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Far-Infrared Active Media Based on Shallow Impurity State Transitions in Silicon

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Two mechanisms of the inverse population of shallow impurity states in silicon under optical pumping have been proposed and analyzed, using a procedure allowing to reduce the number of required matrix elements of transitions. The first mechanism is based on the resonance interaction of the $2p_0$ state in Si:Bi with optical phonons. The other one is based on the suppression of acoustic-phonon-assisted relaxation from the $2p_0$ state in Si:P due to the momentum conservation law. Spontaneous emission was registered from shallow donors in Si:P under photoionization by a CO_2 laser. The dependence of the spontaneous emission intensity on the intensity of pumping radiation confirms the possibility of amplification on impurity transitions.

Introduction. The interest in far-infrared (FIR) active media based on shallow impurity states in silicon is caused by two reasons. The first one is the low level of lattice absorption of FIR radiation in silicon. The second is the cascade character of the main relaxation processes along the excited coulombic impurity states [1], allowing to expect high efficiency of pumping of impurity excited states population, which is important for reaching continuous lasing. Cascade relaxation means that transitions with a small reduction of carrier energy are predominating, and the probability that a heated carrier takes part in the amplification is rather high when one of the first excited states or the group of excited states within the step of phonon relaxation are inversely populated.

On the other hand, the fast acoustical-phonon-assisted relaxation causes the main complication in obtaining the inverse population of impurity states, since it tends to form the equilibrium distribution at lattice temperature. Thus, the inverse population of impurity states implies conditions in which the distribution is formed by processes with threshold character (interaction with optical phonons, optical pumping) and being faster than acoustical-phonon-assisted and Auger processes, or it implies conditions, where the latter are suppressed for particular states. The other complication originates from the fact that absorption for impurity transitions lies in the same frequency region as possible amplification and thus can prevent it. Hence the possibility of amplification depends on the details of nonequilibrium distribution of charge carriers over excited impurity states.

Calculation of Impurity States Population. The calculation of the nonequilibrium impurity states population generally requires the knowledge of numerous matrix elements of transitions between various excited impurity states for different interactions. Solving the system of rate equations for the first several impurity levels is not a correct procedure,

since upper excited states, with density growing fast for smaller binding energies, play a significant role in the forming of lower level population, even when the former are slightly populated, because of the fast transition rates between such states. A procedure is proposed for the calculation of stationary impurity states population, which allows to extract the limited number of transition matrix elements essential for the population of appropriate states. Impurity states are described by the probabilities P_{ijk} that a carrier from the state i reaches the state j before coming to the state k. Instead of solving the system of rate equations for level populations, we solve the system of following equations:

$$P_{ijk} = \frac{\mathbf{W}_{ij} + \sum\limits_{l \neq i,j,k} \mathbf{W}_{il} P_{ljk}}{\sum\limits_{l} \mathbf{W}_{il}} , \tag{1}$$

where W_{jk} are the transitions rate from j- to k-state. The ratio of populations is expressed in terms of probabilities in the following way:

$$\frac{N_k}{N_j} = \frac{W_{jk}^{\text{net}}}{W_{kj}^{\text{net}}} , \tag{2}$$

$$W_{jk}^{\text{net}} = W_{jk} + \sum_{i \neq k,j} \mathbf{W}_{ji} P_{ikj} , \tag{3}$$

where W_{jk}^{net} is the total rate of moving from state j to state k including different possible ways of transitions through the ladder of impurity states. The probabilities of such kind were first introduced by Lax [1] in cascade capture theory as "sticking probabilities" – the probabilities that the electron from a particular state will enter the ground state before escaping – and were calculated assuming that they depend on the impurity level but not on how it was reached. Although the supposition was made by Pickin [2] that the relations of Lax for the sticking probabilities are not explicit, it was found out now that in the present formulation the equations for sticking probabilities from different states to the i-th state are explicit and thoroughly equivalent to the system of rate equations. This is clearly seen from the fact that the matrix of the coefficients of the above system is exactly the transposed matrix of the system of correspondent rate equations,

$$0 = \frac{\partial N_i}{\partial t} = \sum_{l \neq i} N_l \mathbf{W}_{li} - N_i \sum_{l \neq i} \mathbf{W}_{il} , \tag{4}$$

with terms containing N_k and N_j transferred to the left-hand part. At the same time, the formulation in terms of probabilities is more convenient, since it allows to reduce the number of required matrix elements on the base of an analysis of the probabilities of different routs for an excited carrier through the ladder of excited states. Taking into consideration the specific character of cascade processes, which are going predominantly through the neighboring lower excited states, we have found out that only few matrix elements are needed for calculation of ratios of their population.

