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Hydrogen-donor-induced free-exciton splitting in GaAs

M. Capizzi, V. Emiliani, A. Frova, and F. Sarto
Dipartimento di Fisica, Università di Roma "La Sapienza," Piazzale Aldo Moro 2, 00185 Roma, Italy

R. N. Sacks
United Technology Research Center, East Hartford, Connecticut 06108
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Liquid-helium photoluminescence spectra have been taken in nominally undoped, donor-free GaAs grown by molecular-beam epitaxy and exposed to increasing doses of hydrogen irradiation. The narrow single free-exciton line observed in the untreated sample evolves into a broader doublet in the hydrogenated sample in the same way as was observed in high-purity GaAs on going from p-type to weakly n-type material. This behavior is highly suggestive of the activation of an exciton-polariton scattering mechanism by neutral donors, and provides an argument, in addition to existing experimental and theoretical evidence, in favor of a hydrogen-induced donorlike state. Measurements at different exciting wavelengths and bath temperatures support the model.

I. INTRODUCTION

Hydrogen passivates deep nonradiative centers in Si and III-V compounds, as is evidenced by an increase of carrier lifetime and luminescence efficiency.[1–3] The neutralization of the electrical activity of defects is usually explained in terms of a Coulomb interaction between the defect itself and charge states of the H atom, followed by the formation of complexes.[4,5] H-related acceptor and donor states have been predicted theoretically in Si and GaAs,[6–8] and it is also claimed that they account for a number of experimental findings: H-diffusion profiles change when an electric bias is applied during the diffusion process;[9] a H-donor level has been identified in $In_xGa_{1-x}As/GaAs$ multiple quantum wells, whose binding energy adapts well to that obtained from electroreflectance experiments in highly doped, bulk, n-type GaAs ($\sim$ 25 meV).[10,11] Moreover, hydrogenation gives rise to photoluminescence (PL) bands deep in the gap of p-type GaAs and of $In_xGa_{1-x}As/GaAs$ multiple quantum wells.[10,12,13] These bands are due to internal transitions in hydrogen/Ga-vacancy complexes H/V_{Ga}, where the ground state is provided by the Ga vacancy, and the excited state by a donor level introduced by a H atom located probably in one of the four bond-centered sites neighboring the V_{Ga}.[12,13]

In this paper, we report experimental evidence of changes due to H irradiation in the polariton-exciton PL spectra of nominally undoped, donor-free p-type molecular-beam epitaxy (MBE) GaAs. In particular, the free-exciton (FE) line shape evolves from the single narrow line typical of low p-type doping into a well-resolved doublet, 0.3 meV wide, as a function of H irradiation. A similar doublet, formerly interpreted in terms of upper and lower polariton branches,[14] has been shown recently to be the signature of an exciton-polariton scattering by localized electrons.[15,16] The changes of PL spectra with H treatment reported here, therefore, support the insurgence of localized levels for electrons, either due to H donors or to H-induced electron traps. An analysis of PL spectra taken at increasing H doses, as well as at variable exciting laser wavelengths, further substantiates this conclusion.

II. EXPERIMENT

$Ga_{0.83}Al_{0.17}As/GaAs$ heterostructures have been grown by MBE over GaAs semi-insulating substrates grown by a liquid-encapsulated Czochralski (LEC) technique. The $Ga_{1-x}Al_xAs$ capping layer, 1.1 μm thick, was meant to protect the underlying GaAs layer, 0.8 μm thick, from surface bombardment damage. The GaAs epitaxial layers were slightly p-type because of residual nonintentional C and Si acceptors, 10^{14} cm^{-3}, as indicated by secondary ion emission spectroscopy (SIMS).

Hydrogenation was produced, at a temperature of 300 °C, by ion-beam irradiation from a Kaufman source. The H-ion energy was about 100 eV, the current density of order tens of μA cm^{-2}, for H doses impinging on the surface ranging between 10^{16} and 10^{19} ions cm^{-2}. SIMS profiles in deuterated samples show that [D] is nearly constant, of order 10^{17} cm^{-3}, over the two MBE layers and part of the LEC substrate.[13] In the most deuterated samples, a spiky D accumulation has been observed at the MBE-LEC-GaAs interface, at least an order of magnitude higher than the average value, in a region tenths of a micrometer wide. Assuming that D and H behave similarly, we conclude that the average H concentration only weakly depends on the H dose, thus confirming that H solubility is set by trapping processes at defects whose concentration in the untreated material can be estimated[13] to be of order 10^{17} cm^{-3}.

