Magnetic-resonance studies of tellurium-doped $Al_xGa_{1-x}As$

M. Surma, Z. Żytkiewicz, K. Fronc, and M. Godlewski
Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Aleja Lotników 32/46, Poland

P. Stallinga
Van der Waals-Zeeman Laboratory, Amsterdam University, Valckenierstraat 65, 1028 XE Amsterdam, The Netherlands

B. Monemar
Department of Physics and Measurement Technology, Linköping University, 581 83 Linköping, Sweden
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An ESR study performed on a thick $Al_xGa_{1-x}As$ epilayer with removed GaAs substrate is presented. The measurements were performed on LPEE-grown $Al_xGa_{1-x}As$ ($x=0.41$) heavily doped with Te. The detailed photo-ESR investigations of the light-induced conversion of the *DX* centers into the shallow Te donor states are presented. The mechanism of an enhanced photosensitivity of the Te-related electron-spin-resonance signal in $Al_xGa_{1-x}As$ is discussed. The observed anisotropy of the signal allows us to estimate the A_1-E valley-orbit splitting for Te donor. The ODMR experiment indicates that the E-symmetry state of the Te donor participates in electron trapping to the A_1 ground state.

I. INTRODUCTION

The so-called *DX* state of group-IV and group-VI donors in $Al_xGa_{1-x}As$ and GaAs belongs to the most studied deep impurity state in III-V semiconductors.[1] The *DX* state is believed to have a negative-U property[2,3] and is diamagnetic, i.e., it cannot be studied with magnetic-resonance techniques. However, it is accompanied by a metastable effective-mass-like shallow donor state.[1,4] This state is paramagnetic and could be detected with electron-spin-resonance[5] (ESR) and optically detected magnetic-resonance[6,7] (ODMR) techniques. Such experiments are presented in the present work for tellurium donor in $Al_xGa_{1-x}As$ samples. An ESR study of Te-doped $Al_xGa_{1-x}As$ was performed by Bardeleben *et al.*[8] The sensitivity of that experiment was, however, low due to the thin metal-organic vapor-phase epitaxy (MOVPE) samples used by the authors.[8] In our study we used uniform thick liquid-phase-electroepitaxy (LPEE) -grown samples, which increased the sensitivity of the experiment and enabled an ESR study of $Al_xGa_{1-x}As$ with a removed GaAs substrate. The aim of our investigations was (a) to confirm the previous identification of an ESR signal as that of the shallow donor state of Te, and (b) to describe its properties in carrier-trapping processes and radiative recombination transitions. For the latter case, we supplemented ESR by ODMR studies.

II. EXPERIMENTAL PROCEDURE

The ESR and ODMR experiments were performed on conventional *X*-band spectrometers on thick $Al_xGa_{1-x}As$ epilayers grown on semi-insulating (001) GaAs:Cr substrates, by either the modified liquid-phase-electroepitaxy method described elsewhere,[9] or by liquid-phase epitaxy (LPE). Layers with an Al fraction above 0.4 were used to study *X*-minimum conduction-band (CB) states of the Te donor in $Al_xGa_{1-x}As$.

Two different LPEE epilayers were studied (E37/90 and E23/91). The sample E37/90 had 0.41 ($\pm$0.01) Al mole fraction on the whole 190 μm thickness and 2.5×10^{18} cm^{-3} Te concentration. The sample E23/91 had 0.56($\pm$0.01) Al mole fraction on the whole 200 μm thickness, the Te concentration was 2×10^{18} cm^{-3}.

The two LPE samples studied were 45 μm thick, have 0.42 and 0.5 Al-mole fraction, respectively, and were relatively lightly doped with Te to 10^{16} cm^{-3}. The uniformity of the LPE samples was worse than those grown by LPEE. A small increase of the aluminum fraction toward the $Al_xGa_{1-x}As$/GaAs interface was observed.

III. MAGNETIC-RESONANCE EXPERIMENTS

The $g=1.94\pm0.01$ ESR signal observed for two LPE and for E23/91 LPEE epilayers is shown in Figs. 1(a), 1(b), and 1(c), respectively. Due to a larger Te doping level of the LPEE sample and only a partial freeze-out of electrons to the deep *DX* state, the $g=1.94$ signal was consistently observed prior to any illumination. This occurred even for the sample cooled down in total darkness. A similar situation occurred for the $x=0.5$ LPE sample [Fig. 1(b)] if the cooling down was fast. A large thickness of the LPEE epilayer enabled etching of the GaAs substrate. The $g=1.94$ ESR signal was observed both before and after etching the GaAs substrate.

