Direct Evidence for Two-Step Photoionization of DX(Te) Centers in $Al_xGa_{1-x}As$

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A detailed analysis of the photoionization process of DX(Te) centers in $Al_xGa_{1-x}As$ ($0.25 < x < 0.55$) for different temperatures and light intensities revealed, for the first time, that the process goes through two steps. The only possible interpretation of the phenomenon is by means of a negative-U character of the defect; i.e., the center binds two electrons in the ground state, forming a DX^- energy state. An intermediate state for the process is a one-electron localized state of the defect.

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Doping of GaAs or $Al_xGa_{1-x}As$ with Si, Sn, or group-VI elements produces defect states which behave as standard donors in GaAs or $Al_xGa_{1-x}As$ for low ($x < 0.2$) Al concentration. If the Al content in the alloy becomes larger, or equivalently high hydrostatic pressure is applied to GaAs or $Al_xGa_{1-x}As$ with lower x, new defect states directly related to the chemical dopants control the carrier concentration. They are known as the DX centers.[1] In contrast to standard donors, these states, while empty at low temperatures, do not recapture photoexcited carriers. The carriers either stay practically indefinitely in the conduction band at low temperature or become metastably retrapped on the effective-mass-type excited states of the DX centers. The first type of behavior, known as persistent photoconductivity (PPC), is observed in the direct-gap $Al_xGa_{1-x}As$ alloys,[2] while the second is seen in the indirect-gap alloy, when the lowest conduction-band minimum becomes X type and the effective-mass donor state associated with it is deep enough to capture photogenerated carriers without forming an impurity band.[3]

Among many problems related to the properties of DX centers the fundamental ones are the following: (i) the reason of the metastability of DX centers, (ii) their microscopic nature, and (iii) their charge state. Large lattice relaxation around a defect, following the electron capture by a DX-type state, is regarded as a most likely reason for metastability. The barrier preventing the electron from being captured originates from a strong electron-phonon coupling and exists only for a localized DX-type state.[4] It should be mentioned, however, that there are attempts to explain the metastability of DX centers by involving selection rules related to the band structure.[5]

The issue of the microscopic structure of these centers is much less settled. Very recently, Chadi and Chang,[6] and independently Morgan,[7] proposed that a substitutional-interstitial defect reaction may be responsible for large lattice relaxation phenomena. The most essential assumption of the Chadi and Chang model is that the defect must capture two electrons to form the DX state. Therefore the ground state of the DX center should be negatively charged and the whole system should possess a negative electron correlation energy U ($U < 0$).[8] In such a system the neutral DX^0 state must be thermodynamically unstable, but obviously should play a role in all carrier capture and emission processes as an intermediate state ($DX^- \leftrightarrows DX^0 + e^- \leftrightarrows DX^+ + 2e^-$).[9] It is our aim to provide a direct proof of the existence of such an intermediate state. Several characteristic phenomena of DX centers can be well explained by invoking the existence of such states. For example, it is well known that the activation energy of electron emission from the DX centers almost does not depend on the alloy composition of $Al_xGa_{1-x}As$, while the capture barrier exhibits a pronounced minimum at $x = 0.37$.[10] Such behavior can be easily explained if the carrier capture and emission proceeds via an intermediate DX^0 state whose energy in respect to the DX^- state does not depend on composition. Such a state must be resonant with the conduction band. A similar conclusion can be reached noting that the capture rate depends exponentially on the quasi Fermi level.[11] Finally, the hot electron capture by the DX centers in GaAs can be most simply interpreted as capture via an intermediate state.[12] None of the above experiments, however, provides direct evidence for the existence of such intermediate states and can be interpreted in a much less elegant way but without invoking a negative-U concept of the DX centers.

In our experiments we studied temperature evolution of the photoionization transients of the DX centers in $Al_xGa_{1-x}As$:Te. They are double exponential with the ratio of the two exponential components strongly depending on temperature and light intensity.

The $Al_xGa_{1-x}As$:Te samples used in our experiments were grown by liquid-phase epitaxy on n-type Te-doped GaAs substrates with net electron concentration $n > 10^{19}$ cm^{-3} (⟨100⟩ surface plane orientation). The samples consisted of a 3-μm n-type $Al_xGa_{1-x}As$ ($0.25 < x < 0.55$) layer doped with 2×10^{17} cm^{-3} Te and a subsequent 4-μm p-type top layer of GaAs doped with about 10^{19} cm^{-3} Ge. The structure forms an asymmetric p-n junction with a depletion region (approximately 0.2 μm thick) in an $Al_xGa_{1-x}As$ layer. The deep-level transient spectroscopy spectra of the samples showed only one dominant peak related to the DX(Te) center.

The capacitance of the sample measured as a function of temperature (C-T curve) exhibits a strong step around 100 K. This step is not due to any change within the space-charge region of the diode but represents a substantial increase of the diode series resistance caused by the freeze-out of conducting electrons on the ground states of DX centers in $Al_xGa_{1-x}As$, which are outside the space-charge region. For thin $Al_xGa_{1-x}As$ layers (less than 0.5 μm) there are attempts to interpret this effect as due to the recapture of electrons from the free-carrier tail by the DX centers being at the edge of the space-charge region;[13] however, for structures used in the study, the diode series resistance must dominate.

