Charge state of the *DX* center in aluminum gallium arsenide from photo-Hall measurements

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We report the temperature dependence of the Hall mobility in the dark and in the persistent-photoconductivity (PPC) states of $Al_xGa_{1-x}As$:Te and $Al_xGa_{1-x}As$:Si samples, which incorporate buffer layers separating the epilayer from the substrate. The mobility of the Si-doped sample is higher in the PPC state than in the dark, whereas for the Te-doped sample the mobility in the dark is higher. The results for the Si-doped sample can be explained equally well by the positive-*U* and the negative-*U* models of the *DX* center and hence are not suitable for drawing definitive conclusions about the charge state of the *DX* center. On the other hand, the results for the Te-doped sample are shown to be conclusively in favor of the neutral charge state (positive-*U*) model of the *DX* center.

The *DX* center has been the focus of considerable research interest in the last few years.[1] It has invoked both fundamental and technological interest alike, due to its unusual properties and its manifestation in modern devices such as high electron mobility transistors. It is now widely accepted that the *DX* center is a highly localized state of the isolated donor atom possibly distorted from its substitutional configuration and is not a complex involving the donor atom and a native defect. Yet, the physics of an isolated donor atom having a highly localized state and a strong coupling to the lattice is not well understood. Among the different models for the *DX* center, the negative-*U* model proposed by Chadi and Chang[2,3] has received considerable attention in recent years since this model has a built-in large lattice distortion around the donor atom. In this model, the charge state of the occupied *DX* center is negative (DX^-) which results from the capture of two electrons by an ionized donor (d^+), i.e.,

$$d^+ + 2e^- \rightarrow DX^- \ . \qquad (1)$$

In the conventional position-*U* models, the occupied *DX* state is neutral (DX^0) formed by the capture of one electron by an ionized donor, i.e.,

$$d^+ + e^- \rightarrow DX^0 \ . \qquad (2)$$

An experimental determination of the charge state of the *DX* center is therefore crucial to further progress in the microscopic understanding of the *DX* center. In this paper, we report the temperature-dependent Hall mobility measurements on $Al_xGa_{1-x}As$:Te and $Al_xGa_{1-x}As$:Si samples to probe the charge state of the *DX* center.

It is well known that ionized impurity scattering dominates the Hall mobility at temperatures below about 100 K. Since the concentration of scattering impurity centers is obviously different for the DX^0 and DX^- models, one would expect to obtain unambiguous information on the charge state of the *DX* center from low-temperature Hall mobility measurements. Unfortunately, this has not been possible in practice because the mobility data analysis is complicated by the generally unknown compensating acceptor concentration in the sample. The role of compensating acceptors in the analysis of mobility measured by photo-Hall measurements has been recently pointed out.[4,5] It has been shown[4] that the DX^0 model predicts either an increase or a decrease in mobility upon photoionization of the *DX* center depending upon whether the compensation in the sample is high or low, respectively. On the other hand, the DX^- model predicts an increase in mobility after photoionization for all compensation. Thus, if an increase in mobility upon photoionization is observed in a photo-Hall measurement, it is not possible to conclusively establish the charge state of the *DX* center in the absence of an independent measure of compensation in the sample.

Most of the published experimental data on $Al_xGa_{1-x}As$:Si show an increase in mobility after photoionization of the *DX* center.[6] While these results have been generally argued in favor of the DX^- model,[7] they can as well be argued in support of the DX^0 model by assuming a high degree of compensation in the sample. Therefore, compensated samples are not particularly suitable for the determination of the charge state of the *DX* center from photo-Hall measurements.

More recently, Leith, Zukatynski, and SpringThorpe[5] have shown that the mobility of a weakly compensated sample of $Al_xGa_{1-x}As$:Si remains almost constant upon photoexcitation supporting the DX^0 model. However, ideally one should use a very low compensation sample for definitive conclusions from photo-Hall measurements, since in that case the DX^0 and DX^- models predict opposite signs of the photoinduced change in mobility. Samples containing group-IV dopants (Si, Ge, Sn) generally tend to be more compensated due to the amphoteric doping behavior of group-IV elements in III-V compounds. On the other hand, samples doped with group-VI donors (Te, Se, S) may be expected to be less compensated since in this case the compensation arises only from the background acceptor impurities and defects whose concentration may be carefully controlled by optimizing the growth conditions.