PL measurements have been made at temperatures ranging between 1.9 and 15 K, using as a pump either an Ar^+ or a Ti-sapphire laser, corresponding to characteristic light penetration depths of 0.2 and 0.7 μm, respectively. In the former case, the GaAs-layer emission is only due to carriers generated in the cap layer and diffusing through the $Ga_{1-x}Al_xAs$-GaAs interface; in the latter

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case there is also a substantial contribution from carriers directly excited in the GaAs epilayer. Emission was analyzed by a 1-m McPherson monochromator, detected by a Hamamatsu photomultiplier working in a photon-counting mode. A final spectral resolution as high as 0.07 meV was achieved, whenever needed.

III. RESULTS AND DISCUSSION

The liquid-helium PL spectrum of the untreated sample V, shown in Fig. 1, is typical of nonintentionally doped p-type GaAs. Conduction-band-to-acceptor transitions at 1.49 eV, not shown here, dominate the spectrum, while excitons bound to neutral acceptor, (A^0, X) at 1.5124 eV, and free excitons, at 1.5153 eV, are also visible. The absence of exciton bound to neutral donor (D^0, X) transitions or of donor to valence-band (D, h) transitions sets an upper limit on the residual donor concentration ($\sim 1\times10^{12}$ cm^{-3} taking into account the different Bohr radii and exciton capture cross sections of acceptors and donors). The small full width at half maximum of the FE and of the (A^0, X) lines (0.4 and 0.25 meV, respectively) as well as the high intensity ratio of free excitons to A^0 bound excitons (≥ 1, even at the lowest level of power excitation) are clear signs[17] of an acceptor concentration of the order of 1×10^{14} cm^{-3}, in agreement with crystal growth conditions. Finally, the well-resolved j-j splitting (5/2-3/2) of the (A^0, X) line proves[18] that internal strain and/or microscopic electric fields, such as those due to medium-high concentration of impurities, are absent.

The changes of the exciton emission with increasing H doses are shown in Fig. 2(a). For low to medium H doses, samples AB through BC, the FE line splits into two lines, 0.2–0.3 meV apart, and starts to broaden. At the same time, the whole PL spectrum shifts rigidly toward lower energies by a few tenths of a meV, more noticeably for the (A^0, X) line. At higher H doses, sample C, the (A^0, X) line disappears while the FE spectrum shifts back to higher energy and broadens to such an extent that the splitting is no longer observed. Whenever detectable at liquid helium, the FE splitting persists at temperatures where the (A^0, X) line has already quenched ($\sim$10 K), thus ruling out the possibility of a new, weakly bound complex below the FE line.

We will now show that these features — FE splitting and overall spectral shift — are well explained in terms of two different effects of hydrogenation: the former by an initial passivation of acceptors which leads the material toward an intrinsic condition, followed by the introduction of localized scattering centers (H-related donors or trapping centers); the latter by the piling up of H at the MBE-LEC-GaAs interface.

As to the FE splitting, spectra nearly equal to those reported here have been measured in intrinsic GaAs samples where the residual doping was varied from barely p-type to n-type material,[15] as shown in Fig. 2(b) from top to bottom. The parallel behavior of Fig. 2(a) vs H treatment and Fig. 2(b) vs donor concentration is very noticeable. This indicates that H not only passivates acceptors by forming neutral complexes, but also introduces donor or donorlike centers in the material. These new states, however, do not give rise to narrow lines just below the FE, as for the case of exciton bound to shallow donor reported in Ref. 15.

The FE doublet reported here has been previously explained, in nonhydrogenated GaAs, in terms of intrinsic effects like recombinations from the upper and lower polariton branches,[14] reabsorption processes,[19] or exciton-electron scattering.[20] More recently, Lee *et al.*[15] have

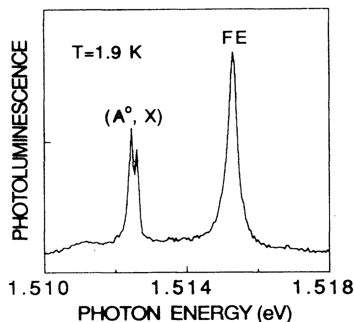

FIG. 1. Liquid-helium photoluminescence spectrum of as-grown, unintentionally doped GaAs ($p \sim 10^{14}$ cm^{-3}). Excitons bound to neutral acceptors (A^0, X) and free excitons FE are indicated. $\lambda_{exc} = 7700$ Å, $P_{exc} = 110$ W cm^{-2}.

