USE OF INDIRECT TRANSITIONS IN SEMICONDUCTORS FOR THE DETERMINATION OF STATES WITH NEGATIVE ABSORPTION COEFFICIENTS

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The conditions for formation of negative temperature states in semiconductors have been obtained for indirect transitions of non-equilibrium carriers in the following two cases: a) indirect recombination of free carriers and b) indirect recombination from exciton states. Possible mechanisms of absorption of radiation are considered and the conditions for appearance of a negative absorption coefficient are derived by taking these processes into account.

INTRODUCTION

AT the present time, three different methods have been suggested to obtain states with negative temperature in semiconductors.[1-3]

The pulse method of obtaining such states[1] is based on the essential difference in the recombination time and the slowing-down time of non-equilibrium carriers inside the band.[4] The conditions for the appearance of states with negative temperature in this method are: a long lifetime of non-equilibrium carriers, high densities of excitation, and low temperature of the specimen.[5] All this strongly limits the selection of superconducting materials and produces a series of technical difficulties.

A method was suggested by Lax[2] of obtaining states with negative temperature in superconductors, based on the non-equidistance of the Landau levels in strong magnetic fields. The comparatively short relaxation times of the non-equilibrium carriers for these levels makes difficult the production of states with negative temperature by this method.

In the present paper a method of producing states with negative temperature in semiconductors, which was earlier suggested by the authors,[3] is investigated in detail. To accomplish this method, as will be shown, comparatively low excitation densities are required.

1. CONDITIONS FOR ESTABLISHING NEGATIVE TEMPERATURES FOR INDIRECT TRANSITIONS

Indirect transitions in semiconductors represent a recombination process or the formation of current carriers — electrons and holes — with simultaneous emission or absorption of a photon and phonons. The long wavelength edge of the absorption band for interband transitions in certain semiconductors (for example, in germanium and silicon) corresponds to precisely such processes, owing to the structure of the fundamental bands.[6,7] In these semiconductors, the minimum energy in the conduction band and the maximum energy in the valence band correspond to different values of the quasimomentum of the electron. It is obvious that the longest wavelength radiation corresponds to a transition of the electron from the minimum of the conduction band to the maximum of the valence band with the emission of a phonon.* The simultaneous absorption of a photon and a phonon is opposite in behavior to the process mentioned above.

If the temperature cf the specimen is sufficiently low, and the phonons necessary for the inverse transition are absent, then the absorption of the long wavelength radiation under consideration will be small. Therefore, one can expect in this case that for comparatively small increase in the carrier concentration (in comparison with the equilibrium value) the occurrence of a state with negative temperature relative to the given transition is possible.

We shall consider this process in more detail. The number of transitions per unit time with simultaneous emission of a photon and a phonon is equal to

$$I^+ = W(n_r+1)(\varphi+1)f_e(\varepsilon_e)f_h(\varepsilon_h), \quad (1)$$

*We shall not consider many-phonon processes since their relative probability is small.

where W is the transition probability, n_r and φ are, respectively, the number of photons and phonons in the given state, $f_e(\epsilon_e)$ and $f_h(\epsilon_h)$ are distribution functions of the electrons in the conduction band and of the holes in the valence band. The number of transitions with absorption of a photon and a phonon is equal to

$$I^- = Wn_r\varphi\,[1 - f_h(\varepsilon_h)]\,[1 - f_e(\varepsilon_e)]. \tag{2}$$

The energy of the electron ϵ_e and of the hole ϵ_h are connected by the law of conservation of energy with that of the photon $\hbar\omega_r$ and of the phonon $\hbar\omega_f$ through the equation

$$\varepsilon_e + \varepsilon_h + \Delta - \hbar\omega_r - \hbar\omega_f = 0, \tag{3}$$

where Δ is the minimum width of the forbidden band. In the state of thermodynamic equilibrium, $I^+ - I^- = 0$, which holds if we insert the corresponding thermodynamic equilibrium distributions for n_r, φ, f_e and f_h in (1) and (2).

