Direct Proof of Two-Electron Occupation of Ge-DX Centers in GaAs Codoped with Ge and Te

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In this paper we present the first direct and unambiguous evidence that the total number of electrons which can be trapped on Ge-DX centers is exactly twice as large as the number of electrons which can be bound on Ge-A_1 donor states. It should be emphasized that our reasoning does not require any technological information, about either doping or the compensation of a sample.

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It is well known that many substitutional donors in semiconducting compounds, beside normal hydrogenlike donor states, can also form highly localized electronic states whose energy relative to the Γ conduction band minimum is highly pressure dependent. For some of these states there exist potential barriers for both electron emission and electron capture processes, leading to nonequilibrium occupation of these states by electrons at low temperatures—i.e., so-called metastable effects. These are called DX states. There are also other localized states with no apparent metastable effects present—see, e.g., the results of anitcrossing between a shallow donor state and a highly localized one, both originating from the same impurity, observed for n-InSb [1] or GaAs:Ge [2]. For simplicity, following some authors, such highly localized states will throughout this paper be called "A_1 states," just to distinguish them from DX-like ones—no matter whether the name is justified or not. There are some rare but very interesting cases for which both types of highly localized states (originating from the same impurity or defect) coexist and can both be populated by electrons in the same experiment. Such a population can be induced, e.g., by hydrostatic pressure which shifts the appropriate electronic levels down with respect to the conduction band minimum and the Fermi level. However, at low temperatures (i.e., well below a certain temperature T_c) due to potential barriers for emission and capture of electrons the population of DX-like states is nonequilibrium (frozen) and the pressure shift of the corresponding energy level does not influence its occupation. At $T \ll T_c$ its population can be changed only in a persistent way by means of illumination. While the pressure shift of the corresponding energy level can change the population of DX-like states only at $T > T_c$, for A_1 states there is no such restriction. Accordingly, in such materials as nominally undoped n-InSb [3], GaSb:S [4], or GaAs:Ge [5], in which both DX-like and A_1 states are present, hydrostatic presure measurements of the Hall coefficient reveal that at low temperatures the pressure-induced capture of free electrons is governed by a level whose energy position as well as pressure shift differ from those observed for temperatures high enough to populate DX states.

One of the most exciting problems related to DX centers was the charge state of the defect occupied with electrons. Since the first suggestions of Khachaturyan, Weber, and Kamińska [6] and Chadi and Chang [7] that DX is a negatively charged donor (i.e., occupied with two electrons) subjected to a large local lattice distortion, a huge number of experiments have been performed to determine the DX-center charge state. Among others, arguments were used based on electron paramagnetic resonance [6,8] and magnetic susceptibility [9] measurements, electron mobility changes due to population and ionization processes of DX centers [10], the kinetics of photoionization of DX centers and that of electron emission or capture [11], and DX-center-related local vibration mode studies performed at high pressure [12] or temperature dependent saturation of photoconductivity [13]. Although most of the papers suggested that DX was a negatively charged center, the arguments used were neither direct nor sufficiently unambiguous to finally close the discussion. It seems that experiments in which the total number of electrons trapped by DX centers could be directly compared to the DX center concentration should be more conclusive. The negative charge state of DX means two electrons trapped on one DX, while neutral DX gives a one-to-one correspondence. To completely saturate even doubly occupied DX centers one has to use samples codoped with other donors providing excess electrons to the system. Fujisawa and co-workers [14] studied GaAs codoped with Ge and Si in the range of hydrostatic pressure in which Ge acted as a DX center and Si as a source of excess free electrons only. Maude and coworkers [15] investigated the persistent photoconductivity effect (PPC) of AlGaAs samples codoped with Si and Sn in which the photoionized Si-DX centers provided excess free carriers to saturate the Sn-DX centers. While the concentration of electrons trapped by DX centers could be measured directly in these experiments, the number of DX centers could not be measured but only predicted from technological data. Beside the uncertain character of technological data, one has also to take into account that the number of introduced impurity atoms can differ from that of DX centers because of the amphoteric character of IV-group elements or possible complex formation.

