Thermally induced hole-electron competition in photorefractive InP:Fe due to the Fe2+ excited state

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The photorefractive coupling gain is limited in InP:Fe even if there is no direct hole-electron competition. One has to take into account the excited state of Fe^{2+} ($^5T_2$) with its strong thermal emission ($1/\beta_{th} \simeq 100$ ns). This leads to an indirect hole-electron competition mechanism and helps to explain experimental results. This coupling gain reduction is inherent to the nature of the Fe dopant in InP for wavelengths below 1.2 μm and temperature above 170 K.

Photorefractive two-wave mixing is an important phenomenon especially for optical processing.[1] Many studies for the enhancement of the photorefractive gain in III-V materials are developed in this context.[2–4] The photorefractive effect for semi-insulating InP:Fe is described by charge redistribution after photoexcitation from a single active center $[Fe^{2+}/Fe^{3+}]$ coupled with both conduction and valence bands. This hole-electron competition leads to a lowering of the gain compared with what would be obtained with a single charge carrier.[5,6] We have conducted two-wave mixing experiments on an InP:Fe sample grown at CNET Lannion for which the electron contribution should be negligible. Indeed, for a sample from the same boule, electron paramagnetic resonance (EPR) and secondary-ion mass spectroscopy (SIMS) measurements[7] gave Fe^{3+} density: $[Fe^{3+}] \simeq 8\times10^{16}$ cm^{-3} and a total iron density $[Fe] \simeq 7\times10^{16}$ cm^{-3}. This indicates the accuracy of these measurements and gives hints on the Fe^{2+} density: $[Fe^{2+}] \leqslant 10^{16}$ cm^{-3}. Similar concentrations have been obtained in our sample in cross measurements.[8] The photoionization cross sections for holes (S_p) and electrons (S_n) are related by $S_n \simeq S_p/10$, with $S_p \simeq 5\times10^{-17}$ cm^2.[9] If we now split the total absorption α_T into electron (α_n) and hole (α_p) contributions, one gets $\alpha_n = S_n\,[Fe^{2+}] \ll \alpha_p = S_p\,[Fe^{3+}]$. Consideration of the expression for the photorefractive gain[5] Γ implies that in our sample the photorefractive effect is mainly due to holes. To our surprise the measured photorefractive gain is much smaller than expected; in these experiments we have used a cw Nd:YAG laser ($\lambda = 1.064$ μm). It is interesting to remark that in diffraction experiments lower efficiencies were also reported.[10] Previous analyses did not consider the excited state of Fe^{2+}. Photoluminescence,[11] deep level optical spectroscopy (DLOS), and deep level transient spectroscopy (DLTS)[12,13] have shown that Fe^{2+} exists under two states: the ^5E ground and the $^5T_2$ excited states. The latter is located 0.35 eV above the ^5E level and is named here Fe^{2+*}. The energy diagram is shown in Fig. 1.[14] To get a physical insight of the influence of this excited state on the photorefractive effect in InP:Fe, we first neglect electron photoionization ($\alpha_n \ll \alpha_p$). Photogeneration of holes changes Fe^{3+} to Fe^{2+} and Fe^{2+*} with photoionization cross sections of the same order of magnitude.[12] The Fe^{2+*} level is quickly emptied by thermal emission of electrons giving rise to a new process of hole-electron competition reducing the photorefractive gain. This is illustrated by the following relations:

$$Fe^{3+} \xrightarrow[h\nu]{} \begin{cases} Fe^{2+} + p_{VB} \xrightarrow{\text{thermal}} Fe^{3+} + n_{CB} + p_{VB}, \\ Fe^{2+*} + p_{VB} \end{cases}$$

To establish the expression of the photorefractive gain we have extended Kukhtarev's model[15] considering both photogeneration and thermal emission of electrons and holes from Fe^{3+}, Fe^{2+}, Fe^{2+*}. In the following, N_T represents the total iron density, N corresponds to $[Fe^{3+}]$, N^* to $[Fe^{2+*}]$, and N_T-N-N^* to $[Fe^{2+}]$. The electron and hole current densities are $\mathbf{j}_n$, $\mathbf{j}_p$ and the free hole and electron densities p and n. $\mathbf{E}$ is the electric field induced by charge redistribution in the crystal. The material equations are

$$\frac{\partial N}{\partial t} = (\beta_n + S_n I)(N_T - N - N^*) - \gamma_n n N + (\beta_n^* + S_n^* I) \times N^* - \gamma_n^* n N - (\beta_p + S_p I) N + \gamma_p p \times (N_T - N - N^*) - (\beta_p^* + S_p^* I) N + \gamma_p^* p N^*$$