Two studies of Hall mobility on $Al_xGa_{1-x}As$:Te have been reported in the literature. In one study, Nelson[8] reported a decrease in mobility of a sample of $Al_{0.36}Ga_{0.64}As$:Te upon photoexcitation. This result can, of course, be argued in favor of the DX^0 model. Attempts to fit the data of Nelson quantitatively have been reported.[4,5] The main reservation about the data of Nelson has been that the sample used in this study does not incorporate a buffer layer between the $Al_xGa_{1-x}As$:Te epilayer and the semi-insulating GaAs substrate to eliminate a possible contribution from an inadvertant two-dimensional electron gas to the measured Hall mobility.

Dmochowski *et al.*[9] have reported Hall mobility data obtained from $Al_xGa_{1-x}As$:Te samples with and without a buffer layer. Without a buffer layer, the mobility of a sample of $Al_{0.3}Ga_{0.7}As$:Te shows a decrease in mobility while that of a sample of $Al_{0.6}Ga_{0.4}As$:Te remains almost constant upon photoexcitation. With a buffer layer, the results are reported only for the $Al_{0.6}Ga_{0.4}As$:Te sample which shows a slight increase in mobility after photoionization. Clearly, it is not possible to draw unambiguous conclusions about the charge state of the *DX* center from these data.

In the present study, we report the temperature dependence of the Hall mobility in the dark and in the persistent-photoconductivity (PPC) state of a sample of $Al_{0.36}Ga_{0.654}As$:Te incorporating a buffer layer. Our results clearly show a decrease in mobility after photoexcitation. We also report for the first time a quantitative fitting of the temperature dependence of mobility using consistent parameters for both dark and PPC conditions in the framework of DX^0 and DX^- models and show that our experimental results are conclusively in favor of the DX^0 model.

The sample used in this study was grown by liquid-phase epitaxy (LPE) at a growth temperature of 780 °C. We chose LPE for the growth of the sample, since LPE is known to be an excellent technique for the growth of materials with a very low background concentration of impurities and defects, and the focus of this work is to study a low compensation sample. The sample structure consists of a buffer layer of ~ 0.5-μm-thick undoped $Al_{0.36}Ga_{0.64}As$ and a ~ 2-μm-thick Te-doped $Al_{0.36}Ga_{0.64}As$ grown sequentially on a semi-insulating GaAs substrate. Ohmic contacts were made at the four corners of the sample by alloying tin balls at ~ 450 °C in a forming gas atmosphere. Hall measurements were performed in an automated measurement system in the temperature range from 20 to 300 K in a liquid-helium-flow cryostat. The sample was always cooled to the lowest temperature and measurements were made at different stabilized temperatures during the warming cycle. Persistent-photoconductivity conditions were created by first cooling the sample to 10 K in the dark, exposing the sample to an intense source of white light, and then returning the sample to the dark.

The measured temperature dependencies of the electron concentration and the Hall mobility for the dark and PPC conditions are shown in Fig. 1. The mobility in the PPC state is clearly seen to be less than the mobility in the dark before the sample was exposed to light. The steep increase in mobility in the PPC states after 60 K is related to the quenching of photoconductivity due to the capture of electrons by the *DX* centers. The mobility curves (as well as carrier concentration plots) for the dark and PPC conditions merge together at temperatures above 90 K when the *DX* centers are in thermal equilibrium with the conduction-band electrons. The decrease in mobility after photoionization or, equivalently, the increase in mobility with increasing occupation of the *DX* centers, is clearly in support of the DX^0 model (for low compensation samples) as argued earlier. We will now substantiate this argument more quantitatively by a theoretical analysis of the observed Hall mobility data in the framework of both the DX^0 and the DX^- models.

