Photoluminescence Transients Due to Hole Capture at *DX* Centers in $Al_xGa_{1-x}As$:Si

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The near-band-gap photoluminescence of AlGaAs:Si shows a slow intensity transient after cooling the sample in darkness to low temperatures. This transient correlates to the Si dopant concentration. By investigating the behavior for below- and above-band-gap illumination we show that the observed transients are caused by hole capture at the *DX* center (hole-capture cross section $\sigma_{DX,h} \gtrsim 2\times10^{-16}$ cm^2). Using the transient to determine the occupation of the *DX* state, we confirm the electron-capture barrier and the photoionization cross section for *DX* centers, observed by Mooney *et al.*

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The *DX* center is present in AlGaAs and other III-V compounds doped with any shallow donor-producing species.[1,2] This defect limits device properties, but it is, on the other hand, important from the point of view of understanding semiconductor defects.[3,4] The *DX* center is a member of a growing family of defects identified as bistable.[5] There are macroscopic[6] and microscopic[7] models for the *DX* center, for which also a negative correlation energy U has been proposed.[7,8] Despite extensive efforts, the *DX* center (and many other complex centers, such as *EL*2 in GaAs) still present formidable difficulties for a consistent interpretation of experiments.

In this Letter, a new method for investigating the *DX* center is presented: near-band-gap photoluminescence (PL) transients due to hole capture at *DX* centers. These transients yield information about the occupation of *DX*, hence its properties can be analyzed under various external influences. All characteristics of the *DX* center were so far tested by measuring electron capture or emission [e.g., deep-level transient capacitance spectroscopy (DLTS) and Hall effect]. Our novel method reveals important properties of the *DX* center under experimental conditions of photoluminescence, which markedly differ from conditions for DLTS (e.g., electric fields). The efficient hole capture itself of the *DX* center, which is able to quench the initial near-band-gap PL, is an important new feature. We first describe the experiment, and then discuss the results to establish the hole capture at the *DX* center by means of the configuration-coordinate diagram (CCD).

Most of the PL measurements selected here for publication are done on a 2-μm-thick $Al_{0.34}Ga_{0.66}As$ sample grown by molecular-beam epitaxy on semi-insulating GaAs:Cr. The sample is doped with a Si concentration of about 1.5×10^{18} cm^{-3}. Because of the formation of an impurity band, the near-band-gap PL at a temperature of $T=2$ K shows a broad peak with the maximum at a wavelength of 660 nm (1.88 eV) and a full width at half height of about 15 nm. A Spex 0.75-m double-grating monochromator and a GaAs photomultiplier are used to detect the signal in most experiments. However, to investigate especially the time dependence of the near-band-gap PL emission at 660 nm, the photomultiplier together with an appropriate interference filter is placed directly in front of the cryostat. This method enhances the measurement sensitivity by a factor of 30.

While cooling to low temperature, the sample is carefully shielded against any light inside the cryostat. As shown in Fig. 1(a), the first above-band-gap illumination with low power ($\sim$10 μW/cm^2) causes a slow transient in the PL intensity, saturating at a final value $I(\infty)$. For different excitation intensities, the evolution of the transient is directly correlated to the integrated photon flux. The total number of photons needed to saturate the PL is approximately equal to the total number of Si in the layer. After the first illumination at low temperature any further measurement does not show a slow transient behavior, but starts immediately at $I(\infty)$, even if the sample is again placed in the dark for up to several hours [Fig. 1(b)]. Only after heating up the sample ($T>100$ K) and cooling down again do we get the same PL transient as for the first illumination. This bistable behavior is directly associated with the *DX*-center properties. We further probe the temperature dependence for converting the illuminated sample back into its initial state. By drawing an Arrhenius plot for the relative electron-capture cross section we get an energy barrier E_b close to 200 meV, in good agreement with data published by Mooney.[3]