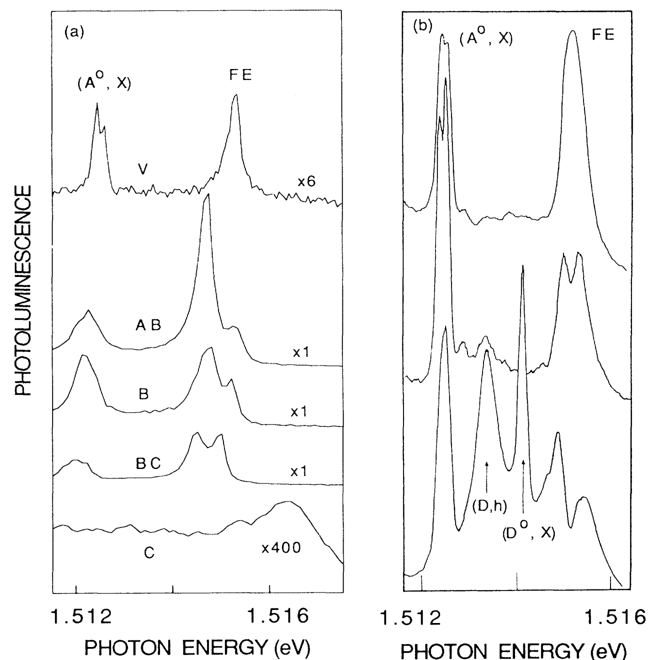

FIG. 2. Liquid-helium photoluminescence in the exciton region as a function of (a) H-dose, and (b) effective donor concentration. Impinging H atom doses are 6×10^{16} cm^{-2}, 1.4×10^{17} cm^{-2}, 7×10^{17} cm^{-2}, and 1.3×10^{18} cm^{-2} for samples AB, B, BC, and C, respectively. Sample V is not hydrogenated. For all samples, $\lambda_{exc} = 7700$ Å, $P_{exc} = 1.1$ W cm^{-2}, $T = 1.9$ K. The data in (b) are from Ref. 15; $\lambda_{exc} = 6328$ Å, $P_{exc} = 0.10$ W cm^{-2}, $T = 5$ K.

pointed out that this splitting is much larger than that predicted for the polariton branches and, furthermore, it cannot be an intrinsic feature as it depends on the type and concentration of dopant, as shown in Fig. 2(b).[15]

The polariton-exciton (PE) line shape measured at the detector is not the "intrinsic" one produced by radiation-matter interaction deep into the bulk, which depends on the quasithermal distribution of PE in the vicinity of the "bottleneck" region. Such distribution is indeed affected by scattering processes as the PE modes move toward the surface: inelastic processes directly affect the PE population distribution; elastic ones give an indirect effect since they change the PE momentum and introduce a variable delay in the arrival of the modes at the surface.

Without going into further details, for which consultation of Refs. 15 and 16 is recommended, it can be foreseen that, due to the dependence on the PE elastic-scattering cross section, the FE line shape will be affected by extrinsic contribution like the type and concentration of impurities and the exciting light penetration depth and power. In particular, numerical calculations have been performed to include the effect of scattering by neutral impurities.[15,16] They have shown that scattering by donors introduces a "dip" in the FE line shape, resulting in a doublet like that observed in n-type or in moderately hydrogenated "p-type" samples, while scattering by acceptors cuts asymmetrically the PL intensity on the FE low-energy side (narrowed line shape), as observed in p-type material and in the present untreated samples.[15] Moreover, in our samples the splitting increases and the line shape keeps broadening as a function of the H dose, while the FE intensity decreases with respect to that of the (A^0,X) line, as expected on the basis of the above model for an increasing concentration of donors.

The same considerations apply to the behavior with exciting laser wavelengths, shown in Fig. 3, where the line-shape asymmetry increases with increasing laser penetration depth (i.e., longer wavelength). This implies a larger number of scattering events suffered by the outgoing FE.

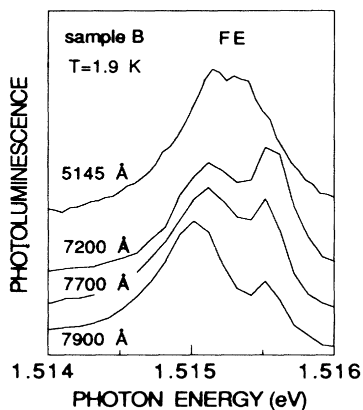

FIG. 3. Liquid-helium photoluminescence in the exciton region of sample B as a function of exciting laser wavelength. Spectra are horizontally shifted in order to have the (A^0,X) peak in Fig. 1 fall at the same energy (in text, see discussion about the influence of interfacial electric fields).

