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Transient and steady decay of persistent photoconductivity in Si-doped $Al_xGa_{1-x}As$

J. F. Sampaio, A. S. Chaves, G. M. Ribeiro, P. S. S. Guimarães, R. P. de Carvalho, and A. G. de Oliveira
Departamento de Física, Universidade Federal de Minas Gerais, Caixa Postal 702, Belo Horizonte, 30161, Minas Gerais, Brazil
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The decay of persistent photoconductivity (PPC) in bulk $Al_{0.3}Ga_{0.7}As$:Si was investigated at 77 K. A transient decay was observed to appear if the light is shut off while the conduction-electron concentration is increasing quickly. The decay of PPC is analyzed based on the negative-U model for the DX center. It is shown that this transient indicates that the decay of the DX center goes via a neutral metastable state DX^0 of silicon.

The DX center has been intensively investigated in the last decade[1,2] because of its truly unique behavior and the way it affects the performance of electronic devices based on III-V semiconductors. This center appears, for example, in Si-doped $Al_xGa_{1-x}As$, and this is, in fact, the most widely studied example of the DX center.

A major step towards the understanding of the microscopic nature of the DX center was the proposal by Kachaturyan, Weber, and Kaminska[3] and by Chadi and Chang[4] of the negative-U character of the DX center. Several studies of the electron mobility[5-8] and of the persistent photoconductivity[9-11] (PPC) were performed, aiming to determine the charge of the ground state of the DX center; but though the bulk of the resulting evidence gives strong support to the negative-U model, the question is not yet settled.

An important issue related to the negative-U model is the nature of the intermediate neutral state and its role on the electron capture and emission by the DX center. The theory by Chadi and co-workers predicts an unrelaxed state, but supplementary calculations[12,13] suggest the existence of both relaxed and unrelaxed neutral states. Theis and Mooney[9] argue for the existence of an unrelaxed neutral state in their analysis of electron capture and emission by the DX center. Dobaczewski and Kaczor[14] fitted photoionization data with a model that required a relaxed (DX^0) neutral state. However, they measured only the resistivity and obtained indirectly the conduction-electron density n. As there is no agreed way to obtain the behavior of the mobility as a function of n, because it depends itself on the defect's model,[5-8] their analysis is not reliable. Furthermore, their samples should present photoinduced electron transfer from the doped alloy to the substrate and this could result in very spurious effects.

This paper reports on a study of both steady and transient decay of PPC in $Al_{0.3}Ga_{0.7}As$. The concept of transient decay of PPC (TDPPC) already was presented in the literature[10,15] with a different meaning from the present one, which we define in the sequence. As the illumination on the sample is shut off, at $t=0$, the electron concentration n starts another regime of variation. The rate of decay dn/dt depends on the values of both n and dn/dt immediately before $t=0$. The contribution to dn/dt resulting from the initial condition $(dn/dt)_{t=0^-}$ is what we call TDPPC. The TDPPC dies out in a few seconds, whereas the steady decay of PPC (SDPPC) can be observed for days and can be theoretically predicted using only the value of n just after the TDPPC has disappeared. Schubert and Ploog[15] have observed a transient photoconductivity in heterojunction structures which they relate to tunneling-assisted electron decay, and Dobson, Scalvi, and Wager[10] denote as TDPPC what is here described as SDPPC. We argue that the TDPPC, as defined here, is very strong evidence for the negative-U model for the DX center and for a decay mechanism from d^+ to DX^- via a metastable neutral state of silicon (DX^0). The evidence does not rely just on model fitting of data, but also, and mostly, on qualitative behavior that seem to require those conclusions.

The experiments reported here were done on a molecular-beam-epitaxy (MBE) sample on semi-insulating (001) GaAs substrate, consisting of a buffer of undoped GaAs layer, a 0.55-μm-thick undoped spacer followed by a 3.8-μm-thick Si-doped ($N_{Si}=1.6\times10^{18}$ cm^{-3}) layer, both of $Al_{0.3}Ga_{0.7}As$, and a 150-Å-thick Si-doped GaAs cap layer. The density n_{2D} of the two-dimensional electron gas at the $GaAs/Al_xGa_{1-x}As$ heterojunction and the consequent spurious effect caused by photoinduced charge transfer are very small. For a spacer of large thickness L_s, the maximum predicted value of n_{2D}, based on a simple capacitor model, is $n_{2D}(\max)=K\epsilon_0\Delta E_c/e^2L_s$, where K is the dielectric constant of the spacer and ΔE_c is the conduction-band offset. For the present sample $n_{2D}(\max)=3\times10^{10}$ cm^{-2}, which is far too small to have any effect in our results. Besides, tests on a sample with $L_s=0.25$ μm and a doped $Al_xGa_{1-x}As$ layer with thickness $\delta=1.0$ μm show the same results of our standard sample.