Next, the photoionization cross section below and just above the band-gap energy E_g is investigated. We use a dye laser with LD700 and 4-(dicyanomethylene)-2-methyl-6-(p-dimethyl-amino-styrl)-4H-pyran (DCM) to illuminate the sample between 625 and 760 nm. After cooling down to 30 K in the dark, the sample is illuminated for 1 min with the dye laser and then a PL

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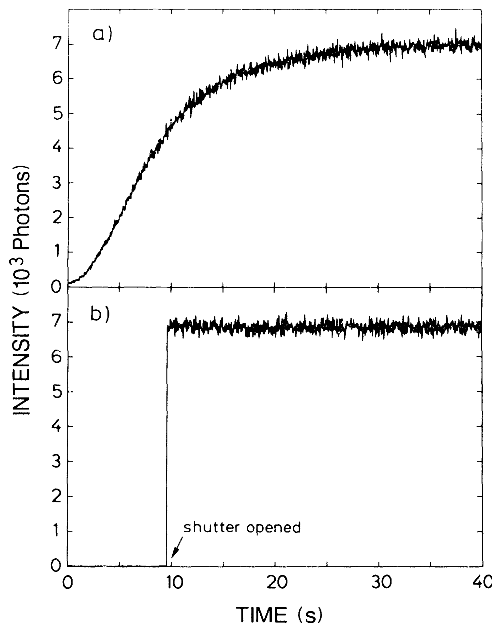

FIG. 1. (a) Transient in the near-band-gap photoluminescence ($h\nu = 1.88$ eV) for the first illumination after cooling down the $Al_{0.34}Ga_{0.66}As$:Si sample in the dark. The noise in the measurement is due to photon flux fluctuation statistics. (b) Any further illumination at low temperature shows no slow transient.

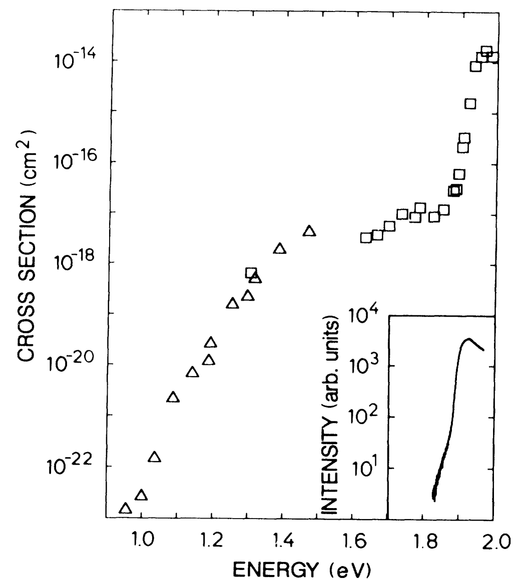

FIG. 2. Below 1.85 eV our data (□) represent the photoionization cross section for the DX center; above 1.85 eV we call the result an apparent cross section dominated by hole capture at the DX center. For comparison, the photoionization cross section after Mooney *et al.* (Ref. 9) (△) is shown.

transient measurement is started as described above, using now a HeNe laser at 632 nm (close above E_g) for excitation. Now the PL transients do not start at zero intensity, but at higher values which depend on the previous dye-laser illumination intensities, energies, and times. For each new measurement the sample has to be heated up ($T > 100$ K) and cooled down in the dark to convert the system again into the initial state. At E_g there is a drastic 3 order-of-magnitude increase in the conversion sensitivity of the DX center due to illumination.

