dz would be given by the more-or-less exponential distribution of pairs produced by the absorption of the light, but, if confinement begins, they both will grow larger. The question of a proper determination of dT_L/dz is difficult because of the open question of the variation with plasma density of the rate of transfer of energy from the plasma to the lattice. Here we shall simply assume dT_L/dz is proportional to dn/dz in the period immediately following the laser pulse. As no mechanism for confining the flow of heat, i.e., the phonons, has been suggested, it seems clear that after some time dT_L/dz will grow small.

Let us now evaluate Eq. (12) using parameters consistent with the measurements[14] of Lo and Compaan for the period immediately following the laser pulse. We take $T_L = 573$ K so that $\Delta S_{cv} = 4.0k$. Then Eq. (12) becomes

$$\frac{J}{D} = 2.5 \times 10^{-3} n\left(1 - \frac{T_L}{T_e}\right)\frac{dT_L}{dz} + \frac{4.0n}{T_e}\frac{dT_e}{dz} - \frac{dn}{dz} \quad . \tag{13}$$

We further assume initial penetration to have a characteristic depth of 100 nm, so that with $n = 10^{21}/\text{cm}^3$, $dn/dz = 10^{26}/\text{cm}^4$, $dT_L/dz = 3 \times 10^7$ K/cm, $T_e \approx 10^4$ K, and $dT_e/dz = 10^9$ K/cm. With these values, Eq. (12) now becomes

$$\begin{aligned} J/D &= (0.75 + 4.0 - 1) \times 10^{26}/\text{cm}^4 \\ &= +3.75 \times 10^{26}/\text{cm}^4 \quad . \end{aligned} \tag{14}$$

The positive value is large enough that the error due to the neglect of degeneracy in using Eq. (9) instead of Eq. (8) could not change the sign of the result. We further note that the dominant positive term is that involving dT_e/dz, which will grow larger with time if confinement occurs, and not that involving dT_L/dz, which will grow smaller after some time. Finally, as was noted in the accompanying paper,[15] the effect of including the effect of degeneracy in the relation between T_e and n is to increase T_e relative to n, so that dT_e/dz will also be increased to dn/dz.

IV. CONCLUSIONS

We conclude that there is no doubt that for the extreme conditions achieved in some pulsed laser annealing experiments there will be an initial period in which the laser generated plasma of electron-hole pairs will not diffuse down its concentration gradient but will be driven to higher densities by the band bending induced by the gradient of the band gap. To understand the time development of this confinement, we will have to develop an understanding of the variation with plasma density of the rate of transfer of energy from the carrier system to the lattice. While progress is being made in this direction[8,13,20,21] a full understanding of this problem, and of the long persistence of the laser-induced plasma, has not yet been attained.

Note added in proof. The phenomenon of carrier confinement during pulsed laser annealing that is predicted herein has evidently now been demonstrated[22] by Aydinli *et al.* By measuring the time-resolved reflectivity and transmission spectra of Si on sapphire and doing the Kramers-Kronig transform, they have concluded that a plasma produced by photon absorption over more than 1 μm becomes confined to about 70 nm for about 60 ns and then expands. They used 1 J/cm^2 of 485-nm light in an 8-ns pulse, which is well above the annealing threshold and near the damage limit.

It seems the phenomenon was also observed[23,24] but not fully understood several years ago by Svantesson, Nilsson, and Huldt. In a study of Auger recombination they noted a 60-ns long spike of band to band luminescence after a 4 J/cm^2 of 694-nm light in a "less than 30-" ns pulse, which is more than twice the energy density at this wavelength needed to disperse[25] P precipitates in Si. Nilsson's analysis of this event could not model the spike of luminescence

(Ref. 24, p. 168), which would correspond to the period of negative diffusion and dense confinement. In the remains of the event he found it necessary to severely reduce D from normally observed values (18 cm^2/s) or the sort of hot carrier values calculated[13] by Yoffa (more than 100 cm^2/s) to 1 cm^2/s, which is approximately the diffusivity of heat at 200 °C. He suggested (p. 168) this might result from intense electron-hole scattering, as in exciton droplet formation at very low temperatures. Although this energy density is well above the threshold at which others have suggested crystalline Si should undergo normal thermal melting,[25] it is obvious the normal molten phase is not present to absorb the luminescence and further that the lattice temperature never rises very far because its spectrum has a sharp edge that is shifted only slightly to longer wavelengths from that observed at room temperature. (Their spectra are time resolved and extend from the peak of the exciting pulse to several 100 ns.) They estimate the lattice temperature to be 450 °C, comparable with the 300 °C measured by Lo and Compaan under different conditions. Nilsson also notes several "unresolved discrepancies" in his analysis and a simple thermal heating analysis that neglect the effects described in our two papers and in Refs. 7, 8, 20, and 21.

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