$$\frac{\partial N^*}{\partial t} = -(\beta_n^* + S_n^* I) N^* + \gamma_n^* n N + (\beta_p^* + S_p^* I) N - \gamma_p^* p N^*$$

$$\mathbf{j}_n = e n \mu_n \mathbf{E} + \mu_n k_B T \overrightarrow{\text{grad}}\, n$$

$$\mathbf{j}_p = e p \mu_p \mathbf{E} - \mu_p k_B T \overrightarrow{\text{grad}}\, p$$

$$\frac{\partial n}{\partial t} = \text{div}\, \mathbf{j}_n / e + (\beta_n + S_n I)(N_T - N - N^*) - \gamma_n n N + (\beta_n^* + S_n^* I) N^* - \gamma_n^* n N$$

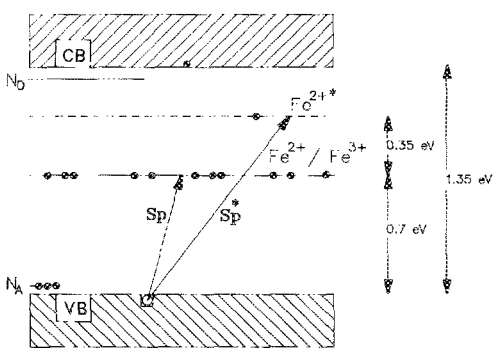

FIG. 1. Energy diagram for InP:Fe at room temperature.

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$$\frac{\partial p}{\partial t} = -\operatorname{div} \mathbf{j}_p/e + (\beta_p + S_p I)N - \gamma_p p(N_T - N - N^*) + (\beta_p^* + S_p^* I)N - \gamma_p^* p N^*$$

$$\operatorname{div} \mathbf{E} = (-e/\epsilon)(N_T - N - N_D + n - p).$$

I is a spatially modulated illumination (photon current in $s^{-1}\,cm^{-2}$). $I(z) = I_0[1 + \mathrm{Re}(me^{ikz})]$. e, μ_n, μ_p are the absolute values of electron and hole charges and mobilities. ϵ is the static dielectric constant of the material [$\epsilon = \epsilon_0\epsilon_R$ with $\epsilon_R = 12.7$ (Ref. 16)] and N_D is the density of compensative donors. In these equations S represents the photoionization cross sections, γ the recombination coefficients, and β the thermal emission rates. The different indices n, p, and * stand for electron, hole, and Fe^{2+*}.

Considering the small modulation of the illumination pattern, $m \ll 1$, we perform the usual linearization of the previous equations, keeping only the zeroth-order term and the spatially modulated, first-order term, expressed as $X = X_0 + \mathrm{Re}(X_1 e^{ikz})$.

In steady state, a general analytical solution can be found. The dark conductivity is mainly due to electrons.[7,14] The thermal emission rate β_n is about 10 s^{-1} (Ref. 17) at ambient temperature (300 K). Since thermal emission rates depend exponentially on the energy difference between the levels and the conduction band, $\beta_n^*(\simeq 10^7\ s^{-1})$ is six orders of magnitude larger than β_n. This is an approximate value as it has been calculated with the same parameters as β_n except level energy. β_p is computed from $p = [Fe^{3+}]\beta_p\tau_p$, with $p < 10^7\ cm^{-3}$ (electrons are dominant in dark current) and the recombination time of holes on Fe^{2+}: $\tau_p \simeq 120$ ns (Ref. 18) giving $\beta_p \simeq 10^{-4}\ s^{-1} \ll \beta_n$. For an illumination of some tens of milliwatts the electron photocurrent is larger than or about equal to the dark current, thus $\beta_n \leqslant S_n I_0$; β_p, $\beta_p^* \ll S_p I_0$, $S_p^* I_0$ and $\beta_n^* \gg S_n^* I_0$. Assuming equal recombination coefficients ($\gamma_p \simeq \gamma_p^*$) for holes on Fe^{2+} and Fe^{2+*}, one has $\beta_n^* \gg \gamma_p^* p_0$ ($\simeq 10^2\ s^{-1}$ for 100 mW cm^{-2}). This means that Fe^{2+*} is primarily changed to Fe^{3+} by thermal excitation of electrons and not by hole recombination. For low irradiance the population of the Fe^{2+*} level is always very small $N_0^* \ll N_0$, $N_T - N_0$. We now make the usual simplifications for low irradiance:

$$n_0, p_0 \ll N_0, N_T - N_0 \quad \text{and} \quad n_1, p_1 \ll N_1.$$

For semiconductors, the diffusion lengths for both electrons and holes are larger than the Debye screening length, i.e.,

$$\gamma_n N_0/\mu_n, \gamma_p(N_T - N_0)/\mu_p \ll (e/\epsilon)N_0(N_T - N_0)/N_T.$$