Some anisotropy of the $g=1.94$ ESR signal of the $x=0.42$ LPE epilayer was observed. The ESR signal varies between $g=1.9475$ for the [001] direction (normal to the heterointerface) and $g=1.9434$ for the [110] direction (in the plane of the heterointerface). No signal anisotropy was observed for thick LPEE epilayers both before and after removing the GaAs substrate. In the former case, the thickness of the LPEE epilayers was above the critical one, i.e., the strain was relaxed by formation of misfit dislocations.

A detailed photo-ESR investigation was performed on

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the E23/91 epilayer, but the same results could be observed also for the second LPEE sample. The signal observed for the LPE samples was too weak for such investigations. The spectral dependence of the signal photosensitivity was measured in the following manner. First, the sample was cooled down to 4 K in complete darkness. Next, the sample was illuminated with a low-intensity monochromatic light of a given photon energy for a fixed time. Then, the light was turned off and the magnitude of the ESR signal was measured. After the light was turned on, the intensity of the ESR signal was decreased or even a complete quenching of the signal was observed. The change of the ESR signal was persistent at low temperatures. The sample during and after the illumination was conducting. A carbon probe sample was used to determine the influence of the decrease of the cavity Q factor on the amplitude of the ESR signal. We found that the observed decrease of the $Al_xGa_{1-x}As$ ESR signal is entirely caused by the decrease of the cavity Q factor occurring when the $Al_xGa_{1-x}As$ sample becomes conducting.

Sample heating up to liquid-nitrogen temperature and then a subsequent cooling down to 4 K (in darkness) was necessary to return to a similar starting magnitude of the ESR signal. Next, another photon energy was selected to measure the effect of the illumination on the ESR signal. As shown in Fig. 2, the photoquenching process becomes effective for the photon energy larger than approximately 0.6 eV. This value coincides very well with the photoionization threshold derived from photoconductivity measurements performed on the tellurium-doped $Al_xGa_{1-x}As$.[3] The kinetics of the ESR signal quenching was measured. Selecting a different initial concentration of the shallow donor center, we could have either pure one-exponential decay or a clear two-exponential behavior.

A tedious experimental procedure was necessary to get the temperature dependence of the ESR signal recovery. First, the magnitude of the ESR signal was measured at 4 K. Then, a white-light illumination was applied for a period of 5 min. This time was selected to ensure that an equilibrium signal magnitude is reached. Once a weak white-light illumination was used, a total photoquenching of the signal could occur after long illumination. Then, the light was turned off and the sample temperature was increased to a selected temperature. Then, after a fixed time, the sample temperature was slowly decreased to 4 K, also at a fixed time. After each such cycle the magni-

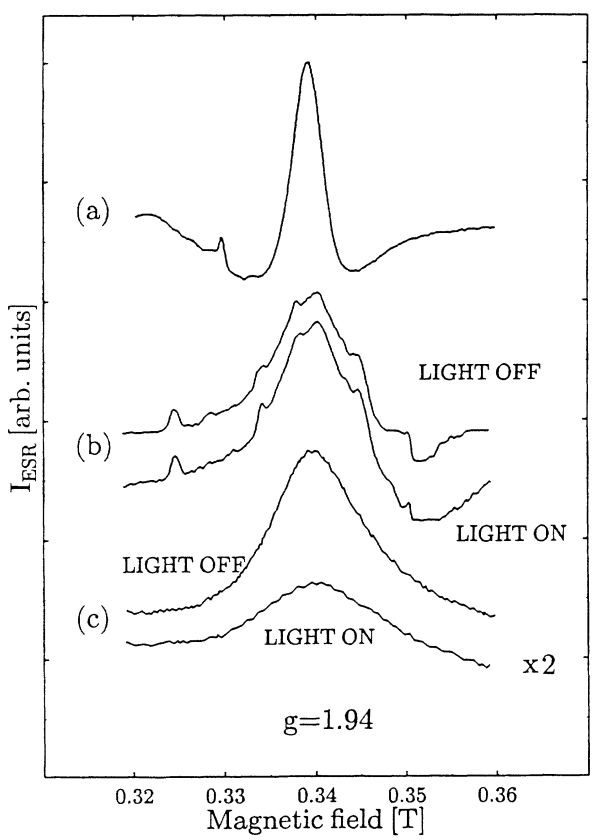

FIG. 1. Electron-spin-resonance spectra of LPE-grown $x=0.42$ (a) and $x=0.5$ (b) $Al_xGa_{1-x}As$ layers. The spectra shown in (b) were measured before and after the illumination. The ESR spectrum shown in (c) was measured for $x=0.41$ LPEE layer after removing the GaAs substrate. The ESR signal shown was observed for sample cooled down to 4 K temperature in total darkness before and after 120 s of white-light illumination.