Assuming at first that the direct photoionization of the DX center takes place for all excitation energies, the optical cross section is

$$\sigma^*(h\nu) = 1/\Phi(h\nu)\tau\,, \tag{1}$$

where $\Phi(h\nu)$ is the photon flux from the dye laser, τ is the time constant according to the illumination time of 1 min, and $h\nu$ is the photon energy. In Fig. 2, we compare our results (marked by squares) with the photoionization cross section for the DX center after Mooney *et al.*[9] (marked by triangles). In the overlapping range the two sets of data agree quite well. As soon as $h\nu > E_g$ (1.9 eV), we see an increase in $\sigma^*(h\nu)$ of about 3 orders of magnitude. At these energies electron-hole pairs are generated and we attribute the increase to a dominating charge transfer due to hole capture at the DX center. We call $\sigma^*(h\nu)$ an *apparent* photoionization cross section because above 1.9 eV the events are dominated by the hole capture. The value $\sigma^*(h\nu)$ directly describes the efficiency of any conversion of the DX center due to illumination with different photon energies. In Fig. 3 we show the usual CCD in a slightly modified form, where an additional electron-hole pair is shown in the total-energy scheme. The lower two parabolas of the picture represent the total energy of the system if one electron is either captured in the large lattice relaxation (LLR) DX^0 state or is free in the conduction band and the DX state has relaxed to a shallow donor state $(d^+ + e^-)$. We label the LLR state with DX^0, but this should not exclude the negative-U model. The upper parabolas, shifted by the gap energy, describe the system if there is an additional electron-hole pair $(e^- + h^+)$ created in the semiconductor. We are able to display all important transients in this picture by explicitly showing these different states of the system.

Cooling the sample in darkness to low temperature brings the system to its lowest energy state, which is DX^0 (in an n-type sample). Illumination with above-band-gap photons creates preferentially free electrons and holes (transition 2 in Fig. 3). The transition from the excited state can occur either by recombination of electron-hole pairs (transition 3) or by capturing a hole into the DX center (transition 4). We propose that this hole-capture mechanism causes the observed PL transients. The PL is initially quenched due to the efficient capture of free holes, but when most of the centers are converted to the d^+ state, further illumination (transi-

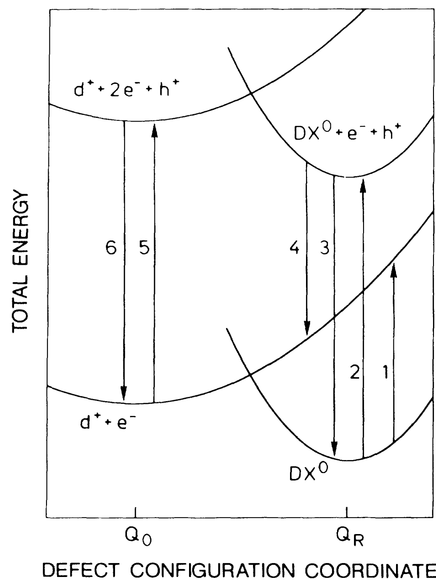

FIG. 3. Total-energy scheme (not scaled) of the system vs defect configuration coordinate. The upper two parabolas represent the system with an additional free electron-hole pair created. All transitions which take place are displayed (for detailed explanation see text).

tion 5) creates electron-hole pairs, which can then undergo the usual near-band-gap recombination process (transition 6). At low temperature, the electrons cannot overcome the barrier between d^+ and DX^0. Only after heating the sample and cooling in the dark the system is again in its lowest total-energy state, i.e., the DX^0.[10]

The initial illumination of the sample with *below*-band-gap photons (transition 1) ionizes a part of *DX* centers directly. Further illumination with *above*-band-gap light (transition 2) then causes a PL transient which starts at a value higher than zero and which, in turn, gives information about how many *DX* centers were ionized by the *below*-band-gap light. By using Eq. (1), we therefore get the photoionization cross section $\sigma(h\nu)$ for the *DX* center.

We also measured the excitation spectrum at the low-energy side of the near-band-gap luminescence peak. The excitation spectrum of the PL intensity at 680 nm (1.82 eV) while tuning the dye laser is shown in the inset in Fig. 2. The excitation of the PL and thus also the creation of free electrons and holes becomes efficient just at the same energy where the *apparent* cross section $\sigma^*(h\nu)$ shows its 3 order-of-magnitude increase. This is a further argument that the initial PL transient is caused by a quenching effect due to very efficient hole capture. In principle, the hole capture can take place also at junctions or inhomogeneities.[11] However, we show that in our case the appearance of the transient is correlated with the Si doping concentration in a series of metalorganic chemical-vapor deposition (MOCVD) samples. The transient is faster in the lower doped samples, because fewer holes are necessary to convert all the *DX* centers.

