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Variation of semiconductor band gaps with lattice temperature and with carrier temperature when these are not equal

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Under conditions of intense optical pumping or electrical injection it is possible to establish a temperature of excited carriers, T_e, larger than the temperature of the lattice, T_L, for periods of time sufficient for many effects to be observed. It is well known that semiconductor band gaps are a function of temperature, but the variation with the two temperatures, T_e and T_L, when these are different seems not to have been discussed previously. Simple thermodynamic arguments may be applied when it is recognized that a band gap is a chemical potential. The simple formula, $\Delta E_{cv}(T_e,T_L)=\Delta H_{cv}(T_L)-T_e\Delta S_{cv}(T_L)$, is deduced. Physically this formula states that the vibronic degeneracy of the electronic states (valence and conduction band or bonding and antibonding) among which the carriers are distributed with characteristic temperature T_e is determined by the lattice temperature, T_L. Thus when $T_e >> T_L$, anomalously large variations in the gap will occur. It is found that under certain conditions loss of energy from the carrier system to the lattice will cause the density of excited carriers to increase, rather than decrease.

I. INTRODUCTION

The forbidden energy gap, ΔE_{cv}, of a semiconductor is identically the chemical potential for the formation of unbound electron-hole pairs.[1,2] Indeed, the normal formula for the thermal equilibrium concentration (when nondegenerate),

$$[e_c][h_v]=N_c(T)N_v(T)\exp[-\Delta E_{cv}(T)/kT] \quad , \qquad (1)$$

is an example of the law of mass action[2,3] for the reaction

$$0 \leftrightarrow e_c+h_v \quad . \qquad (2)$$

Then ΔE_{cv} is, by definition, its standard chemical potential. [Here

$$N_{c,v}(T)=2(2\pi m_{c,v}^{*}kT/h^2)^{3/2} \qquad (3)$$

are the electronic degeneracies, i.e., the effective number of points in the Brillouin zone at which carriers contribute to conduction, for the conduction and valence bands. e_c and h_v represent an electron and a hole excited to the conduction band and valence-band edge distribution of states, respectively, and m_c^* and m_v^* are their density of states effective masses.]

Consequently, the band gap is equal both to the increase in internal energy upon increase of the carrier density by one electron and one hole under conditions of constant entropy and volume and to the increase in free energy upon increase of the carrier density by one electron and one hole under conditions of constant temperature and pressure;

$$\Delta E_{cv}\equiv\mu_{e,h}\equiv\left.\frac{\partial U}{\partial n_{e,h}}\right|_{S,V}\equiv\left.\frac{\partial G}{\partial n_{e,h}}\right|_{T,P} \quad . \qquad (4)$$

(In a forthcoming book chapter[4] there is given a quantum-mechanical derivation of the thermodynamic identity that the increment in free energy measured in thermal experiments is equal to the "no-phonon-line" value of the internal energy increment measured in optical experiments under normal conditions.)

It has previously been noted[5-7] that there are great advantages when discussing the temperature dependence of band gaps to treat the change in free energy rather than the change in internal energy:

$$\Delta E_{cv}=\Delta G_{cv}=\Delta H_{cv}-T\Delta S_{cv} \quad . \qquad (5)$$

The temperature dependence of a free energy is, of course, an entropy, in this case the entropy of the band gap, ΔS_{cv}, or the standard entropy of excitation of an electron across ΔE_{cv}. ΔH_{cv} is the enthalpy of the gap, which must, incidentally, increase with temperature if ΔE_{cv} decreases.[2] The variation of these three thermodynamic variables from $T=0$ to the melting point, 1685 K, for Si is shown in Fig. 1, which is borrowed from Ref. 2.