Photoionization of DX centers creates a persistent photoconductivity in $Al_xGa_{1-x}As$ outside the junction and this effectively changes the capacitance of the structure. A straightforward analysis of such a circuit (a constant capacitor formed by a junction depletion layer and a variable resistor formed by the $Al_xGa_{1-x}As$ layer outside the junction) shows that its measured capacitance equals $C_m = C_0/(1+\omega^2 C_0^2 R^2)$, where C_0 is the capacitance of the diode space-charge region, R is the diode series resistance, and ω is an angular frequency of the capacitance meter. The sensitivity of this method is, of course, not ideal for high electron concentrations, but the experimental setup allowed us to measure even very small changes in the series resistance and observe in this way practically all necessary range of the electron concentrations. Thus, the photocapacitance transients provide a direct measure of the photoinduced electrons.

Photoionization measurements were performed for alloy compositions $x = 0.25$, 0.35, 0.45, and 0.55 at temperatures between 40 and 130 K. The samples were always cooled down in the dark with a controlled cooling rate. No bias voltage was applied either during cooling or during measurement. The photon flux was varied using calibrated neutral density filters. The initial conditions for each of the measurements were reestablished by heating the sample up to 140 K, and then cooling down to the temperature at which the process was investigated. Figure 1 shows examples of the nonexponential transients seen in our experiments. The most extreme case of nonexponential behavior can be observed at higher tempertures and at relatively high photon fluxes, when the transients exhibit "overshoots" (Fig. 2).

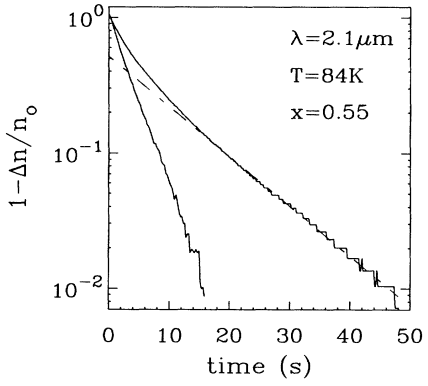

FIG. 1. One of the photoinduced transients observed in the experiments. A fit of a monoexponential function (dashed line) with the tail of the transient gives the lower one of the emission constants. Subtracting this fit from the transient leads to a new monoexponential function, with a higher emission constant. Such a decomposition of the transient is possible only when Eqs. (1) and (2) are linear; i.e., the C_1 and C_2 parameters are small in comparison with e_1 and e_2.

The photoionization kinetics has been fitted by a set of nonlinear equations describing carrier exchange between a two-electron defect and the conduction band. For such a defect the electron concentration n is given by

$$n = N_D - N_A - N_1 - 2N_2 , \tag{1}$$

and the photoionization kinetics is given by

$$dn/dt = e_2 N_2 + e_1 N_1 - c_1 N_0 - c_2 N_1 , \tag{2a}$$

$$dN_2/dt = -e_2 N_2 + c_2 N_1 , \tag{2b}$$

where N_i denotes concentration of defects possessing i electrons. The emission rates e_1 and e_2 are the sums of the thermal emission rates and optical emission rates ($e_o = \sigma_o \Phi$, where σ_o is the photoionization cross section and Φ is the photon flux). Nonlinearity of these equations comes from the proportionality of the capture cross section to the electron concentration. Solution of this set of equations depends critically on the initial conditions and, therefore, on the sign of U. If the sample is cooled in darkness, the initial conditions depend on the sign of U in the following way: for $U < 0$,

$$N_1 = [DX^0] = 0, \quad N_2 = [DX^-] = \tfrac{1}{2}(N_D - N_A) ,$$

for $U > 0$,

$$N_1 = N_D - N_A , \quad N_2 = 0 .$$

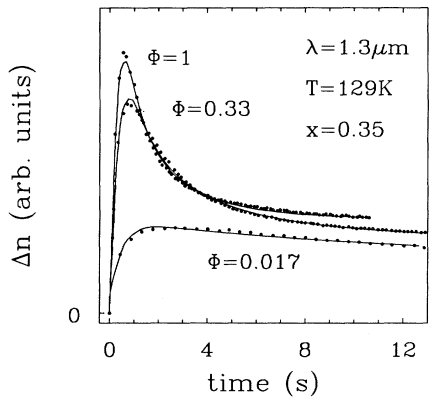

FIG. 2. At higher temperatures, an overshoot behavior of the transient is observed. The lines are fits for different photon fluxes Φ according to the kinetics described in the text.