Population of higher excited states and conduction band states was calculated using the quasiclassical approach [3], which is appropriate for impurity states with energy separation less than the characteristic energy of the emitted acoustical phonon. Within the frame of this approach, the density of impurity states is considered to be a continuous function of energy; the distribution of carriers is described by the Boltzmann equation and is considered to depend only on the total energy E of electrons in the field of

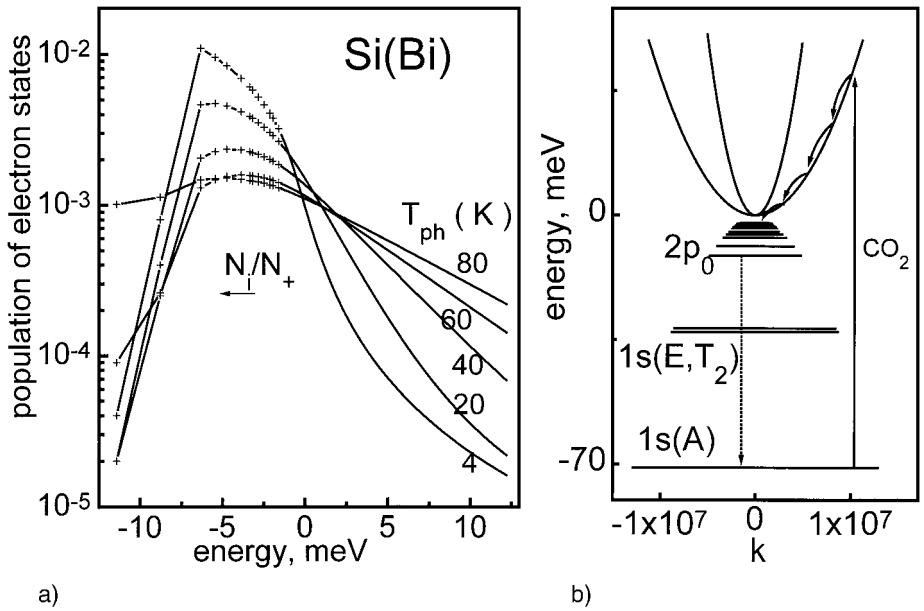

Fig. 1. a) Occupation probabilities of free-electron states and the concentration of electrons at impurity levels N_i divided by the concentration of charged donors N_+ (crosses) in Si:Bi for pumping intensity of CO_2-laser $I = 100\,\mathrm{W/cm^2}$, doping concentration $N_{Bi} = 10^{16}\,\mathrm{cm^{-3}}$, and compensation level 1%. b) Scheme of transitions in Si:Bi under optical pumping by a CO_2-laser

the attractive centers. This approach allows to determine the overlap of the orbits of the neighboring centers by averaging the Boltzmann equation in the phase space layer between $E = \mathrm{const}$ and $E + \mathrm{d}E = \mathrm{const}$, considering the distribution of attractive centers to be uniform. The influence of the discrete character of the first excited impurity states spectrum on the carrier distribution is determined by using the ratio of impurity states population, calculated with the probabilities technique described above, as a boundary condition for the quasiclassical distribution function.

Inverse Population of Impurity States in Si:Bi and Si:P. Two mechanisms of the inverse population of shallow impurity states in silicon have been proposed and analyzed.