The final line shape corresponds therefore to that observed for an increasing concentration of scattering centers, at fixed laser wavelength (see Fig. 2), or for increasing sample thickness.[15] In the limiting case of argon excitation, carriers recombine mainly at the $Ga_{1-x}Al_xAs$-GaAs interface so that no appreciable scattering is possible and the splitting is absent.

The above arguments strongly suggest that the observed FE splittings are due to scattering by a neutral H donor. Its binding energy cannot be established on the basis of the present data, although the mentioned absence of H-related lines just below the FE is suggestive of a quite different value from those known for typical substitutional donor impurities. However, a number of claims of a semishallow H-related donor have been recently made. PL measurements in $In_xGa_{1-x}As$-GaAs QW's have clearly given evidence for a H-induced bound state, 15–20 meV below the fundamental excitonic transition depending on well width, which is suggestive of a somewhat larger binding energy in three-dimensional material.[10,13] Electroreflectance measurements in heavily doped, hydrogenated GaAs have detected a state 25 meV below the band gap.[11]

In the present GaAs material, for heavy hydrogenation (i.e., impinging H-ion doses $\geq 10^{18}$ cm^{-2}) a strong PL band develops near 1.2 eV.[12,13,21] This band is thoroughly similar to the well-known emission from the Ga-vacancy/donor complex observed in n-type degenerate GaAs, pointing to a binding energy for the H-induced level that cannot be exceedingly different from that of normal substitutional donors. For intermediate H doses ($\sim 10^{17}$ cm^{-2}), when the exciton doublet is present, and prior to the appearance of the Ga-vacancy band, our material emits mostly in a band 50–60 meV below the gap, which presents the typical behavior of transitions within donor-acceptor (D-A) pairs.[8,12,13,22] This same band, totally absent in the virgin material, has been independently observed in other unintentionally doped p-type GaAs, grown elsewhere.[23,24] It is consistent with the insurgence of a donorlike level of energy close to that of the partner acceptor state which takes part in the transition (e.g., 27 meV for C).

The only exception to all the above pieces of evidence, far-infrared absorption measurements in GaAs and GaP, are indicative of a much deeper donor, i.e., 0.5 eV above the valence band.[25,26]

The present PL measurements do not allow discriminating between these two possibilities. In the case of a semishallow donor, a (D,h) transition would essentially overlap the (e,A) one, whose intensity would itself be affected by hydrogenation in a complex manner: it should decrease due to acceptor passivation and increase due to passivation of nonradiative centers, thus precluding straightforward conclusions. Recent results by Sobiesierski in weakly Si-doped (3×10^{14} cm^{-3}) n-type GaAs (Ref. 23) are more meaningful. The ensemble of the (e,A) transitions is initially weaker than the (D^0,X) line, the ratio being 1:6. For a H dose of 5×10^{18} cm^{-2} at 150 °C, the exciton bound to the Si donor reduces its intensity, while the emission at or about the energy of the (e,A) transition becomes relatively stronger, for a final

ratio 1:1. Even more marked is the effect, in particular cases, for a 2×10^{16}-cm^{-3} Si-doped sample deposited on a Si substrate. We see no alternative, plain explanation to that of the creation of a new center, induced by H, giving rise to radiative recombination at nearly the same energy.

From the theoretical standpoint, both deep and moderately shallow H-donor states are predicted. In particular, a donor state 0.6 eV above the valence-band extremum has been predicted for H at the stable equilibrium site, the As antibonding site located along the [111] direction in the umbrella formed by the Ga-As bonds.[7,8] A shallower donor state is instead predicted when the H atom is located at the metastable bond-centered site, between a Ga and its nearest-neighbor As atom, which may be occupied at room temperature as a consequence of fast cooling from higher temperatures.[7,8]

To conclude this section, it should be mentioned that the somewhat peculiar nature of the H-donor state, for instance, its not being very shallow, might not allow a straight extension of the donor-polariton scattering model to the present case. Detailed calculations such as those undertaken in Ref. 15 would help provide conclusive support to our interpretation. It is worth mentioning also that the same behavior for the FE line reported in this paper — splitting and rigid shift downward for increasing H doses — has been observed in our laboratory also in other nominally undoped GaAs layers grown in a different MBE apparatus: this occurred not only in luminescence, but also in straight transmission measurements (data not shown here for the sake of brevity).