To calculate the temperature dependence of a particular band gap from first principles, one may consider the effect of the excitation of the carriers upon the frequency of the phonon modes rather than the effect of the phonons upon the electronic states.[5] The number of phonon modes excited is always several orders of magnitude greater than the number of carriers excited across the gap. At the melting point of a covalent semiconductor, typically 2.6 times the Debye temperature, all phonon modes are multiply excited whereas only 10^{-4} of the carriers are excited. Whereas simple, tractable and analytic

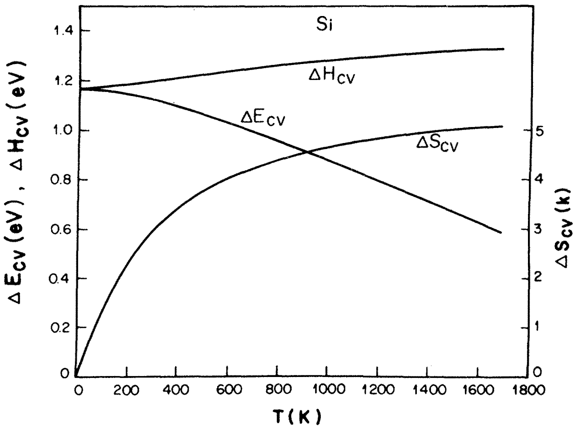

FIG. 1. Variation with temperature of the fundamental band gap, ΔE_{cv} of Si. As ΔE_{cv} is the standard chemical potential for the creation of (unbound) electron-hole pairs, it is equal to a free energy. The corresponding standard enthalpy and standard entropy of this reaction, ΔH_{cv} and ΔS_{cv},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

bond-charge-model[8] formulas are available for the frequency of the various phonon branches in terms of the magnitude of the bond charge and the wave vector, a proper estimate of the effect of the phonons upon the the electronic states would have to treat three independent effects—reduction of direct interband scattering (Debye-Waller or Brooks-Yu effect), increase of indirect interband scattering, and increase of indirect intraband scattering (Fan effect) with increasing temperature—for every one of the phonons in all branches.[5] [The (anharmonic) effect of the variation of lattice parameter with temperature should also be treated, but it is smalller than these effects in the common semiconductors.] It is easier to treat the effect of the excited carriers on the phonon modes.

Under normal conditions the temperatuare of the phonon distribution, the lattice temperature, T_L, the temperatures which characterize the distribution of carriers within the valence and conduction bands, $T_{e,v}$ and $T_{e,c}$, respectively, and the temperature characterizing the excitation of carriers across the gap, the electron temperature, T_e, are all the same. For this situation ΔE_{cv} can be measured by any of several independent methods from $T=0$ K to the melting point, and from these measurements $\Delta H_{cv}(T)$ and $\Delta S_{cv}(T)$ can be deduced. Thurmond has reviewed these data and tabulated the parameters for several semiconductors in Ref. 2.

However, many semiconductor phenomena are observed under "hot-electron" conditions for which, due to optical pumping or electrical injection, the three temperatures describing the excited carriers are much greater than that of the lattice.[9–12] As the various direct, indirect, and fundamental band gaps, as well as the ionization energies of defects, impurities, etc., are all functions of temperature, the condition

$$T_e >> T_L \tag{6}$$

would seem to beg the question of the variation of these chemical potentials with T_e and with T_L; what is $\Delta E_{cv}(T_e,T_L)$? Is ΔE_{cv} a function of $T_{e,v}$ and $T_{e,c}$?

One approach to the description of nonequilibrium carrier distributions that is well established in the literature is that of the introduction[13] of "quasi-Fermi levels." Now, the real Fermi level is the chemical potential of electrons and of holes. (Of course, a hole is nothing but the absence of an electron; as chemical potentials are defined by derivatives of total system energies with respect to the number of particles of a given species, electrons and holes must always have the same chemical potential, or Fermi level.) In the (normal, one fitted parameter) "quasi-Fermi-level" approach, one seeks to describe a nonequilibrium, i.e., $T_e \neq T_L$, concentration of electrons and/or holes by introducing separate values for the electron and hole Fermi levels that are adjusted so that the conventional formula gives the actual concentration when the ambient lattice temperature, T_L, and the corresponding value of $\Delta E_{ev}(T_L)$ are inserted. There is no evident thermodynamic significance to these "quasi-Fermi levels." The approach is normally used to describe the action of injection lasers or transistors under moderate conditions of injection or optical pumping for which $T_L < T_{e,v} < T_{e,c} << T_e$, because the excited carrier density is not so high that recombination is as fast as energy transfer between carriers or to the lattice. It gives no accurate description of the distribution of carriers within the bands.[13] It could be improved by introducing $T_{e,c}$ or $T_{e,v}$ as a second fitted parameter in addition to the "quasi-Fermi level," in which case the corresponding band gap and exponential factors ought logically to be employed, so a different value of the "quasi-Fermi level" would have to be used. It seems quite artificial, but it may be useful when one does not care to develop a thermodynamic description. When none of the four temperatures in the problem are equal, or when, due, e.g., to strong electric fields, the distribution of carriers is not accurately described by a thermal distribution with any choice of temperature and chemical potential, this would seem prudent.