In these conditions the photoinduced space-charge field is $E_1 = imE_{sc}$ with

$$E_{sc} = \frac{-k_B T}{e} k \left[\frac{(\alpha_n - \alpha_p)k^2}{A_n\alpha_n + \alpha_p + 2\alpha_p^*} + \frac{(\alpha_n + \alpha_p^*)\kappa_p^2 - (\alpha_p + \alpha_p^*)\kappa_n^2}{A_n\alpha_n + \alpha_p + 2\alpha_p^*} \right] \Bigg/ \left[k^2 + \frac{k^4}{k_0^2}\left(\frac{A_n\alpha_n + \alpha_p + \alpha_p^*}{A_n\alpha_n + \alpha_p + 2\alpha_p^*} \right) + \frac{(A_n\alpha_n + \alpha_p^*)\kappa_p^2 + (\alpha_p + \alpha_p^*)\kappa_n^2}{A_n\alpha_n + \alpha_p + 2\alpha_p^*} \right]$$

and

$$n_0 = \frac{(\beta_n + S_n I_0)(N_T - N_0) + S_p^* I_0 N_0}{\gamma_n N_0},$$

$$p_0 = \frac{(S_p^* + S_p) I_0 N_0}{\gamma_p (N_T - N_0)}$$

$$N_0^* = \frac{\gamma_n^*}{\gamma_n \beta_n^*}(\beta_n + S_n I_0)(N_T - N_0) + \frac{(\gamma_n + \gamma_n^*)}{\gamma_n \beta_n^*} S_p^* I_0 N_0$$

with

$$k_0^2 = (e^2/\epsilon k_B T)[N_0(N_T - N_0)/N_T],$$

$$\kappa_n^2 = \frac{e}{k_B T}\frac{\gamma_n N_0}{\mu_n} = \frac{e}{k_B T}\frac{1}{\mu_n \tau_n},$$

$$\kappa_p^2 = \frac{e}{k_B T}\frac{\gamma_p (N_T - N_0)}{\mu_p} = \frac{e}{k_B T}\frac{1}{\mu_p \tau_p},$$

and $N_0 = N_T - N_D$, $\alpha_n = S_n(N_T - N_0)$, $\alpha_p = S_p N_0$, $\alpha_p^* = S_p^* N_0$, $A_n = (\beta_n + S_n I_0)/S_n I_0$.

The photorefractive gain is $\Gamma = 2\pi n_0^3 r_{41} E_{sc}/\lambda \cos\theta$, where n_0 is the refractive index, r_{41} the electro-optic coefficient, λ is the wavelength of pump and signal beams, and θ is the half angle between the two interfering beams inside the crystal.

In our experiments the illumination was chosen large enough so that the gain no longer depends on the illumination. Then, as the electron photocurrent is stronger than the dark current, A_n is equal to 1. We can write the gain as

$$|\Gamma| = |A|\, k \frac{|\xi_0 k^2 + b - c|}{k^2 + k^4/k_0'^2 + b + c},$$

with

$$\xi_0 = (\alpha_n - \alpha_p)/(\alpha_T + \alpha_p^*),$$

$$k_0'^2 = k_0^2[(\alpha_T + \alpha_p^*)/\alpha_T],$$

$$b = [(\alpha_n + \alpha_p^*)/(\alpha_T + \alpha_p^*)]\kappa_p^2,$$

$$c = [(\alpha_p + \alpha_p^*)/(\alpha_T + \alpha_p^*)]\kappa_n^2, \qquad (1)$$

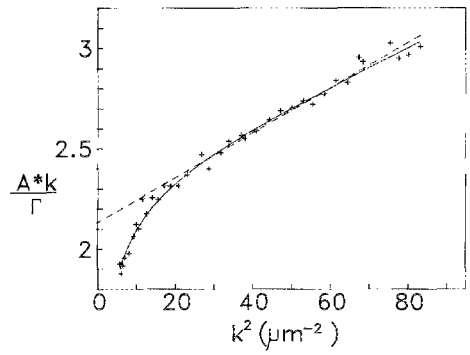

FIG. 2. Measured beam coupling gain Γ (+) plotted in the form Ak/Γ in function of k^2 with the fitted straight line (---) and the best fit with the whole expression of the gain (—).

and $A = 2\pi k_B T n_0^3 r_{41}/e\lambda \cos\theta$ and $\alpha_T = \alpha_n + \alpha_p + \alpha_p^*$. With $r_{41} = 1.34$ pm V^{-1},[16] $n_0 = 3.29$,[16] and $\cos\theta \simeq 1$, we have $A = 7.11\times10^{-2}$ cm^{-1} μm.