A Hall bridge was photolithographically fabricated for the transport measurements and the sample illumination was done with an infrared ($h\nu=1.32$ eV) light-emitting diode. The experiments were all done at $T=77$ K after slow cooling in the dark. For light intensity above a given threshold the conduction-electron density saturates at the same value; this value is most probably equal to the Si doping concentration. As the light is shut off at $t=0$ the electron density n decays as shown in Fig. 1. The decay is clearly nonexponential and the ratio $(-n^{-1}dn/dt)$ decreases rapidly as n decreases. However, this quick initial decay from an initial saturated n is not related to TDPPC. The data in Fig. 1 represent the SDPPC and are similar to

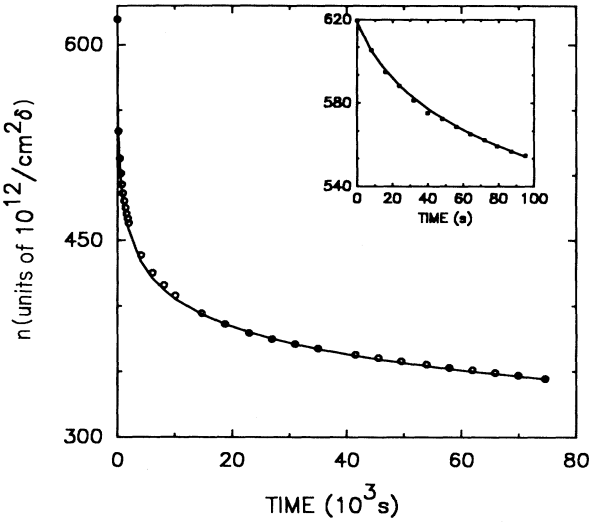

FIG. 1. Experimental data of the decay of the photoconductivity after saturation under intense illumination (circles) and fitting with the SDPPC equation (9) (solid line). δ is the thickness of the Si-doped layer.

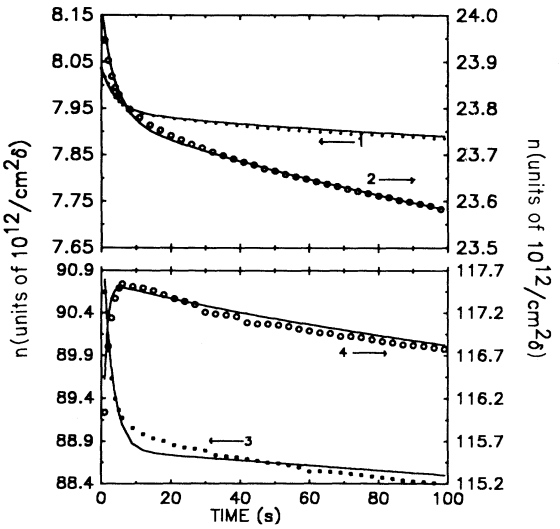

FIG. 2. Experimental data of the decay of the photoconductivity after light shutdown ($t=0$) while n is still increasing quickly (circles). The two regimes, TDPPC and SDPPC, are clearly observed. The fitting (solid lines) was done with Eq. (10).

data found in the literature.[9,10] On the other hand, the system shows different kinetics if the light is shut off, at $t=0$, while n is still increasing quickly. In this case it shows a transient behavior that lasts for a few seconds and which is clearly distinct from the SDPPC. The change Δn_{tr} on n during this transient (with the normal SDPPC already subtracted) depends both on $n_0 \equiv n(t=0)$ and the intensity I of light. The decay which is responsible for Δn_{tr} is what we call TDPPC. For small values of n_0, Δn_{tr} was observed to be negative (positive TDPPC), whereas for large values of n_0 Δn_{tr} is positive (negative TDPPC), i.e., for large n_0, n stays increasing for a while after the light is shut off. For a given n_0, $|\Delta n_{tr}|$ seems to be proportional to I, though this relation was not checked out rigorously. Figure 2 shows examples of decays of PPC demonstrating the presence of both regimes TDPPC and SDPPC. The existence of TDPPC demonstrates that the decay of conduction electrons cannot be described by an ordinary differential equation of first order of the form $dn/dt = f(n,T)$, where f is a function of n and temperature only. In fact, the solution of this equation for a given initial value n_0 is unique, in contradiction with the existence of the TDPPC. This contradiction can be easily seen in an examination of Fig. 2. During the TDPPC, i.e., in the first few seconds, the value of $-dn/dt$ in curve 1 (3) is larger than the value of $-dn/dt$ in curve 2 (4) during the SDPPC in spite of the fact that n in curve 1 (3) is always smaller than in curve 2 (4). As the decay mechanism cannot involve inertial terms of the form d^2n/dt^2, one has to assume that a coupling exists between n and another dynamical variable.