However, a proper thermodynamic description is tractable and desirable when the excited carrier concentration is sufficiently high that for times relevant to the experiments of interest, the carrier-carrier interaction is so much stronger than the carrier-phonon interaction that the carrier and phonon systems can be considered to be weakly coupled. Then the carriers will thermalize among themselves before they thermalize with the lattice. Then, when $T_{e,v} \approx T_{e,c} \approx T_e$, we would have $T_e >> T_L$ for times long enough for many interesting effects to be observed.

Indeed, Lo and Compaan have shown[14] by direct Raman measure of the surface lattice temperature that T_L does not rise more than about 300 °C for crystalline Si exposed to laser pulses well above the threshold energy density for annealing ion implantation damage.[15–22] They also observed a background scattering characteristic of Raman scattering from carriers with a $T_e >> 2000$ K. Yoffa has shown[23] that, for the the excited carrier concentrations that seem to persist during laser annealing experiments, the carriers would thermalize among themselves much more rapidly than with the lattice, so that the condition discussed here, $T_{e,c} = T_{e,h} = T_e >> T_L$, would obtain. It may also occur for intense electrical injection.

II. DERIVATION

For this case that the carriers may be considered strongly coupled to each other, (so that $T_{e,v} \approx T_{e,c}$) and sufficiently dense that the rates of Auger recombination and impact ionization are rapid on the scale of the experiments of interest (so that $T_{e,c} \approx T_e$), but weakly coupled to the phonons (so that $T_e >> T_L$) for times of interest, a simple formula in terms of the values of $\Delta H_{cv}(T)$ and $\Delta S_{cv}(T)$ measured under the normal conditions that $T_e = T_L$ can be deduced from simple consideration of the law of mass action and the number of carriers excited. This formula is

$$\Delta E_{cv}(T_e, T_L) = \Delta H_{cv}(T_L) - T_e \Delta S_{cv}(T_L) \ . \tag{7}$$

To see that this is the correct formula we invite the reader to consider Fig. 2. For simplicity the band structure of the semiconductor has been replaced by a single electronic transition between two electronic states. When the effect of the lattice phonons are added , these two levels become two parabolas (in the harmonic approximation) of vibronic levels. The lattice temperature, T_L, determines the distribution of carriers within whichever vibronic parabola they may be found. At $T_L = 0$ K all carriers must be in the lowest vibronic state because there are no phonons excited. Then the vibronic degeneracy of both states would be the same and the carriers would be distributed between these two parabolas according to the normal Fermi-Dirac expression as a function of the carrier temperature T_e. When $T_L \neq 0$, phonons are excited and carriers in either electronic level are distributed among the corresponding vibronic levels according to the normal Bose-Einstein expression as a funciton of T_L. In general the lattice stiffness and the phonon energies will be different for the two electronic states, i.e., there is an electron-phonon interaction. Exciting electrons from the valence to the conduction band usually softens the lattice modes of a tetrahedral semiconductor, like Si or GaAs. Cases, like HgTe, where the excitation stiffens the lattice are also known; in such cases ΔE_{cv} should and does have the opposite temperature dependence. These cases are easily understood in terms of the band structures of the various materials.[5]