In order that the system be in a state with negative temperature, it is necessary to disrupt the thermodynamic equilibrium so that the induced emission exceeds the absorption, which leads to the condition

$$(\varphi + 1)\,f_e(\varepsilon_e)\,f_h(\varepsilon_h) - \varphi\,[1 - f_h(\varepsilon_h)]\,[1 - f_e(\varepsilon_e)] > 0. \tag{4}$$

Taking the temperature of the lattice equal to T° K, we get from (4)

$$f_e(\varepsilon_e)\,f_h(\varepsilon_h)\,[1 - f_h(\varepsilon_h)]^{-1}\,[1 - f_e(\varepsilon_e)]^{-1} > e^{-\hbar\omega_f/kT} \tag{5}$$

In the case in which there is no degeneracy of the free carriers, Eq. (5) is simplified:

$$f_e(\varepsilon_e)\,f_h(\varepsilon_h) > e^{-\hbar\omega_f/kT} \tag{6}$$

The electron and hole distribution functions which enter on the left side of Eq. (6) can be found by solution of the kinetic equation with account of the production of carriers by an external source, by the process of their slowing down, and by recombination. The slowing down of non-equilibrium carriers has been investigated previously,[4] where it was shown that the time for establishing thermal equilibrium between the lattice and the non-equilibrium carriers is small and, for germanium and silicon, has a magnitude of the order of 10^{-10}sec, which is significantly less than the lifetimes of the non-equilibrium carriers in these materials. Therefore, it can be assumed that the electrons and holes inside the corresponding bands have a Boltzmann distribution (no degeneracy) with a crystal temperature T. Carrying out integration on the left side of (6) over the range $\sim kT$ of energies of electrons and holes, we get the following inequality for the concentration of electrons n and of holes p:

$$np > n_{\text{eff}}\,p_{\text{eff}}\,e^{-\hbar\omega_f/kT}, \tag{7}$$

where

$$n_{\text{eff}} = 2\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2} \approx 4.8\cdot 10^{15}\left(\frac{m_e}{m}T\right)^{3/2}, \quad p_{\text{eff}} = 2\left(\frac{m_h kT}{2\pi\hbar^2}\right)^{3/2}.$$

(We note that we have $n_0p_0 = n_{\text{eff}}p_{\text{eff}}e^{-\Delta/kT}$ for the equilibrium values $n = n_0$, $p = p_0$). The conditions (7) are easily established in germanium and silicon at a temperature of $T \sim 10°$ K, since they require that $np > 10^{22}$ ($\hbar\omega_f \sim 0.03$ ev).

We now consider the conditions for the generation of a negative temperature for indirect transitions from exciton states. The density of electrons ν_0 in the state of thermodynamic equilibrium can be determined from the condition[8] $\mu_\nu = \mu_e + \mu_h = 0$ (μ_ν, μ_e, μ_h are the chemical potentials of excitons, electrons and holes, respectively), which leads to the expression

$$\nu_0 = \nu_{\text{eff}}\exp\left\{-\frac{\Delta - U_\nu}{kT}\right\}, \tag{8}$$

or, if there is no degeneracy of free carriers,

$$\nu_0 / n_0p_0 = \tfrac{1}{4}\,(m_\nu / m_e m_h)^{3/2}\,(2\pi\hbar^2/kT)^{3/2} e^{U_\nu/kT},$$

where U_ν is the binding energy of the exciton ($U_\nu > 0$), m_ν is the effective mass of the exciton, and $\nu_{\text{eff}} = (m_\nu kT/2\pi\hbar^2)^{3/2}$. The conditions for the production of a negative temperature for the indirect transition from the exciton state leads to the inequality

$$\nu > \nu_{\text{eff}}\,e^{-\hbar\omega_f/kT}. \tag{9}$$

Assuming that the additional carriers formed by the external source are in thermal equilibrium with the crystal lattice and with the exciton states of electrons and holes (which is valid, inasmuch as the probability of formation of an exciton is large in comparison with the probability of its recombination), we get for the non-equilibrium concentration of excitons

$$\nu = \nu_{\text{eff}}\,(pn / p_{\text{eff}}n_{\text{eff}})\,e^{U_\nu/kT}. \tag{10}$$

In this case, the condition for formation of a negative temperature takes the form

$$pn > p_{\text{eff}}n_{\text{eff}}\exp\left\{-\frac{\hbar\omega_f + U_\nu}{kT}\right\}, \tag{11}$$

which practically coincides with (7).