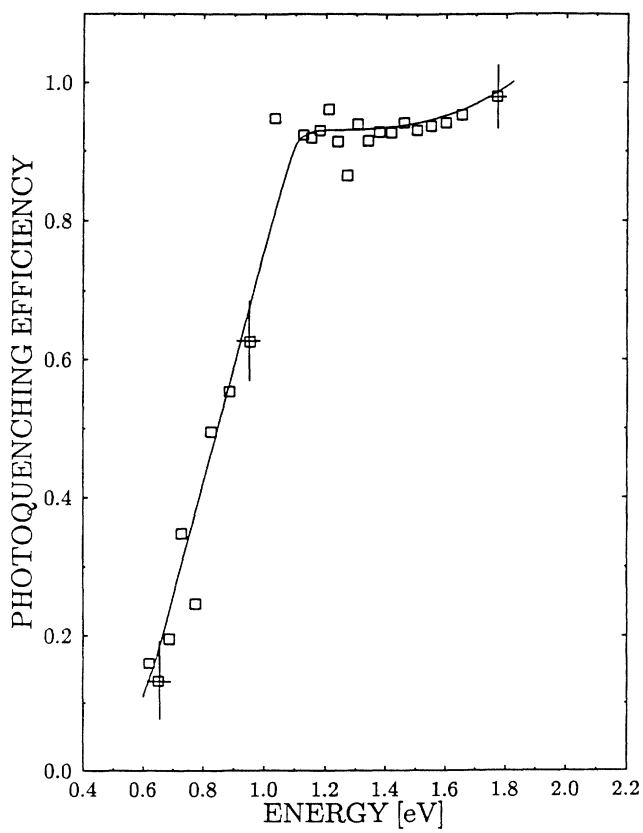

FIG. 2. Spectral dependence of the $g=1.94$ ESR signal photoquenching observed for the $x=0.41$ $Al_xGa_{1-x}As$ LPEE epilayer under illumination. The sequence of steps of the experiment is described in the text. 1 stands for total photoquenching of the signal.

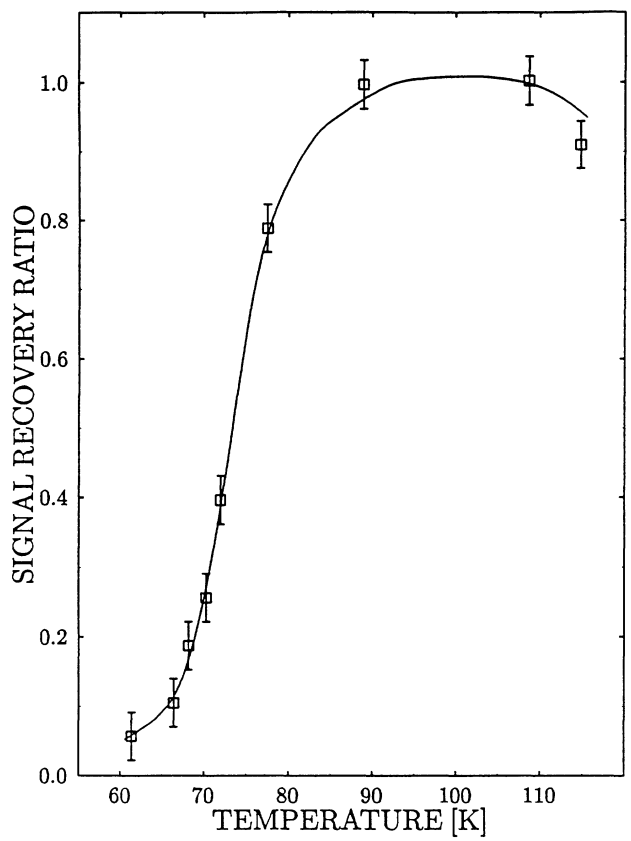

FIG. 3. Temperature dependence of the ESR signal recovery measured for the $x=0.41$ $Al_xGa_{1-x}As$ LPEE epilayer. The sequence of steps of the experiment is described in the text.

tude of the ESR signal was measured to determine the fraction of the ESR signal which was recovered after the annealing. A similar sequence of experimental steps was necessary for each next annealing temperature. The temperature dependence of the ESR signal annealing is presented in Fig. 3.