In this paper, to avoid the above mentioned problems,

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we have chosen for investigation a semiconducting material for which (1) there exists an impurity having both DX-like and A_1 electronic levels; (2) at ambient pressure both levels are resonant with the conduction band but close enough to its bottom to be easily populated with electrons at hydrostatic pressures not exceeding 1.5 GPa; (3) another, always ionized donor impurity can be introduced to serve as an additional source of electrons and thus to enable the full saturation of even doubly occupied DX centers. GaAs codoped with Ge and Te appeared to be such an ideal system.

The germanium impurity in GaAs forms both DX and A_1 electronic levels which at ambient pressure lie approximately 100 meV [5] and 70 meV [2,5] above the bottom of the conduction band (CB), respectively. At high pressure they move downwards with respect to the CB, approaching one another, and at pressures exceeding 1 GPa they cross close to the CB edge [5]. This means that in order to have at ambient pressure completely empty levels, the Fermi level cannot exceed 30–40 meV which corresponds to the free electron concentration n not higher than a few times 10^{17} cm^{-3}. On the other hand, to completely saturate even doubly occupied Ge-DX centers, n must be higher than $2N_{\text{Ge-}DX}$, where $N_{\text{Ge-}DX}$ is the concentration of Ge-DX centers. This leads to the conclusion that the concentration of additional, always ionized donors must exceed $N_{\text{Ge-}DX}$. We chose Te as the additional donor since the DX level of Te in GaAs lies exceptionally high (more than 400 meV above the CB edge [16]) in comparison with the DX levels of other donors. Therefore, for samples with $E_f < 40$ meV and at pressures not higher than 1.5 GPa, Te donors always remain completely ionized.

The crystal, specially designed for our experiment, was grown by the conventional liquid encapsulated Czochralski (LEC) technique. The Hall concentration and Hall mobility measured at $T=77$ K and at ambient pressure on the sample for which we present the results in this paper were $n_H = 2.93\times10^{17}$ cm^{-3}, $\mu_H = 2560$ cm^2/Vs. We performed the measurements of n_H and μ_H as a function of hydrostatic presure up to 1.45 GPa at two different temperatures, $T=100$ and 77 K. At $T=100$ K the capture and emission of electrons on and from the Ge-DX is sufficiently fast to allow an easy change of its occupation by means of pressure. On the contrary, at $T=77$ K its occupation is practically frozen and only the population of the Ge-A_1 level can vary with pressure [5]. Hence, depending on the initial conditions we could, at $T=77$ K, pressure tune the occupation of the Ge-A_1 level for various (but fixed) concentrations of occupied Ge-DX centers. In the experiment we used a helium gas pressure system which allowed the value of the pressure acting upon a sample to be changed at a constant low temperature. In our pressure cell we mounted an infrared GaAs light emitting diode (LED) which could be used to persistently ionize Ge-DX centers. To avoid a nonhomogeneous distribution of photoionized DX centers this LED was applied only in such cases when full persistent DX photoionization (emptying) was needed at $T=77$ K. To obtain various partial persistent occupations of Ge-DX centers at $T=77$ K we used the following procedure: (1) First the pressure was raised at $T>100$ K to the value which assured the required occupation of DX centers; (2) then the temperature was lowered to $T=77$ K and thus the DX occupation was frozen.

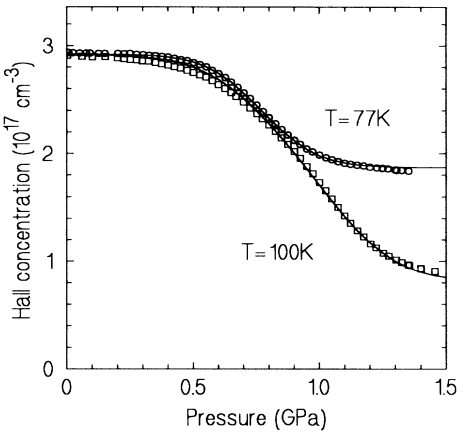

FIG. 1. Steplike dependences of the Hall concentration measured as a function of hydrostatic pressure at $T=77$ and 100 K. Solid lines show the results of calculations.