2. INDIRECT INTERBAND TRANSITIONS AND ABSORPTION OF RADIATION BY FREE CARRIERS

As was noted earlier,[5] the condition for formation of a negative absorption coefficient in a medium which is in a state with negative temperature

relative to the transition under consideration is that the radiation induced by a light quantum propagating in the medium exceed the absorption of this quantum by the other levels of the system which are in a state with positive temperature.

The probability W_{ij} of indirect recombination of an electron in the state i with a hole in the state j with radiation of a photon was considered by Dumke.[9] This probability takes into account both the absorption of the phonon and its emission; however, it is evident that at the lattice temperature for which $kT \ll \hbar\omega_f$ the probability of transition with absorption of the phonon $\hbar\omega_f$ is small.

The total number of radiative transitions in a unit volume of a crystal with emission of a light quantum of frequency ω_r per unit time is equal to

$$dn/dt = \sum_{ij} W_{ij} f_e(\varepsilon_i) f_h(\varepsilon_j). \quad (12)$$

Summation in (12) should be carried out only over such values of i and j which are consistent with the conservation of energy:

$$\varepsilon_i + \varepsilon_j + \Delta = \hbar\omega_r + \hbar\omega_f. \quad (13)$$

Proceeding to a continuous spectrum, and taking into account radiation in this case for the range of frequencies from ω_r to $\omega_r + \Delta\omega$ we get the following expression for the number of quanta N radiated as a result of induced transitions per unit time in a unit volume of the specimen:

$$\left(\frac{dN}{dt}\right)^+ = n_r \hbar \Delta\omega \int W_{ij}(\varepsilon_i, \varepsilon_j) f_e(\varepsilon_i) f_h(\varepsilon_j) \rho(\varepsilon_i) \rho(\varepsilon_j) d\varepsilon_i, \quad (14)$$

where $\rho(\epsilon)$ is the density of states per unit energy interval, n_r the average number of quanta per radiation oscillator with frequency ω_r, and

$$N = \int_{\omega}^{\omega+\Delta\omega} n_r \rho(\omega) d\omega \approx n_r \rho(\omega) \Delta\omega.$$

In Eq. (14), ϵ_j takes on the values determined by Eq. (13). In the absence of degeneracy, and if the electrons and holes inside the corresponding bands are in thermal equilibrium with the lattice, but have non-equilibrium concentrations n and p, integration in (14) gives

$$\left(\frac{dN}{dt}\right)^+ = n_r \overline{W}_{ij} \frac{4np}{\pi kT} e^{-y} y^2 \frac{\Gamma^2(3/2)}{\Gamma(3)} \hbar\Delta\omega, \quad (15)$$

where $\overline{W}_{ij}$ is the mean value of the transition probability and

$$y = (\hbar\omega_f + \hbar\omega_r - \Delta)/kT.$$

The question of the line shape of spontaneous emission of a system which has the form

$$J(\omega) \sim \left(\frac{\hbar\omega_r + \hbar\omega_f - \Delta}{kT}\right)^2 \exp\left\{-\frac{\hbar\omega_r + \hbar\omega_f - \Delta}{kT}\right\} \quad (16)$$

is solved by Eq. (15).

Thus the maximum intensity of spontaneous radiation corresponds to the frequency determined by the condition

$$\hbar\omega_r = \Delta + 2kT - \hbar\omega_f,$$

and the width of the spontaneous radiation line is $\sim kT$.