We propose that the population of an intermediate neutral state for silicon, DX^0, is the dynamical variable which couples to n. Figure 3 shows our proposed configuration diagram for the DX center. The TDPPC forced us to postulate the existence of an energy barrier Δ_1, therefore, a finite time for decay of the intermediate state into d^+, though the barrier Δ_2 for decay into DX^- may or may not exist. Also, from the observation that the TDPPC can be positive or negative, i.e., n can either decrease or increase just after the light is shut off, we were forced to admit that the intermediate state can either take one electron from, or else give one electron to, the conduction band; thus it must be neutral silicon.

The kinetic equations of this model, through simple approximations, will describe explicitly our experimental observations. Ignoring for simplicity the state d^0, i.e., neutral extended state, the kinetics is represented by

$$\frac{dN^+}{dt} = -c_n N^+ + eN^0, \tag{1}$$

$$\frac{dN^0}{dt} = -(e+c_n')N^0 + c_n N^+ + \alpha_2 I N^- - \alpha_1 I N^0, \tag{2}$$

subject to the constraints $N_D = N^+ + N^0 + N^-$ and N^+

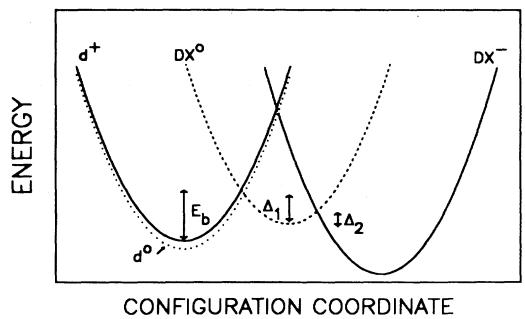

FIG. 3. Proposed configuration diagram for the DX center. The different element in this diagram is the metastability of the neutral state DX^0. Clear evidence was found for the barrier Δ_1 but not for Δ_2.

$=N^- + n$. In these equations, N^+, N^0, and N^- are the concentrations of d^+, DX^0, and DX^-, respectively, N_D is the total concentration of silicon, I is the light intensity, and everything else are kinetic coefficients. Because of the above constraints we do not have an independent equation for dN^-/dt. We have made many simplifications in writing Eqs. (1) and (2), including the neglect of light-induced conversion between the states d^+ and DX^0, double ionization of DX^- by light, and direct thermal conversion from d^+ to DX^-. In our judgment these simplifications, though not appropriate in a more rigorous treatment, still allow us to draw valid conclusions from the model. For $I=0$, Eqs. (1) and (2) are equivalent to

$$\frac{dn}{dt} = -\tfrac{1}{2} c_n (N_D + n) + (e - c_n' + \tfrac{1}{2} c_n) N^0 , \tag{3}$$

$$\frac{dN^0}{dt} = -(e + c_n' + \tfrac{1}{2} c_n) N^0 + \tfrac{1}{2} c_n (N_D + n) , \tag{4}$$

and the coupled Eqs. (3) and (4) describe the decay of PPC. The electron capture coefficients c_n and c_n' are given by $\sigma n \langle v \rangle$ and $\sigma' n \langle v \rangle$, respectively, and thus we can write approximately for the metallic regime

$$c_n = \sigma_\infty k T D(\varepsilon_F) v(\varepsilon_F) \exp\left[-\frac{E_b - \varepsilon_F}{kT} \right] , \tag{5}$$

$$e = e_\infty \exp(-\Delta_1 / kT) , \tag{6}$$

$$c_n' = \sigma_\infty' k T D(\varepsilon_F) v(\varepsilon_F) \exp\left[-\frac{\Delta_2}{kT} \right] \exp\left[-\frac{E_b - \varepsilon_F}{kT} \right] , \tag{7}$$