Figure 1 presents the pressure dependences of the Hall concentration measured at $T=77$ and 100 K. The results obtained at $T=77$ K correspond to fully photoionized DX centers. The steplike character of the curves means that Ge localized states were completely empty at low pressure, gradually populated at intermediate pressures, and finally almost completely saturated with electrons at high pressure (the highest value of pressure was slightly too low to observe full saturation—especially at $T=100$ K). Since at $T=77$ K the DX was persistently empty, the amplitude of the step, equal to the concentration of electrons trapped on Ge-A_1 states, gave in this case the total concentration of Ge donors (provided that each A_1 state can be populated with one electron). Thus we obtained $N_{\text{Ge}} = 1.05\times10^{17}$ cm^{-3}. On the other hand at $T=100$ K, when the DX states were active, the total concentration of electrons trapped by Ge donors appeared to be twice as large. To confirm that the above experimental results really mean that each DX center can be occupied with two electrons, we checked the correlation (if any) between the concentration of electrons persistently trapped on the Ge-DX level and that of electrons which could be trapped on remaining Ge-A_1 states. Figure 2 presents the pressure dependences of the Hall concentration measured at $T=77$ K for various persistent occupations of DX centers obtained by means of the method described above. The highest curve is the same as in Fig. 1 (DX fully photoionized). The rest of the curves corre-

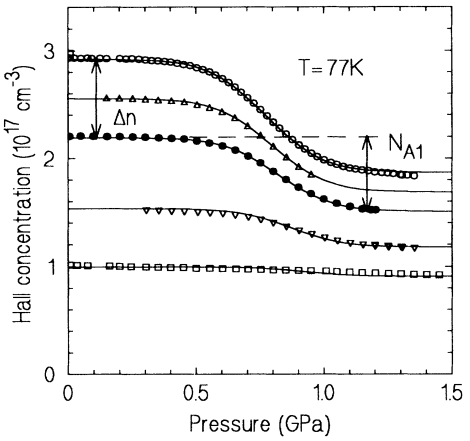

FIG. 2. Hall concentration versus hydrostatic pressure measured at $T=77$ K for various partial persistent occupations of DX centers. The highest curve corresponds to full persistent photoionization of DX centers. Solid lines are the results of calculations.

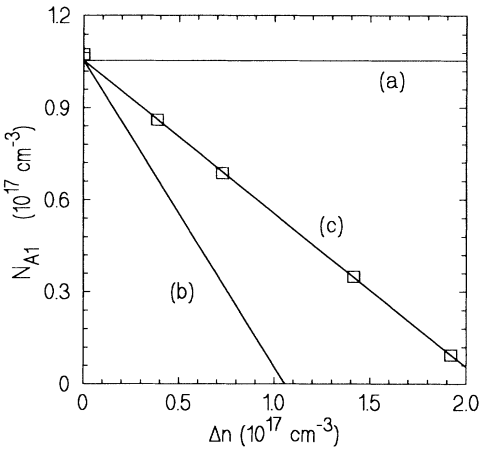

FIG. 3. Accessible number of A_1 states N_{A_1} versus the number of electrons persistently trapped on DX states, Δn. Straight lines correspond to the following cases: (a) A_1 and DX states given by two different defect centers. (b) Both states are given by the same defect with DX trapping only one electron. (c) The same as (b) but with two electrons trapped per each DX state.

spond to partial persistent DX center occupation. In particular, the lowest curve was obtained after cooling the sample at $p=1.45$ GPa, at which pressure the DX was already saturated (see Fig. 1, $T=100$ K), and thus it corresponds to a practically full persistent occupation of DX centers. It is clear that the higher the concentration of electrons persistently trapped on DX centers, Δn (marked as an example for one of the curves in Fig. 2), the lower the concentration of A_1 states, N_{A_1}, given by the height of the steps seen in Fig. 2. To visualize this correlation we plotted in Fig. 3 N_{A_1} versus Δn, taken from Fig. 2. If the DX and A_1 states originated from two different defects instead of the same one, the population of DX states should not influence the number of accessible A_1 states —i.e., N_{A_1} should not depend on Δn in Fig. 3. In such a situation the experimental points should lie along line (a), which is certainly not the case. Since, as is clear from the above results, both DX and A_1 do originate from the same defect, the following condition must be fulfilled: $N_{A_1}+N_{DX}=N_{\mathrm{Ge}}$, where N_{DX} is the concentration of persistently occupied DX centers. If each DX traps k electrons, then $kN_{DX}=\Delta n$, and we end up with the equation $N_{A_1}=N_{\mathrm{Ge}}-\Delta n/k$. Thus the slope of the straight line from Fig. 3 must give the inverse of k. Line (b) from Fig. 3 is drawn for $k=1$, i.e., for the case when each DX traps only one electron, while line (c) corresponds to $k=2$—double occupation of DX centers. Obviously, the experimental points give a perfect confirmation of the latter case. All the pressure dependences of Hall mobility obtained at both $T=77$ and 100 K are qualitatively entirely consistent with the above finding. The experimental results and the analysis of the mobility will be published elsewhere.