Absorption of radiation in the case that we have considered will be principally determined by the absorption by free current carriers, whose investigation has been treated in a number of works.[10-12] The change in the number of quanta per unit volume as a result of absorption by the free carriers is determined by the equation

$$(dN/dt)^- = -\varkappa cN, \quad (17)$$

where c is the velocity of light in the material, and the absorption coefficient κ is equal to $\kappa = n\sigma_e + p\sigma_h$ (σ_e and σ_h are cross sections for the absorption of the photon by the electron and hole).

The condition for the formation of a negative coefficient of absorption gives

$$(dN/dt)^+ > (dN/dt)^-. \quad (18)$$

If we substitute here value $(dN/dt)^{\pm}$ from Eqs. (15) and (17), the condition for the appearance of a negative absorption coefficient takes on the form

$$\overline{W}_{ij} \hbar\lambda^2 npe^{-y} y^2 / 8kTD\,(n\sigma_e + p\sigma_h) > 1, \quad (19)$$

where λ is the wavelength of the radiation in vacuum, and D the dielectric constant of the material. One can express the averaged probability $\overline{W}_{ij}$ in terms of the spontaneous radiation lifetime τ_R relative to the indirect transition at the temperature of interest to us:

$$\tau_R^{-1} = \overline{W}_{ij}(n_0 + p_0). \quad (20)$$

In the case in which $n\sigma_e > p\sigma_h$, the condition (19) gives

$$p > 8kTD\sigma_e / \hbar\lambda^2 e^{-y} y^2 \overline{W}_{ij}. \quad (21)$$

For $n\sigma_e < p\sigma_h$, we must make the substitution $p \rightarrow n$, $\sigma_e \rightarrow \sigma_h$ in (21). An estimate made by Eq. (21) for germanium at $\lambda \sim 10^{-4}$ cm, $D \sim 10$, $T \sim 4°$K, $\tau_R \sim 0.75$ sec[9]* (for $n \sim 2.4 \times 10^{13}$ cm^{-3}), $\sigma_e \sim 10^{-19}$ cm^2,[11] gives the condition $p > 5 \times 10^{15}$ cm^{-3} for the concentration of non-equilibrium carriers. If it is assumed that the absorption coefficient of the generated light is $\sim 10^3$ cm^{-1} and the

*The quantity τ_R was given in reference 9 for $T \sim 300°$K; it is more correct to take τ_R at 4°K.

lifetime of the non-equilibrium carriers is $\sim 10^{-4}$ sec, the inequality given above will be satisfied for an excitation density $i > 5 \times 10^{16}$ quanta/cm^2-sec, which is practically attainable. However, the lifetime for such high excitation densities will be much less than 10^{-4} sec, which requires high excitation density, and consequently, difficulties of cooling the specimen arise. Therefore, from our point of view, a more appropriate method of obtaining the negative absorption coefficient lies in processes connected with indirect transitions from exciton states.

3. INDIRECT TRANSITIONS FROM EXCITON STATES

We now consider the condition of formation of a negative absorption coefficient in the case of indirect transitions from exciton states, when the criteria for generation of a negative temperature (9) are satisfied. In this case, the absorption of radiation takes place as a result of ionization of the exciton by the photon into an electron and hole (absorption by impurities and by the lattice will be considered later).

Let the lifetime of the exciton relative to radiation decay in the range of radiation frequencies from ω_r to $\omega_r + \Delta\omega$ be equal to τ. Then the number of quanta N produced by induced radiation per unit volume is determined by the equation

$$(dN/dt)^{+} = n_{\omega}\nu/\tau. \tag{22}$$

On the other hand, the number of quanta absorbed per unit volume of the specimen is equal to

$$(dN/dt)^{-} = -c\sigma_i\nu N, \tag{23}$$

where σ_i is the cross section for ionization of an exciton by the photon. The conditions for production of a negative absorption coefficient lead to the inequality