For small grating spacings, corresponding to large k, we have $k^2 \gg \kappa_n^2, \kappa_p^2$ and $b \simeq c \simeq 0$. Then, the plot of Ak/Γ in function of k^2 is a straight line. For $k^2 \geqslant 20$ μm^{-2} our experimental data can be fitted with a straight line (Fig. 2) and permit the determination[6] of $\xi_0 = -0.47$ and $k_0'^2 = 190$ μm^{-2}. For $k^2 < 20$ μm^{-2} the departure from a straight line is apparent. This is the influence of κ_n^2, κ_p^2 (or b and c) in the above expression of the gain. The best fit with this expression gives the parameters $\xi_0 = -0.424 \pm 0.03$, $k_0'^2 = 260 \pm 50$ μm^{-2}, $b \leqslant 0.05$ μm^{-2}, $c = 1.4 \pm 0.5$ μm^{-2}, and is shown in Fig. 2. The values of ξ_0 and $k_0'^2$ are only a little different from the values determined above. For b we can only give an upper limit. It could also be set to zero without visible influence on the plot; i.e., the data can be perfectly fitted with three parameters. The sign of the quantity ξ_0 has been determined by an additional experiment, as explained in Refs. 19 and 20. It is found to be negative. The total absorption has been measured independently and its value is $\alpha_T \simeq 1.95 \pm 0.04$ cm^{-1}.

With relations (1) and $\alpha_n \ll \alpha_p, \alpha_p^*$, as previously discussed, we then deduce $\alpha_p = 1.16 \pm 0.05$ cm^{-1}, $\alpha_p^* = 0.79 \pm 0.05$ cm^{-1}, $k_0^2 = 185 \pm 40$ μm^{-2}, $\kappa_p^2 \leqslant 0.2$ μm^{-2}, $\kappa_n^2 = 2 \pm 1.5$ μm^{-2}.

The orders of magnitude of κ_n^2, κ_p^2 are in accordance with those calculated by taking the values of mobilities and recombination times for iron known from the literature.[7,18]

k_0^2 gives $[Fe^{2+}] = (3.2 \pm 0.5) \times 10^{15}$ cm^{-3} and α_p and α_p^* give $S_p = 0.6 S_p', S_p^* = 0.4 S_p'$, where $S_p' = S_p + S_p^*$ is the photoexcitation cross section determined by DLOS ($S_p' \simeq 5\times10^{-17}$ cm^2).[9] With $[Fe^{3+}] \simeq 8\times10^{16}$ cm^{-3}, we find $S_p' \simeq 2.5\times10^{-17}$ cm^2.

In conclusion, we propose a new model for the unexpected reduction of the photorefractive gain in two-wave mixing. This model takes into account the influence of the Fe^{2+*} state. Due to the strong thermal emission of this state an indirect hole-electron competition appears, which lowers the photorefractive coupling gain below the value expected from the current one-trap–two-bands charge-transport model. The experimental results confirm our theoretical model and permit us to determine two characteristics of the crystal hardly accessible directly by other methods: $[Fe^{2+}] = 3.2\times10^{15}$ cm^{-3} and the ratio $S_p/S_p^* = 1.5$ (at $\lambda = 1.06$ μm).

The gain limitation of the indirect hole-electron competition is very drastic, since it is inherent to the nature of the iron dopant. Its influence could be less important for undercompensated crystals with $[Fe^{2+}] \gg [Fe^{3+}]$ and $\alpha_n \gg \alpha_p$, but then the dark current caused mainly by electrons will be larger, requiring an increase of the optical irradiance. The only reasonable possibilities to suppress this gain limitation are to decrease the light frequency or the temperature. For $h\nu < 1.05$ eV, α_p^* is negligible before α_p (Ref. 12) as the excitation energy to raise the electrons from the valence band to Fe^{2+*} is not reached, and for temperatures below 170 K the thermal emission rate β_n^* is negligible compared to the recombination rate $\gamma_p p_0$ of holes on Fe^{2+*}. Then our expression for the gain becomes equal to one of the current charge-transport model. It could be interesting to do a temperature-dependent study of the photorefractive coupling gain for further confirmation of the model.

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