The first one (see Fig. 1b) is realized in Si:Bi under the conditions of optical pumping. The resonance interaction with optical phonons of the $2p_0$ donor state [4] causes the depletion of this state, while the population of higher excited states, formed mainly by the relaxation due to interaction with acoustical phonons, is higher under the conditions of optical pumping. The calculation of impurity states population was performed using the procedure described above in the simplified model of a nondegenerate parabolic spherical band with an effective mass providing the same density of states as in the real conduction band minima, $m_h = 0.33m_0$ (m_0 is the mass of the free electron). The rates of acoustical-phonon-assisted transitions were estimated within a hydrogen-like center model [5], the rate of optical-phonon-assisted transition from $2p_0$ state was estimated from the lineshape of $1s \rightarrow 2p_0$ optical transitions [4]. It is shown that under the conditions of optical pumping the inverse population is realized (Fig. 1) on the

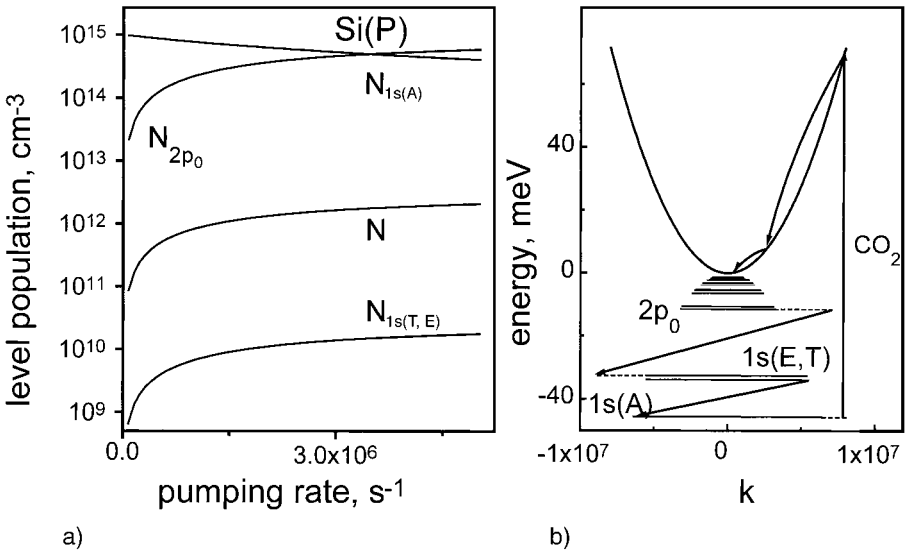

Fig. 2. a) Calculated populations of 1s(A), 1s(E, T), and $2p_0$ donor states in Si:P and free-electron concentration N versus optical pumping rate for lattice temperature $T = 4.2$ K, doping concentration $N_P = 10^{15}$ cm^{-3}, and compensation level 1%. b) Scheme of transitions in Si:P under optical pumping by a CO_2-laser

transitions leading to the $2p_0$ Bi-donor states from higher excited impurity states and continuum states with energies $E \leq kT$ as well, with lattice temperatures $kT \leq E_{op}/\ln(\nu_{op}/\nu_{oi})$, where E_{op} is the energy of the optical phonon, ν_{op} and ν_{oi} are the rates of transition from $2p_0$ state due to optical phonon spontaneous emission and optical ionization from the ground state, respectively. An amplification up to 2 cm^{-1} is expected in the frequency range of 25 to 100 cm^{-1} for pumping intensities of the CO_2-

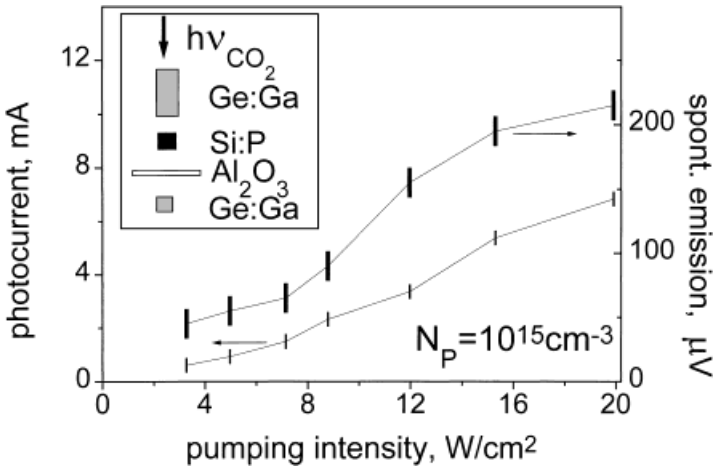

Fig. 3. Experimental dependencies of photocurrent and spontaneous emission versus pumping intensity; inset: experimental set-up scheme

laser $I \geq 100$ W/cm^2, concentration of Bi-donor centers $N_d \approx 10^{16}$ cm^{-3}, and lattice temperatures $kT \leq 60$ K.