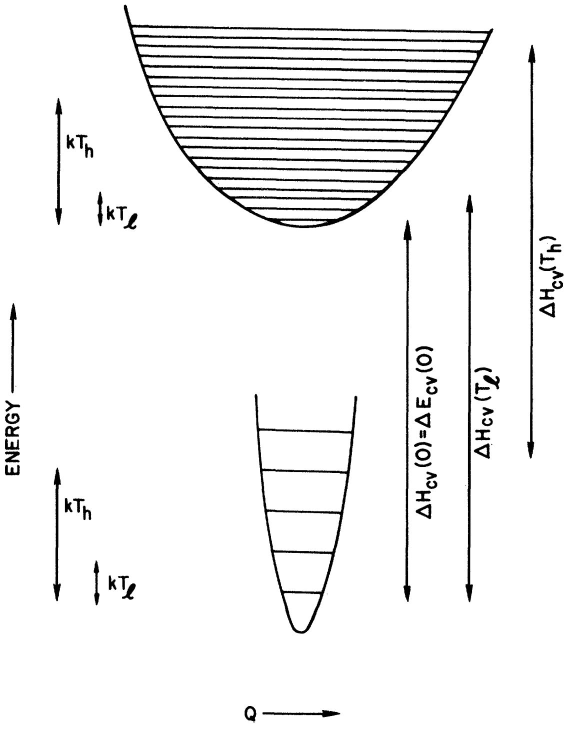

FIG. 2. Configuration coordinate diagram to illustrate how it is that when the entropy of formation of electron-hole pairs is positive (as it is in Si and most other semiconductors), then, in the harmonic approximation: the vibronic eigenvalues change not at all; the enthalpy difference between the two electronic states must increase with carrier temperature, T_e, to a saturation value; and the free energy difference between the two electronic levels will decrease without limit as the T_e increases. T_l and T_h denote lattice temperatures which are, respectively, low and high with respect to the Debye temperature. Also, the value of ΔS_{cv}, and therefore of ΔH_{cv}, is entirely a function of the number of vibrational modes excited for each electronic state. These entropies and enthalpies will always be functions of T_L, and will, until the carrier density becomes great enough to significantly alter phonon frequencies, be functions only of T_L.

Figure 2 is drawn for the usual case that the excitation softens the lattice so the upper parabola is broader than the lower. Consequently the vibronic degeneracy, i.e., the number of states of the total system available to a carrier, is greater for the excited state than for the ground state. By the law of the equipartition of states, this will increase the probability of finding the carrier in the excited state for any positive value of T_e.

There are other consequences also. Because the vibronic levels are more closely spaced in the excited electronic state, the excited vibronic levels will begin to be populated to a significant extent at lower values of T_L in the excited state. This means that the average energy of the distribution of carriers in the excited electronic state *increases* relative to the average distribution in the ground state when ΔE_{cv} decreases with rising temperature, T_L. This difference between the mean energy of two distributions is just the difference in internal energy for excitation across the gap, which is effectively equal to ΔH_{cv} because pressure times volume change terms are quite negligible in all ordinary circumstances. Indeed, 1 atm is only 0.632×10^{-6} eV/Å.[3] (It was noted above that thermodynamics requires ΔH to increase when ΔG decreases.[2])

The standard entropy, ΔS_{sv}, of the excitation reaction is defined in terms of the ratio of the probable number of vibronic states in the two electronic states. As the number of electronic states does not change, this is a function only of the probable number of phonons excited. Therefore, the value of ΔS_{cv}, and thus of ΔH_{cv}, required for $\Delta E_{cv}(T_e, T_L)$ must be functions of T_L. They will be the same functions of T_L as those measured under normal furnace conditions provided that the number of excited carriers in excess of that which would obtain if the two temperatures were equal is not so large that the effect on the phonons becomes nonlinear in the number of carriers. (The intrinsic carrier concentration at the melting point of Si, and most other common semiconductors, is about 2×10^{19} cm^{-3}.) When nonlinearity sets in one would expect the effect to be greater for the excited electronic states because atoms whose bonding electrons have been excited to nonbinding or antibonding electronic states will make larger excursions in their thermal motion than fully bonded atoms and thus will sense the more anharmonic portions of the lattice potential. It follows that our assumption of $\Delta S_{cv}(T_L)$ will underestimate the correct value. This can be seen from Fig. 1 and the fact that ΔS_{cv} does not saturate above the Debye temperature, Θ, as it would in the harmonic approximation,[5] but continues to increase moderately all the way to the melting point. At this point it should be clear that the values of the enthalpy and entropy of the gap in Eq. (7) are functions only of the excitation of phonons.