The mobility analysis was performed in the relaxation-time approximation. The total scattering rate obtained from the sum of the polar-optic, deformation-potential, piezoelectric, ionized impurity, neutral impurity, and alloy scattering rates was averaged over the energy distribution of electrons using Fermi-Dirac statistics by nu-

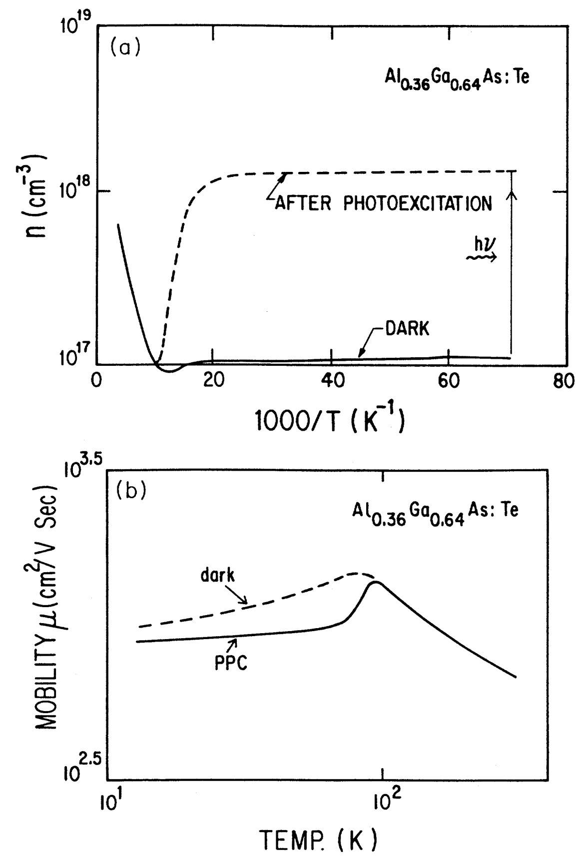

FIG. 1. Measured temperature dependence of electron concentration (a) and mobility (b) of $Al_{0.36}Ga_{0.64}As$:Te under dark and PPC conditions.

merical integration. Both drift and Hall mobilities were calculated and the comparison of the experimental data was made with the calculated Hall mobility values.

In the calculation of ionized impurity scattering, the dynamic screening of the impurity potential by the electronic cloud was taken into account by the Takimoto-Hall approach.[10,11] For large electron concentrations ($\sim 10^{18}$ cm^{-3}) typically observed under PPC conditions in our experiment, the Brooks-Herring theory considerably overestimates the screening owing to the neglect of the polarization due to the colliding electron.[12]

The ionized impurity concentration for the two models is determined as follows. For the DX^0 model, $N_i(DX^0)$ is given by

$$N_i(DX^0)=N_d^+ + N_A^- = 2N_A + n \ , \quad (3)$$

where n is the free-electron concentration measured in the experiment and the acceptor concentration N_A is treated as fitting parameter. For the DX^- model, $N_i(DX^-)$ is given by

$$N_i(DX^-)=N_d^+ + N_{DX}^- + N_A^- = N_D + N_A \ , \quad (4)$$

where N_D and N_A are the total donor and acceptor concentrations, respectively. It is seen from Eq. (4) that $N_i(DX^-)$ is the same for both dark and PPC conditions and it remains constant at all temperatures. If all the donors are assumed to be ionized ($N_D = N_d^+$) under saturated PPC conditions at the lowest temperature with a maximum electron concentration $n_{\max}^{\mathrm{PPC}}$, then

$$N_i(DX^-)=2N_A + n_{\max}^{\mathrm{PPC}} \ . \quad (5)$$

Once again, N_A is seen to be the only fitting parameter.