The maximum value for $\sigma^*(h\nu)$ of about 10^{-14} cm^2 does not correspond to a value for the *DX* hole-capture cross section. This *apparent* cross section results from efficient creation of free holes due to the large above-band-gap absorption coefficient. In order to estimate the true hole-capture cross section $\sigma_{DX,h}$ at the *DX* center, the observed transients are fitted by solving the occupation rate equations of the system. This gives a hole capture at the *DX* center which is about 5 times more efficient than the competing recombination processes for holes. From time-resolved measurements with a streak-camera system we get a time constant of about 3 ns for the near-band-gap PL lifetime under much higher excitation conditions. This gives an upper limit for the lifetime at very low excitation intensities. By combining these results we estimate a lower limit for $\sigma_{DX,h}$ of about 2×10^{-16} cm^2.

Watanabe *et al.*[12] estimated $\sigma_{DX,h}\simeq2\times10^{-17}$ cm^2 in n-$Al_{0.3}Ga_{0.7}As$ from DLTS measurements performed around 200 K. The measurements there show a strong temperature dependence of $\sigma_{DX,h}$ which suggests a capture barrier for holes of 0.14 eV. This is in disagreement with our results where we get, at 30 K, an even larger value for $\sigma_{DX,h}$. There is a very recent paper about hole capture in GaAs. Leroux *et al.*[13] estimated for GaAs:Sn a value of $\sigma_{DX,h}\simeq10^{-16}$ cm^2 from lifetime measurements under high pressure at room temperature, which is close to the low-temperature limit we estimated.

There are two reports about hole capture at *DX* centers in GaAsP. The first one gives a capacitance-measurement–derived ratio of $\sigma_{DX,h}/\sigma_{DX,e}\simeq10^6$ near 200 K for sulfur centers, which implies $\sigma_{DX,h}\simeq10^{-13}$ cm^2 and it is noted that $\sigma_{DX,h}$ is essentially temperature independent.[14] The second paper gives $\sigma_{DX,h}/\sigma_{DX,e} > 10^7$ at a temperature between 10 and 34 K and they also estimate that the hole-capture cross section has little temperature dependence.[15] The electron-capture cross section $\sigma_{DX,e}$ for $Al_{0.35}Ga_{0.65}As$:Si is about 10^{-22} cm^2 at 100 K but due to the thermally activated capture process it has a strong temperature dependence, and it is therefore unreasonable to combine the data for different temperatures to estimate $\sigma_{DX,h}$ for AlGaAs.

Stoneham[16] showed that a large capture cross section of about 10^{-16} cm^2 is due to a phonon-assisted nonradiative capture process, and he gives a value between 10^{-17} and 10^{-15} cm^2 for neutral centers and 10^{-15} to 10^{-12} cm^2 for Coulomb-attractive centers. However, to make further conclusions about the charge state of the *DX* center it would be necessary to investigate the hole-capture cross section of the *DX* center in more detail.

In conclusion, we have observed near-band-gap PL transients in AlGaAs:Si. By investigating a set of samples with different Si concentrations we showed that the bistable effect, manifested by the transient, is correlated with the Si concentration. The measurement of the con-

version efficiency for the *DX* state for below- and above-band-gap illumination gives a difference of 3 orders of magnitude from which we conclude that the hole capture at the *DX* center causes the transients in the near-band-gap PL. By fitting the transients and performing lifetime measurements we estimate a lower bound for the hole-capture cross section $\sigma_{DX,h}$ of 2×10^{-16} cm^2. This value is close to the boundary between neutral and Coulomb-attractive centers and does not allow one to distinguish between the two cases.

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