[We might note that, when viewed as a free energy, ΔE_{cv} decreases without limit as T_e increases because the entropy factor in the definition of a free energy, Eq. (7), is multiplied by the temperature relevant to the species being excited, here T_e. When viewed as an enthalpy or internal energy difference, as in optical excitation experiments, ΔE_{cv} decreases because the mean number of phonons excited increases and the optical band gap, when defined as the entropy conserving no-phonon line, connects states with the same number of phonons excited, but each phonon excitation raises the level of the ground electronic state (valence band) more than the excited electronic state (conduction band). The eigenvalues of individual ground and excited vibronic states do not in general approach each other as temperature varies. In the harmonic approximation the eigenvalues do not vary at all.]

The carrier temperature T_e is defined by the distribution of the carriers between the two vibronic systems, the two parabolas, for which the degeneracy is different. If one considers now just that distribution, as if there were only one temperature in the problem but levels of degeneracy determined in the same way, then it is evident the temperature which multiplies the entropy factor for the free energy, Eq. (7), must be exactly T_e. Thus Eq. (1) becomes

$$[e_c][h_v] = N_c(T_{e,c}) N_v(T_{e,v}) \exp\left(\frac{\Delta S_{cv}(T_L)}{k}\right) \times \exp\left(\frac{-\Delta H_{cv}(T_L)}{kT_e}\right) . \tag{8}$$

[Note that we have here a product of electronic degeneracy factors, N_c and N_v, which are determined by the intraband carrier temperatures, $T_{e,c}$ and $T_{e,v}$, and the vibronic degeneracy factor, $\exp(\Delta S_{cv}/k)$, which is determined by the lattice temperature T_L.] Again, at the very high carrier densities, such as those achieved in laser annealing experiments,[14,18] Yoffa has shown[23] that the three carrier temperatures should approach each other much more rapidly than any of them approaches T_L; the condition $T_{e,v} \approx T_{e,c} \approx T_e >> T_L$ obtains for some time. Equation (8) simply states that the vibronic degeneracy of the ground and excited electronic states (i.e., the valence and conduction bands or the bonding and antibonding states) is a function of T_L, but the carriers are distributed between these electronic states according to T_e. The ratio of the density of vibronic states available, $\exp(\Delta S_{cv}/k)$, is a factor in the determination of the number of carriers excited. The ratio T_L/T_e does not appear.

III. DISCUSSION

One should note that, when $T_e \neq T_L$, the optical no-phonon line ("optical gap"), $\partial U/\partial n_{e,h}|_{S,V}$, is not equal to the thermal, or chemical potential, band gap, $\partial G/\partial n_{e,h}|_{T,P}$. This may be seen in Fig. 2 from the fact that the optical no-phonon line will depend only on the excitation number of the phonons, and thus T_L; the optical no-phonon line will not decrease without limit as T_e increases. Except for the contribution of free carriers, the optical-absorption edge will shift to lower energy only to the degree characteristic of T_L. However, as the chemical potential and the density of carriers determine diffusion and most other interesting properties, it is the thermal or chemical potential band gap, described by Eq. (7), that is relevant to our discussion.

Another interesting point is that, since $\Delta S_{cv} \rightarrow 0$ as $T_L \rightarrow 0$, as do all other entropies, no major variation of the band gaps should be expected in low-energy pulsed laser experiments done with liquid He ambients. Picosecond pulse experiments have commonly been done with samples cooled to liquid He temperatures. If such experiments were repeated with T_L a substantial fraction of Θ, a significant variation of band gaps, optical reflectivity, and related phenomena should be observed.

For the same reason, the threshold laser intensity for pulse laser annealing should be sensitive to the initial lattice temperature. If one started from $T_L = 0$ K and the laser pulse raised it to 300 K, rather than from 300 K to about 600 K, as measured[14] by Compaan and Lo, then from the relative values of ΔS_{cv} (Fig. 1), we see we would need about twice as large a value for T_e to achieve the same band gap and carrier concentration.