The other mechanism of excited states overpopulation (see Fig. 2b) is based on the suppression of the acoustical-phonon-assisted relaxation from deep impurity states due to the momentum conservation law. In the case of Si:P, the inversion population of the $2p_0$ state (Fig. 2) is expected under photoionization by CO_2 laser radiation. The lifetime of the P-donor $2p_0$ state was estimated from the saturation of optical $1s(A) \rightarrow 2p_0$ transition $\tau_{2p_0} = 3 \times 10^{-7}$ s [6]. Far-infrared (168 to 180 cm^{-1}) amplification (0.3 cm^{-1}) on $1s(E) \rightarrow 2p_0$ and $1s(T) \rightarrow 2p_0$ optical transitions is expected for doping concentration $N_D \approx 10^{15}$ cm^{-3} for cryogenic temperatures ($kT \leq 10$ K) under 10 W/cm^2 CO_2 laser radiation density, considering the photoionization cross-section $\sigma = 2 \times 10^{-16}$ cm^2 for $\lambda = 10.6$ μm.

Experimental Set-Up and Results. Spontaneous emission was registered from shallow donors in silicon (Si:P) under photoionization by a CO_2-laser ($\lambda = 10.6$ μm).

The scheme of the experimental set-up is presented in the inset of Fig. 3. A silicon sample ($V = 5 \times 5 \times 5$ mm^3), with doping concentration $N_P \approx 10^{15}$ cm^{-3} and B compensation on the level $N_B \approx 10^{13}$ cm^{-3}, and a Ge:Ga photodetector, with acceptor concentration $N_{Ga} \approx 10^{14}$ cm^{-3} and dimensions $V = 4 \times 3 \times 1$ mm^3, were introduced in liquid He. Photoexcitation was provided on the wavelength 10.6 μm with a pulse duration of 3 to 10 μs and a repetition rate of 150 to 50 Hz, correspondingly. The maximum power density was about 20 W/cm^2 (10^{21} quants/cm^2 s). The influence of CO_2 laser radiation on the photodetector was prevented by the sapphire filter, and the room-temperature background far-infrared radiation was cut by the Ge:Ga filter with appropriate doping concentration.

The measured dependencies of the photocurrent under bias voltage 30 V/cm and of the spontaneous emission intensity from Si:P on the photoexcitation power are presented in Fig. 3. Taking into account the electron mobility $\mu = 3 \times 10^4$ cm^2/Vs (see [7]), the estimated photoelectron concentration does not exceed $n = 2 \times 10^{11}$ cm^{-3}, that is much less than the compensation level. Considering the capture rate $W_r \approx 0.7 \times 10^9$ s^{-1} (the corresponding pumping rate is $W_p \approx 1.4 \times 10^5$ s^{-1}), the electron concentration captured on $2p_0$ state can be estimated as $N_{2p_0} \approx 4 \times 10^{13}$ cm^{-3}. For the amplification cross-section $\sigma = 10^{-14}$ cm^2 [8] on $1s(E, T) \rightarrow 2p_0$ optical transitions, a spontaneous emission amplification of about 0.4 cm^{-1} is expected. This fact can explain the nonlinear enhancement of the spontaneous emission signal on the pumping power.

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References

[1] M. Lax, Phys. Rev. **119**, 1502 (1960).
[2] W. Pickin, Phys. Rev. B **20**, 2451 (1979).
[3] V.N. Abakumov, V.I. Perel, and I.N. Yassievich, Nonradiative Recombination in Semiconductors, North-Holland Publ. Co., Oxford 1991.
[4] N.R. Butler, P. Fisher, and A.K. Ramdas, Phys. Rev. B **12**, 3200 (1975).
[5] G. Ascarelly and S. Rodriquez, Phys. Rev. **124**, 1321 (1961).
[6] K. Geerinck, Doctor degree thesis, Technical University of Delft (1995).
[7] F.J. Morin and J.P. Maita, Phys. Rev. **96**, 28 (1954).
[8] A.K. Ramdas and S. Rodriguez, Rep. Progr. Phys. **44**, 1297 (1981).