Detailed ODMR investigations were performed for $x=0.42$ LPE sample. An ODMR signal with $g=1.95\pm0.01$ was observed for the optical detection set at the *C*-related (DAP) emission of GaAs and at the 1.988-eV DAP emission of the $Al_xGa_{1-x}As$ epilayer. The $g=1.95$ spectrum was observed only under direct photoexcitation of the $Al_xGa_{1-x}As$ epilayer.

For an increased microwave power, both the $Al_xGa_{1-x}As$ and GaAs emissions are reduced and then, for further increased power, started to oscillate. This is evidence of the impact ionization of shallow centers and of exciton breakdown caused by collision with microwave-accelerated free carriers.[10,11]

IV. DISCUSSION

The ODMR and the ESR investigations prove that the $g=1.94$ magnetic resonance comes from the $Al_xGa_{1-x}As$ epilayer. This signal attribution is unambiguous since the ESR studies were performed on the epilayer with removed GaAs substrate. The ESR spectrum has an identical *g* factor as the signal observed previously in the ESR studies by Bardeleben *et al.* for MOVPE-grown epilayers.[8] All features of the $g=1.94$ ESR signal are consistent with those expected for the X_1 CB minimum—related shallow Te donor in $Al_xGa_{1-x}As$.

The above conclusion is not questioned by the fact that the $g=1.94$ signal could also be observed in dark, i.e., after the sample was cooled in total darkness down to the liquid-helium temperature. As already mentioned, some of the donors may remain in the nonequilibrium shallow donor state.[12] Controlling the cooling time (fast cooling) we could even freeze nearly all donors in a nonequilibrium shallow donor state. In that case no photosensitivity of the ESR signal was observed (see Fig. 1), which reflects a known property of shallow donors in $Al_xGa_{1-x}As$—the shallow donor state cannot be light converted to the deep *DX* state.

The photosensitivity of the ESR signal is usually interpreted as evidence for the direct photoionization of the center studied. This may not always be true and a pseudosensitivity was observed in some cases.[13,14] By a pseudophotosensitivity of an ESR signal we mean here the change of the ESR signal, which is not related to direct ionization of the center. Such photosensitivity can be related to the appearance of free or quasi-free-electrons in the sample caused by the illumination. These electrons absorb radiation and may screen the interior of the sample from microwaves and/or cause a decrease of the cavity *Q* factor. A reduced penetration depth of the sample by microwaves (skin effect[14]) and a reduced cavity *Q* factor both result in a reduction of the amplitude of any ESR signal of a bulk center, also for those centers which are not directly affected by the illumination.[14] Experiments performed with the probe sample mounted in the cavity indicated that the major contribution to the observed decrease of the ESR signal is due to the decrease of the cavity *Q* factor.

An asymmetrical ESR line is expected for a conducting sample. An asymmetry factor of between 3 and 4 is expected in the case of metallic samples. The value about 1.2 was observed in our case of quasi-free-carriers hopping via shallow donor states. A Dyson-type ESR signal was also observed by Bardeleben *et al.*[8]

The ESR signal of the A_1 donor state of Te should be isotropic. The observed anisotropy of the ESR signal relates to the strain-induced mixing of the upper-lying *E*-symmetry state with the ground A_1 state of the group-VI donor, i.e., the anisotropy observed reflects the anisotropy of the *E* state. Its magnitude depends on the strain value and on the energy distance between the two donor states. Under common assumptions, made also for S and Se donors in $Al_xGa_{1-x}As$,[7] we obtained the value of about 20 meV for A_1-*E* splitting.

An experimental method was applied to determine the role played by the *E*-symmetry excited state in carrier-trapping processes. We have observed that the impact ionization of a two level by the microwave-accelerated free-carriers system may lead to the chaotic oscillations in the carrier density.[11] In our experimental setup, free carriers could gain the energy sufficient for the dissocia-

tion of the bound excitons and the E-symmetry excited donor state. The temporal changes of the DAP photoluminescence intensity observed in our ODMR experiment suggest, thus, that the E-symmetry state may act as an intermediate, relatively long-lived state for carrier trapping to the ground A_1-symmetry state.