Neutral impurity scattering is important only for the DX^0 model. The scattering cross section by the nonhydrogenic DX center is calculated by using an effective Bohr radius estimated from the experimentally measured binding energy E_d of the DX center rather than using the Bohr radius given by the density-of-states effective mass, as suggested by Drummond and Hjalmarson[13] and McGill and Baron.[14] While the inclusion of the neutral impurity scattering is found to improve the overall quality of the fit, it is not essential for the fitting of the experimental data. The value of the fitting parameter N_A is found to change only slightly if the neutral impurity scattering is not included in the mobility analysis.

The calculated Hall mobility plots for both the DX^0 and DX^- models along with the experimental data in the temperature range from 20 to 150 K are shown in Fig. 2. We restrict the present discussion to this temperature range since the ionized impurity scattering is less dominant above 150 K. The ionized impurity concentration at the lowest temperature under the saturated PPC condition is the same for both models as seen from Eqs. (3) and (5). In the temperature range $T<60$ K, in which the decay rate of PPC is extremely small in the time scale of the experiment, $N_i(DX^0)$ and $N_i(DX^-)$ are nearly equal and hence the calculated mobility plots for the PPC state for both the models are coincident. At the onset of electron capture by the DX centers, $N_i(DX^0)$ and $N_i(DX^-)$ begin to differ and the calculated mobility curves for the

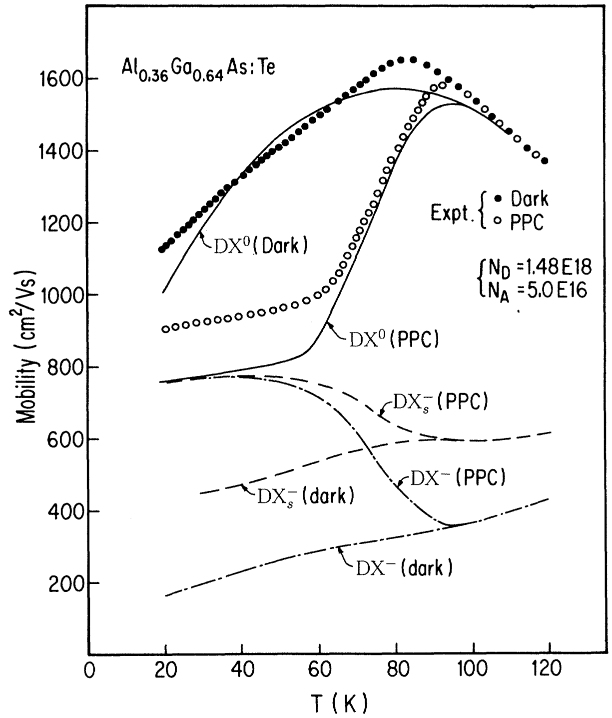

FIG. 2. Experimental data and simulated plots of mobility for the DX^0 and DX^- models under dark and PPC conditions for $Al_{0.36}Ga_{0.64}As$:Te.

two models branch in different directions. The fit of the calculated mobility curve for the DX^0 model to the experiment is particularly striking at temperatures above 60 K at which the mobility rises sharply before merging with the dark curve. On the other hand, the DX^- model shows the opposite trend of decreasing mobility after 60 K with increasing occupation of the DX centers, contrary to experiment. The values of the donor and acceptor concentration used in the present calculation are 1.48×10^{18} and 5.0×10^{16} cm^{-3}, respectively, giving a compensation ratio of $K=N_A/N_D=0.033$ which is indeed very small. This low value of compensation realized in the present sample is crucial to the definitive conclusion of this experiment. Finally, it may be mentioned that it is impossible to fit the dark experimental data using the DX^- model with parameters consistent with the electron concentration observed under the PPC conditions in the experiment.

In the calculations above, screening by mobile electrons only was taken into account. For the DX^- model, it may be argued that the static screening by the electrons bound to the DX center may also be quite important. To model this effect, we assumed the screening by the DX centers to be similar to the screening by negatively charged acceptors in the Brooks-Herring theory as discussed by Fallicov and Cuevas.[15] The results of this calculation are shown in Fig. 2 by the curves labeled DX_s^- (dark) and DX_s^- (PPC). It is seen that though the calculated mobilities for the DX_s^- model are considerably higher than those of the DX^- model, they still lie far short of the experimental curve.