When large densities of carriers are excited, the effects of the exclusion principle for electrons and holes, i.e., of carrier degeneracy, must be considered. Equations (2) and (8) must be replaced with more complicated expressions involving the product of two Fermi-Dirac functions,[24]

$$[e_c][h_v] = 4\left(\frac{kT_e}{2\pi\hbar^2}\right)^3 (m_c^* m_v^*)^{3/2}\frac{4}{\pi}F_{1/2} \times (\eta' - \eta_0)F_{1/2}(-\eta') , \tag{9}$$

where, of course,

$$F_{1/2}(\eta) = \int_{x=0}^{\infty} dx \frac{x^{1/2}}{\exp(x-\eta)+1} . \tag{10}$$

Here we have $\eta_0 = \Delta E_{cv}(T_e, T_L)/kT_e$ and $\eta' = E_F/kT_e$, where E_F, is, of course, the Fermi level measured from the valence-band edge. When the arguments of the Fermi-Dirac functions are large and negative, these expressions reduce to the Boltzmann expressions given above. When the arguments of these functions become positive (i.e., the band gap becomes negative), the effects of degeneracy become important; for a given concentration of excited carriers, T_e will actually be larger than the value obtained from Eq. (8). However, such complication does not affect qualitatively the foregoing discussion, which would hold for a system of discrete electronic levels as well as for bands.

One expedient would be to use the Ehrenberg approximation[24,25]

$$F_{1/2}(x) = 2\pi^{1/2}\exp(x)/[4+\exp(x)] , \tag{11}$$

which is accurate when $x < 2.5$, or the approximation[26]

$$F_{1/2}(x) = (4x^{3/2}/3\pi^{1/2}) + \pi^{3/2}/6x^{1/2} , \tag{12}$$

which is accurate when $x > 1.5$. The effect of degeneracy could be accounted for in Eqs. (1) and (8) by simply dividing the classical result by the factor

$$y = (\pi/4)\exp(-\eta_0)/F_{1/2}(\eta' - \eta_0)F_{1/2}(-\eta') , \tag{13}$$

which is plotted in Fig. 3. As long as $-\Delta E_{cv}/kT_e < 2.5$, we may use the Ehrenberg approximation and have

$$y = \frac{16 + 4\exp(\eta' - \eta_0) + 4\exp(-\eta') + \exp(-\eta_0)}{16\exp(-\eta_0)} . \tag{14}$$

Reference to Fig. 1 shows that indeed $x < 2.5$ as long as $T_L < 0.7\Theta$ and/or $kT_e < 1$ eV. Therefore, the Ehrenberg approximation should be reasonably adequate for almost all experimental circumstances.

Under pulsed laser annealing conditions, one may contemplate[14,18] the situation where $T_e \approx 10\,000$ K while $T_L \approx 500$ K. Referring again to Fig. 1, we see that such values of T_e and T_L would produce a decrease in ΔE_{cv} of more than 3 eV from its normal room-temperature value of 1.1 eV, so that we would have $x = 1.9$ in the Fermi-Dirac function. [Note that negative values of ΔE_{cv} have significance only in the

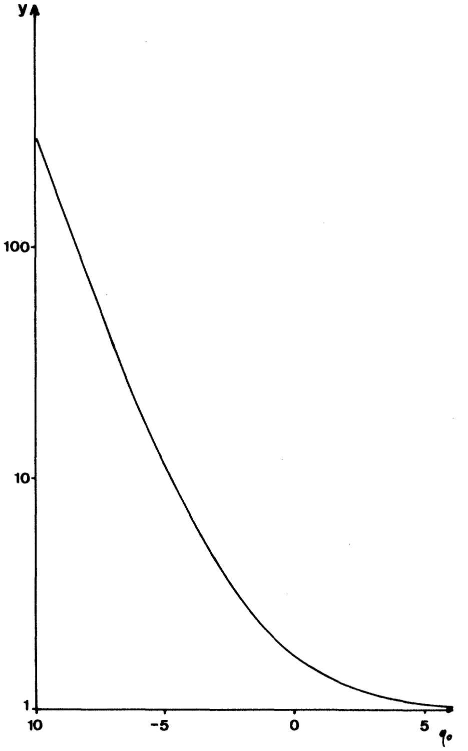

FIG. 3. Variation of degeneracy correction factor, y, from Eq. (13) with $\eta_0 = \Delta E_{cv}(T_e, T_L)/kT_e$, into the range of very high excitation, as during pulsed laser annealing, where the band gap becomes negative.