$$\sigma_i < \lambda^2/4D\Delta\omega\tau. \tag{24}$$

Numerical estimates for this case in silicon[13] at $\lambda \sim 10^{-4}$ cm, $D \sim 10$, $\Delta\omega \sim 10^{12}$ sec^{-1} and $\tau \sim 10^{-5}$ sec give

$$\sigma_i < 0.25\cdot 10^{-16}\ \text{cm}^2. \tag{25}$$

The photo-ionization cross section of the exciton* is evidently less than the quantity on the right side of the inequality (25), so that the conditions for producing a negative absorption coefficient in transitions from exciton states are satisfied in this case.

*The exciton photo-ionization cross section can be estimated from the formula for ordinary photoeffect in the atom.[14] In this case, the inequality (25) is satisfied by a wide margin. Evidently, the more probable process is the photo-ionization of the exciton with emission of a phonon, a process whose cross section is equal in order of magnitude to the cross section of absorption by free carriers.

It is easy to estimate the role of absorption of radiation by impurities and by the lattice. Actually, the number of quanta absorbed per unit time per unit volume is equal to

$$(dN/dt)^{-} = -c\varkappa_c N, \tag{26}$$

where κ_c is the coefficient of absorption of radiation by the lattice and by impurities for wavelengths corresponding to the indirect transition. To obtain a negative absorption coefficient from (22) and (26), we shall determine the condition for the concentration of excitons:

$$\nu > 4D\Delta\omega\tau\lambda^{-2}\varkappa_c. \tag{27}$$

A numerical estimate by means of the values of parameters used in (25) gives

$$\nu > 4\cdot 10^{16}\varkappa_c. \tag{28}$$

The width of the radiation line of the exciton, $\Delta\omega$, which enters into the expressions (24) and (27), is determined by the temperature of the specimen and is of the order kT. Upon lowering the temperature, $\Delta\omega$ is decreased, which improves the condition for obtaining a negative absorption coefficient.

CONCLUSION

The investigation carried out above shows that the methods considered in the present research for obtaining states with negative temperature arise in the case of comparatively low concentrations of non-equilibrium current carriers, which is connected with a significant decrease in the probability of absorption at low temperature in indirect transitions. The concentrations of carriers necessary for the production of the negative temperature can be obtained relatively easily by experiment. The low concentrations of carriers make it possible to expect the possibility of obtaining negative temperatures in semiconducting specimens not only under pulse conditions but also in continuous operation.

The production of states with negative temperature can evidently also be observed in the absence of amplification of the light passing through the specimen (when the probability of absorption of quanta by free carriers exceeds the probability of induced radiation) by the narrowing of the width of the spectral line as a consequence of regeneration. The total amplification of radiation of quanta

passing through the specimen can in principle always be obtained for certain concentrations of carriers, inasmuch as absorption by free carriers increases linearly with concentration, while radiation is proportional to the square of the concentration. However, the concentrations of free carriers necessary to obtain amplification of radiation appreciably exceed the concentrations necessary for formation of negative temperature. Therefore the creation of such concentrations requires additional investigation of the problem connected with the cooling of the specimen at high intensity of exciting radiation, although this difficulty is not one of principle, inasmuch as a changeover to pulse excitation with sufficiently short pulses is always possible.

To obtain amplification of radiation for exciton transitions, lower densities of excitation are required because of the significant increase in the radiation probability which removes the difficulties associated with heating of the specimen.

The shape of the line obtained in Sec. 2 shows that its figure of merit is of the order of $\hbar\omega_r/kT$ and has a value of $\sim 10^3$ for a temperature of $T \sim 10°$K. Using a magnetic field, one can change the frequency of radiation by an amount of order $\Delta\omega \approx eH/mc$,[15] which, for example, at fields of $H \sim 10^4$ oe amounts to 10 percent of the frequency of radiation for germanium. Thus, a change in the magnetic field can be a very useful method for changing the frequency of quantum generators and amplifiers using indirect transitions in semiconductors.

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202