We have also not included in this present analysis the role of any photoinduced new states related to the *DX* center in the framework of the DX^- model. Such new states have been observed only under the conditions of steady background light shining on the sample. There is no evidence of the presence of these states in the PPC state which results after the illumination is turned off. Even if one assumes that such states are present under the PPC conditions (in the dark), the analysis remains unchanged if these new states are also negatively charged trapping two electrons. On the other hand, if they are neutral (having one electron), then the calculated DX^- (dark) curve would lie even lower than that shown in Fig. 2 making the fit to the experimental data worse.

To complete this study, we now present results for a sample of $Al_{0.33}Ga_{0.67}As$:Si grown on a 0.3-μm undoped $Al_{0.33}Ga_{0.67}As$ buffer layer by molecular-beam epitaxy, which shows the opposite behavior of an increase in mobility after photoexcitation. Figure 3 shows the experimental data and the calculated curves for the DX^0 and the DX^- models. It is seen that the experimental data can be fit equally well by both models by the appropriate choice of values for N_D and N_A. For the DX^- model, the fit is slightly poorer at low temperatures under saturated PPC conditions, whereas for the DX^0 model the fit is good for both the dark and the PPC conditions. This emphasizes our earlier noted point that it is not possible to draw a definitive conclusion in favor of any one model in the absence of independent information on the compensation in the sample, if an increase in mobility is observed after photoexcitation in a photo-Hall measurement.

In conclusion, we have measured the temperature dependence of mobility of a sample of $Al_{0.36}Ga_{0.64}As$:Te in the dark and in persistent-photoconductivity conditions. The measured mobility after photoexcitation is found to be less than the mobility in the dark before the sample was exposed to light in the temperature range in which the capture rate of the electrons by the *DX* center is negligible. The experimental data of mobility fits very well with the neutral charge state model of the *DX* center, whereas the negative charge state model predicts a temperature dependence opposite of that of the experimentally observed trend. We, therefore, conclude unambiguously that the charge state of the occupied *DX* center is neutral. Our conclusion is in agreement with the results of magenetic-susceptibility measurements[16] but is in variance with the conclusions from electron paramagnetic resonance,[17] local vibrational mode spectroscopy,[18] and some deep-level transient spectroscopy[19] measurements. More work is needed to resolve the inconsistency between the results obtained from the two sets of measurements.

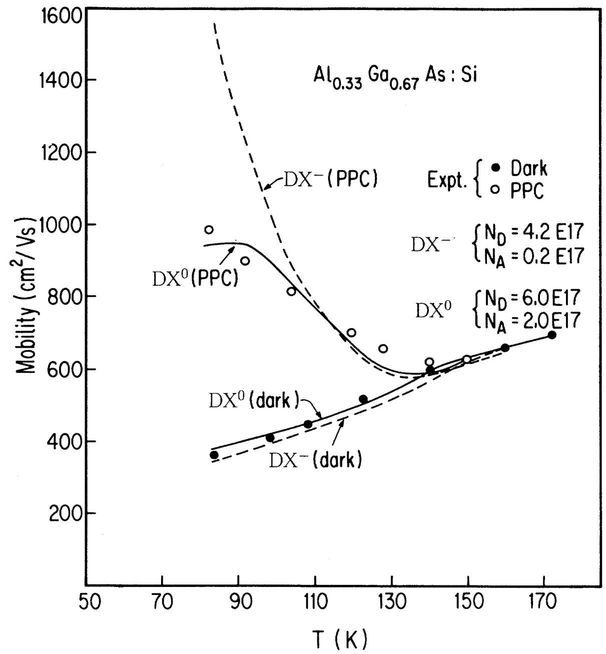

FIG. 3. Experimental data and simulated plots of mobility for the DX^0 and DX^- models under dark and PPC conditions for $Al_{0.33}Ga_{0.67}As$:Si.

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