way they affect the magnitude of the exponential in Eqs. (1) and (8). They do not imply any crossing of eigenvalues.] Thus, pulsed laser annealing conditions can produce anomalously large variations to the thermodynamic band gap. Due to the enormous gradient in the plasma density resulting from the very short absorption lengths of the intense laser pulse, the gradient of the band gap may be very large indeed, of order 10^5 eV/cm (3 eV over 300 nm). As the band gap is smallest where the carriers are the densest and hottest, this field opposes the expansion of the plasma and may even produce negative carrier diffusion, i.e., produce plasma self-confinement. This point will be discussed further in a separate publication.[27]

Another interesting point to consider is the variation of the carrier concentration with time as the carriers do scatter emitting phonons and lose energy to the lattice. Of course, this causes a decrease in T_e and an increase in T_L. The former tends to make $[e_c][h_v]$ decrease through the density-of-states terms and the denominator of the exponential in Eq. (8). The latter tends to make this product of excited carrier concentrations increase through the $\Delta S_{cv}(T_L/k)$ term in the argument of the exponential. Returning to Fig. 1, we see that, particularly at temperatures below $\Theta/2$, ΔS_{cv} varies rapidly with T_L. If one considers progressively lower values of T_L, the lattice specific heat becomes progressively less. Then a given quantity of energy from the carrier system may produce a progressively larger increase in T_L with a relatively modest decrease in T_e. Thus, we may reach the amusing conclusion that, under certain conditions, a loss of energy from the carrier system will cause the concentration of excited carriers to increase, rather than decrease.

Let us investigate this point more quantitatively. For simplicity let us first treat the nondegenerate expression for $n^2=[e_c][h_v]$. We obtain (using $T =_{e,c} = T_{e,v} = T_e$)

$$\frac{\partial n^2}{\partial T_L}=\frac{n^2}{k}\frac{\partial \Delta H_{cv}}{\partial T_L}\left(\frac{1}{T_L}-\frac{1}{T_e}\right) , \tag{15}$$

and

$$\frac{\partial n^2}{\partial T_e}=\frac{n^2}{T_e}\left(3+\frac{\Delta H_{cv}}{kT_e}\right) . \tag{16}$$

Therefore,

$$\begin{aligned}\Delta(n^2)&=\frac{\partial n^2}{\partial T_L}\Delta T_L+\frac{\partial n^2}{\partial T_e}\Delta T_e\\&=\frac{n^2}{T_e}\left[\frac{\partial \Delta H_{cv}}{k\partial T_L}\left(\frac{T_e}{T_L}\right)\Delta T_L+\left(3+\frac{\Delta H_{cv}}{kT_e}\right)\Delta T_e\right] .\end{aligned} \tag{17}$$

Using Varshni's equation[28] and Thurmond's data,[2] we have

$$\frac{\partial \Delta H_{cv}}{\partial T_L}=\frac{2\alpha\beta^2 T_L}{(T_L+\beta)^3} , \tag{18}$$

with $\alpha=4.73\times10^{-4}$ eV/K $=5.49k$ and $\beta=636$ K for Si. Moreover,

$$\Delta T_e=-\Delta T_L\frac{C_L}{C_e} , \tag{19}$$

where C_L and C_e are the lattice and carrier specific heats. Around $T_L=100\,^{\circ}\mathrm{C}$ and at constant pressure, $C_L=0.81$ cal/g $=2.55R$ for Si.[29] For a free-electron gas at constant volume,

$$C_e=1.5R(\pi^2 kT_e/3\mu_e) , \tag{20}$$

where

$$\mu_e=\hbar^2/2m(3\pi^2 n)^{2/3} . \tag{21}$$

Let us make the most conservative estimate for Δn^2 by choosing the maximum plausible value of μ_e, which would obtain if all the $2\times10^{23}/\mathrm{cm}^3$ valence electrons would be participating in the gas, so $\mu_e=12.5$ eV and we find $C_e|_V=0.39R$. Then we would have $C_e|_P=1.39R$, the carrier specific heat at constant pressure, to be compared with the lattice specific heat $C_L=2.55R$. Then, evaluating Eq. (16) we find,

$$\Delta n^2=53\Delta T_L n^2/T_e , \tag{22}$$

i.e., while these extreme conditions remain, the loss of energy from the carrier system to the lattice causes the density of excited carriers to increase rather than decrease. Again, this is simply the result of increasing the vibronic degeneracy of the excited electronic states, which increases the probability that they be occupied.