To check if the parameters describing both A_1 and DX levels which can be extracted from the data presented in Fig. 1 are similar to those already published [2,5] we fitted the energies of the levels, $\mathcal{E}^{0/+}$ and $\mathcal{E}^{-/0}$ and their pressure coefficients, $\partial\mathcal{E}^{0/+}/\partial p$ and $\partial\mathcal{E}^{-/0}/\partial p$, to have the best agreement between the calculated curves and the experimental points. For concentrations of Ge and Te donors $N_{\mathrm{Ge}}=1.05\times10^{17}$ cm^{-3} and $N_{\mathrm{Te}}=1.87\times10^{17}$ cm^{-3}, respectively, and for assumed degeneracy factors of positive, neutral, and negative charge states of the Ge donor equal to 1, 2 (spin doublet), and 4 (spin singlet, orientational degeneracy only), respectively, as well as assuming a δ-like density of states for both levels, we obtained $\mathcal{E}^{0/+}=80$ meV, $\partial\mathcal{E}^{0/+}/\partial p=-75$ meV/GPa, $\mathcal{E}^{-/0}=112$ meV, $\partial\mathcal{E}^{-/0}/\partial p=-90$ meV/GPa, where all the values are given with respect to the conduction band edge. The solid lines in Fig. 1 and Fig. 2 are calculated with the above parameters. Each line in Fig. 2 corresponds to a different concentration of electrons persistently trapped on DX centers, Δn, which was taken directly from the experimental data. Although the fit is very good, the obtained values of the parameters should be treated with some caution, since we have not taken into account the possible broadening of the density of states due to disorder or spatial correlation of impurity charges. Moreover, we are not absolutely sure if the degeneracy factor of the negatively charged DX is really equal to 4. Anyway, the above values of energies and pressure coefficients mean that at low pressure $\mathcal{E}^{-/0}>\mathcal{E}^{0/+}$, i.e., that the effective Hubbard correlation energy U is positive $(U>0)$ and only at very high pressure U might change its sign (negative U case). In our case, due to codoping, all Ge donors can be doubly occupied. However, even without additional source of electrons, if only $\mathcal{E}^{0/+}$ and $\mathcal{E}^{-/0}$ levels lie close enough to one another and are

both close to the Fermi level, a fraction of Ge donors can be negatively charged (i.e., doubly occupied) even for $U > 0$ and all the three charge states can coexist. It seems that the double occupation of *DX* centers (which was explicitly shown in our paper for the Ge donor) is characteristic for many other donors in GaAs and GaAlAs. However, it should be pointed out that this is not a general behavior for *DX*-like centers. A very interesting exception is an unidentified *DX*-like center in nominally undoped *n*-type InSb which was reported about twenty years ago [3] and was believed to be related to an oxygen contamination or a structural defect. This defect forms three localized electronic levels—a shallow hydrogenic one, associated with the Γ CB minimum [1], as well as A_1- and *DX*-like ones, both resonant with the CB at ambient pressure [3]. However, in contrast to our finding for the Ge donor in GaAs, it can easily be deduced from pressure measurements performed at $T = 77$ K [3] that both A_1- and *DX*-like states given by this unidentified defect in *n*-InSb capture the same number of electrons.

In conclusion, from our results it unambiguously follows that each Ge-*DX* state is occupied by two electrons. Such double occupation does not necessarily mean that for every *DX* center the effective Hubbard correlation energy *U* is negative. Moreover, not all of the so-called *DX*-like states must be occupied by two electrons—e.g., the above mentioned *n*-InSb case [3] interpreted by the authors within a large lattice relaxation model which was of the same type as the models used nowadays to explain *DX*-like behavior of donors.

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