where $D(\varepsilon_F)$ is the density of electron states at the Fermi energy and E_b, Δ_1, and Δ_2 are barriers indicated in Fig. 3. It should be noticed that even for $\Delta_2 = 0$ the coefficient c_n' depends on temperature. Thus, it is surprising that Dobaczewski and Kaczor could fit their data with C_2 (equivalent to our c_n'/n) independent of temperature. Supposing that Δ_1 is small enough to have the conditions $e \gg c_n'$ and $e \gg c_n/2$ the pair of Eqs. (3) and (4) result in

$$\frac{dn}{dt} = -\frac{c_n c_n'}{e} (N_D + n) - \frac{dN^0}{dt} . \tag{8}$$

If the light is shut off at $t=0$ after the system has stabilized in a given thermodynamic state, then at $t=0^-$, dn/dt and dN^0/dt are both equal to zero and $N^0 \ll n$. Therefore, in an integration of Eq. (8) the term dN^0/dt is negligible and thus we have, from Eqs. (5)–(8), the equation to describe approximately the SDPPC:

$$\frac{dn}{dt} = -A(T)(N_D + n) n^{4/3} \exp(2an^{2/3}/kT) . \tag{9}$$

Figure (1) shows the fitting of SDPPC with Eq. (9). The value of a can be obtained from the values of the effective mass and the nominal value of the thickness δ of the doped layer and thus the only free parameter in (9) is $A(T)$. To obtain the fit shown in Fig. 1 it was necessary to use a value for a 30% higher than the one predicted using the nominal thickness. However, this is not very significant as we do not have a precise calibration for the growth rate.

The TDPPC arises as a contribution of the term dN^0/dt in Eq. (8). When n and N^0 are changing quickly by light pumping, their relative values can become very different from the quasistatic ones. Thus, N^0 will probably change very quickly just after the light is shut off in order to adjust to its correct value. Defining ΔN^0 as the difference between N^0 and its "balanced" value we can find the approximate equation,

$$\frac{dn}{dt} = -A(T)(N_D + n) n^{4/3} \exp(2an^{2/3}/kT) + e \Delta N_0^0 \exp(-et) , \tag{10}$$

for the decay of PPC.

The second term in Eq. (10) represents the TDPPC. If $\Delta N_0^0 \equiv \Delta N^0$ $(t=0)$ is positive, n will have a quick increase just after $t=0$ (negative TDPPC), before the SDPPC is observed. If ΔN_0^0 is negative, a quick decrease in n (positive TDPPC) is observed, followed by the SDPPC. Both behaviors are seen in Fig. 2. Equation (10) was used to fit the data of Fig. 2, which could not be fitted with Eq. (9) describing the SDPPC, only. In turn, the parameter a used to fit Eq. (10) was not the same for different curves. Its value increased for decreasing n, becoming more and more different from the one predicted with the nominal value δ of the Si-doped layer thickness. If a is kept the same for all curves, the experimental value of d^2n/dt^2, for small n, becomes much bigger than the theoretical prediction. The same problem can be observed in the work by Theis and Mooney,[9] who fitted their data with a formula very similar to (9). This discrepancy could result from the neglect of the state d^0 and the simplified expression for the Fermi energy. We have not yet checked for these possibilities. They, however, would not rule out the need of the second term in Eq. (10) which describes the TDPPC.

In addition to TDPPC shown in Fig. 2, for small n we have observed a very quick transient in which n decreases considerably in a time scale less than 1s. Thus, it could be that there is more than one DX^0 state. The existence of two DX^0 states, one decaying in 10^2s and the other in 10^3s at 4 K, is also strongly suggested by the observation of two electron paramagnetic resonance lines in Sn-doped $Al_xGa_{1-x}As$ under illumination.[16] The quickly decaying DX^0 state suggested by our unresolved transient experiment could be an unrelaxed or slightly relaxed neutral state for silicon as proposed earlier.[4,9]

In conclusion, we have observed the TDPPC, related to the DX center in Si-doped $Al_xGa_{1-x}As$. The effect can be explained based on the negative-U model for the DX center, with the additional hypothesis that the decay of positive into negative silicon involves a metastable neutral state DX^0 of that atom. The metastability of this neutral state, completely necessary to explain the effect of TDPPC, is a fact that has to be incorporated to the negative-U model for the DX center.

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