Of course, degeneracy will generally have significant effect under the conditions relevant to this discussion. Physically, it is clear that an effect of degeneracy is to *increase* the magnitude of the phenomenon just discussed, whereby loss of energy from the carriers to the lattice causes the concentration of excited carriers to increase. This is simply because degeneracy decreases the rate of change of n^2 with T_e, and thus lessens the effect of decreasing T_e. However, the effect of increasing T_L with the transferred energy is to increase the number of vibronic states available, and thus serves to relieve the restriction of the exclusion principle.

Let us denote the correct value of $[e_c][h_v]$, taking degeneracy into account, as n^2/y, where y is defined in Eq. (13). If we then use the Ehrenberg approximation, Eq. (11), for the Fermi-Dirac function in order to take account of electronic degeneracy, then we find Eq. (16) should be modified to

$$\Delta\left(\frac{n^2}{y}\right)=\frac{n^2}{yk}\frac{\partial\Delta H_{cv}}{\partial T_L}\left(\frac{1}{T_L}-\frac{1}{T_e}\right)\left(1+\frac{f(\eta_0,\eta')}{y}\right)\Delta T_L+\frac{n^2}{yT_e}\left[3+\left(1+\frac{f(\eta_0,\eta')}{y}\right)\frac{\Delta H_{cv}}{kT_e}\right]\Delta T_e\ , \tag{23}$$

and

$$F(\eta_0,\eta')=\frac{1}{4}\left(4+\frac{\eta_0-\eta'}{\eta_0}\exp(-\eta')+\frac{\eta'}{\eta_0}\exp[-(\eta_0-\eta')]\right)\ . \tag{24}$$

$F(\eta_0,\eta')$ is always positive and becomes large when η_0 becomes large and negative, i.e., when the band gap becomes large and negative, as will occur under intense excitation, as in pulsed laser annealing. If the approximation of Eq. (12) were used, a much more complicated expression would be obtained, but the qualitative effect would be the same. The whole of the ΔT_L term, which causes an increase in carrier concentration would be multiplied by a factor greater than unity, while only a portion of the ΔT_e term, which causes a decrease in carrier concentration, is multiplied by the same factor. Note that the portion of that term which is multiplied by the factor is the smaller of the two under pulsed laser annealing conditions.

Note added in proof. Throughout this statistical-mechanical discussion it has been assumed that the eigenvalues and eigenfunctions of the electronic states are unaffected by the intense irradiation, the excitation of significant numbers of electrons, and the softening of the lattice. Of course, this is an approximation. Exchange interactions and free-carrier induced shifts of phonon frequencies will contribute to band-gap narrowing. Ferry gives a discussion of these effects[30] with reference to Ge subject to 4×10^8 W/cm^2 of 1.06-μm light. He finds these effects narrow the optical band gap by an amount of order 0.1 eV; he did not discuss the free-energy gap. If the exchange correction is only this large, then we are justified in neglecting this contribution to the total variation (several eV) in free-energy gap due to the statistical effects described herein. In any case, the two effects have the same sign and thus reinforce each other.

Some direct experimental evidence supporting the assumption that large changes in free-energy gap are concomitant with only small changes in optical-absorption edge, but large changes is the distribution of optical-absorption strength, has come to light since submission of this manuscript. Aydinli *et al.* determined the density of carriers excited during the pulsed laser annealing of Si on sapphire by measuring both the reflectivity and the transmission spectra (time resolved) and doing the Kramers-Kronig transform.[31] (See the Note added in proof to the following paper.) They measured excited carrier densities as high as 5×10^{22} cm^{-3} with a shift of the optical-absorption edge of only about 0.1 eV. With the Raman scattering measured lattice temperature of 300 °C, this corresponds to a carrier temperature of $kT_e=1.8$ eV and a free-energy gap of −6 eV.

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