The observed spectral dependence of the signal photosensitivity and of its thermal recovery agrees well with the data obtained by other authors from different experiments. The present ESR study verifies, thus, that the phenomena observed in those experiments relate to the conversion of the deep DX state into the shallow donor state of Te in $Al_xGa_{1-x}As$. Detailed discussions of these processes can be found elsewhere.[3,8]

The observed kinetics of the signal quenching requires some comment. The calculations of Chadi and Chang[2] predicted that the intermediate DX^0 state is unstable and relaxes immediately to the substitutional state of the neutral shallow donor. The recent calculations of Dabrowski and Scheffler[15] suggested that a small energy barrier may exist, which will stabilize the DX^0 state of the Te donor. This should result in observation of two-exponential ionization kinetics. Recently such kinetics were reported by Dobaczewski and Kaczor[3] but were not confirmed by Su, Farmer, and Mizuta.[16] Our experiments indicate that depending on the shallow donor concentration either the double- or single-exponential kinetics can be observed. By changing the cooling time, we could select different initial concentrations of the nonequilibrium shallow donor state and observe the influence of the initial conditions on the photo-ESR kinetics. This result can be accounted for convincingly by the recent models of the DX photoionization assuming that this process proceeds via an intermediate state of a neutral Te donor.[3]

V. CONCLUSIONS

As a main conclusion, we would like to point out that the present results demonstrate how misleading the interpretation of ESR and photo-ESR data can be for conducting $Al_xGa_{1-x}As$ epilayers. All possible misinterpretation could occur since the ESR signal was also observed in the dark; at some conditions it showed a very strong photosensitivity, while in some, the magnitude of the ESR signal was decreased by the illumination, even though the center concentration was increased. All these facts could be interpreted erroneously and, speaking ironically, could easily be adapted for confirmation of any of conflicting models of the DX center in $Al_xGa_{1-x}As$. A clear demonstration and explanation of the abovementioned effects is, in our opinion, one of the most important aspects of the present ESR study. The results obtained confirm the present understanding of the Te-related donor states in $Al_xGa_{1-x}As$.

[1]P. M. Mooney, J. Appl. Phys. **67**, R1 (1990).

[2]D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988); Phys. Rev. B **39**, 10 063 (1989).

[3]L. Dobaczewski and P. Kaczor, Phys. Rev. B **44**, 8621 (1991).

[4]T. N. Theis, T. F. Kuech, L. F. Palmateer, and P. M. Mooney, in *Gallium Arsenide and Related Compounds 1984,* IOP Conf. Proc. No. 74 (Institute of Physics and Physical Society, London, 1984), p. 241.

[5]H. J. von Bardeleben, in *Solid State Phenomena,* edited by J. C. Bourgoin (Science Tech, Vaduz, Liechtenstein, 1989), Vol. 10, p. 181.

[6]T. A. Kennedy and E. Glaser, in *Solid State Phenomena* (Ref. 5), p. 53.

[7]E. Glaser, T. A. Kennedy, B. Molnar, and M. Mizuta, in *Impurities, Defects and Diffusion in Semiconductors: Bulk and Layered Structures,* edited by J. Bernholc, E. E. Haller, and D. J. Wolford, MRS Symposia Proceedings No. 163 (Materials Research Society, Pittsburgh, 1990).

[8]H. J. von Bardeleben, M. Zazoui, S. Alaya, and P. Gibart, Phys. Rev. B **42**, 1500 (1990).

[9]Z. R. Żytkiewicz and S. Miotkowska, J. Cryst. Growth **121**, 457 (1992).

[10]H. Weman, M. Godlewski, and B. Monemar, Phys. Rev. B **38**, 12 525 (1979).

[11]M. Godlewski, K. Fronc, M. Gajewska, W. M. Chen, and B. Monemar, Phys. Rev. B **44**, 8357 (1991).

[12]P. W. M. Blom, P. M. Koenraad, F. A. P. Blom, and J. H. Wolter, J. Appl. Phys. **66**, 4269 (1989).

[13]M. Godlewski, Phys. Status Solidi A **90**, 11 (1985).

[14]M. Godlewski, H. Przybylińska, and J. M. Langer, Appl. Phys. A **30**, 105 (1983).

[15]J. Dabrowski and M. Scheffler, Mater. Sci. Forum **83-87**, 735 (1992).

[16]Z. Su, J. W. Farmer, and M. Mizuta, Phys. Rev. B **48**, 4412 (1993).