The fitting was performed for both sets of initial conditions. During the fitting procedure we redefined the capture cross section to make it independent of the electron concentration, $c_i = C_i n/N_D$, and furthermore the C_i parameter has been used as a constant. As an acceptable fit for both models could be obtained for each individual kinetics, the light intensity was varied by up to 3 orders of magnitude. It turned out that only for $U<0$ all fitting parameters, i.e., the capture cross sections C_i and photoionization cross sections σ_{oi}, were independent of the light intensity. For $U>0$ all kinetics parameters strongly changed with the light flux. This result provides a strong support for the negative-U model of the DX center. The most surprising finding was that the emission constant e_1 of the neutral DX^0 state was dominated for all temperatures and illumination conditions by the photoionization process. This result indicates the existence of a relatively high barrier for the thermal ionization of this state, which is obviously not the case of the hydrogenlike, excited, effective-mass states of the DX centers.

The capture cross section C_1 strongly depends on temperature and vanishes below 50 K, which represents the inability of the empty DX center (DX^+) to recapture carriers at low temperatures. Interestingly, the capture cross section C_2, i.e., the capture cross section of the second electron by the DX center in its neutral charge state, very weakly depends on temperature and even for $T=40$ K it is close to 1 s^{-1}, which means that even in the PPC regime the photogenerated DX^0 state efficiently captures the second electron. It also means that the barrier between DX^0 and DX^- cannot be high but a barrier must exist between DX^0 and the conduction band, in agreement with the emission data discussed above.

The spectral dependences of the low-temperature photoionization cross sections of the DX^- (σ_{o2}) and DX^0 (σ_{o1}) states for direct ($x=0.25$) and indirect ($x=0.55$) $Al_xGa_{1-x}As$ alloys are shown in Fig. 3. The most striking feature is their overall similarity. The spectral shape of the photoionization cross section σ_{o2} of the ground DX^- state is the same as determined in many previous experiments. As its shape is characteristic for a center with a strong electron-phonon coupling and the spectral shape of the photoionization cross section σ_{o1} (neutral DX^0 state) is quite similar, we may conclude that the neutral DX^0 state, acting as the intermediate state for the carrier exchange between the ground DX^- state and the conduction band, is also a localized state and is different from the well-known effective-mass, X-like or Γ-like, hydrogenic, excited neutral charge states of the DX centers. A detailed shape analysis of σ_{o2} and σ_{o1}, which will be presented elsewhere together with the details of the fitting procedure, show that the optical ionization threshold and the electron-phonon coupling of the DX^0 state are slightly larger than for the DX^- state. It is consistent with the large and weakly temperature-dependent cross section C_2 for the electron capture in the reaction $DX^0 + e^- \leftrightarrows DX^-$. This result indicates that the capture of the second electron occurs while the DX center is already in the relaxed state. This is again consistent with the pseudopotential calculations of Chadi and Chang, which suggest that the capture of the second electron of the Si-induced DX center proceeds while the neutral Si is already highly displaced towards the interstitial position.

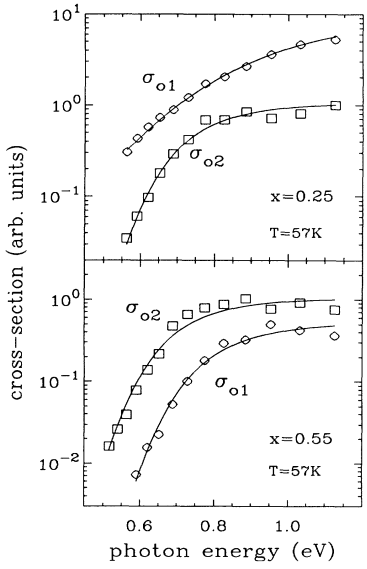

FIG. 3. Photoionization cross sections for one-electron (circles) and two-electron (squares) energy states of the DX center.

There is a very important question about the role of the shallow X-like hydrogen effective-mass excited states of the DX centers in the ionization and capture processes for crystals with an indirect band gap. In these crystals at lower temperatures the X-like states cause partial freeze-out of electrons and reduce the concentration of electrons in the band. However, due to the fact that they are in thermal equilibrium with the band, it is not possible to see them in the transients. The capture rates C_2 found in the crystals with an indirect band gap are indeed lower than for the direct one and probably this apparent effect can be simply nothing else but a manifestation of the X-like effective-mass states of the DX center. To observe a direct (i.e., when the defect is in the DX^+ charge state) participation of these shallow states in the capture process it would be necessary to go to higher temperatures, above the PPC regime, where the thermal emission is non-negligible and it is not possible to study the photoionization process. Different methods, e.g., those presented in Refs. 11 and 12, are then more appropriate.

The nonexponential photoionization transient can have

another origin. A two-donor system can be easily ruled out as tellurium has been a dominant donor dopant in our samples. Analysis of a case when one donor has two energy states of the same charge state shows that, although the individual transients can be reasonably fitted (except for overshoots as in Fig. 2) to appropriate kinetics equations, it is not possible to do it for different light intensities with the same set of cross-section parameters.

In conclusion, we have shown that the carrier exchange between the DX centers and the conduction band is a two-step process and the intermediate state is not the effective-mass X- or Γ-like excited state of the DX center, but a neutral DX^0, most likely resonant, state strongly coupled to the lattice, similarly to the ground DX^- state. These experimental findings are fully consistent with the recent model calculations of the DX centers made by Chadi and Chang.

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