For what concerns the rigid shift of the whole spectrum, we correlate it with the H piling up observed by SIMS measurements (in deuterated material) at the MBE-LEC-GaAs interface, most likely due to trapping at the highly defected interface.[13] One part over one thousand of those H atoms, if charged, would give rise to an electric field E high enough to ionize the FE ($E_i \sim 6000$ V/cm),[27] as observed in sample C. For $0.1\leq E/E_i \leq 0.6$ the broadening of the bound and free-exciton lines begins to be appreciable (the former faster than the latter) and the whole near-edge spectrum shifts to lower energy up to about one-tenth of the Rydberg energy; for $E/E_i \sim 1$, the shift changes sign. The behavior well reproduces that observed here as a function of the H dose. The role of interfacial H piling up of H is further confirmed by study of a sample hydrogenated at 400 °C, where H diffusion is larger and H accumulation less pronounced. In this case the luminescence efficiency of the FE line, depressed in sample C with respect to sample BC by a factor $\sim$200, keeps to a reasonably high level, although the hydrogen dose is the same as for sample C (data not shown).

IV. CONCLUSIONS

We have reported evidence for a change in the FE line shape, due to H irradiation, of nominally undoped p-type GaAs of different origin. The evolution of the line shape, as observed both in PL and absorption spectroscopy, corresponds to a broadening and splitting of the original single narrow peak. It has been tentatively explained in terms of a recent model for the effects of polariton-exciton scattering by neutral impurities on FE photoluminescence. This attribution gets support from measurements as a function of exciting laser wavelength and sample temperature. The extension of the polariton-donor scattering model to the case of a moderately shallow donor, such as the one related to H, is not straightforward. However, we wish to stress that the splitting effect is observed in that very same region of intermediate H doses where the strong H-induced D-A-type band is detected. It is hard to believe that this can be merely a coincidental occurrence.

Finally, in the limit of heavy hydrogenation, the effect of H piling up at defected interfaces is evidenced through its strong action on the emission intensity and line shape of exciton-related states.

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[1] *Hydrogen in Semiconductors: Bulk and Surface Properties,* Proceedings of the Sixth Trieste Semiconductor Symposium, Trieste, 1990 (Elsevier, Amsterdam, 1991).

[2] *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic, San Diego, 1991).

[3] S.J. Pearton, J.W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Berlin, 1991).

[4] S.T. Pantelides, Appl. Phys. Lett. **50**, 995 (1987).

[5] M. Capizzi and A. Mittiga, Appl. Phys. Lett. **50**, 918 (1987).

[6] Chris G. Van de Walle, P.J.H. Denteneer, Y. Bar-Yam, and S. Pantelides, Phys. Rev. B **39**, 10 791 (1989).

[7] L. Pavesi (private communication); see also Doctoral thesis, Ecole Polytechnique Fédérale Lausanne, 1990.

[8] A. Amore Bonapasta, M. Capizzi, A. Frova, and F. Sarto (unpublished).

[9] A.J. Tavendale, D. Alexiev, and A.A. Williams, Appl. Phys. Lett. **47**, 316 (1985).

[10] Z. Sobiesierski, D.A. Woolf, D.I. Westwood, A. Frova, and C. Coluzza, Solid State Commun. **81**, 125 (1992).

[11] L. Kassel, J.W. Garland, P.M. Raccah, C. Coluzza, A. Neglia, and A. DiCarlo, Appl. Surf. Sci. **56-58**, 356 (1992).

[12] M. Capizzi, C. Coluzza, V. Emiliani, P. Frankl, A. Frova, and F. Sarto, Mater. Sci. Forum **83-87**, 599 (1992).

[13] M. Capizzi, C. Coluzza, V. Emiliani, P. Frankl, A. Frova, F. Sarto, A. Amore Bonapasta, Z. Sobiesierski, and R.N. Sacks, J. Appl. Phys. **72**, 1454 (1992).

[14] D.D. Sell, S.E. Stokowski, R. Dingle, and D.V. Di Lorenzo, Phys. Rev. B **7**, 4568 (1973).

[15]J. Lee, E.S. Koteles, M.O. Vassel, and J.P. Salerno, Phys. Rev. Lett. **55**, 867 (1985); W.L. Bloss, E.S. Koteles, E.M. Brody, B.J. Sowell, J.P. Salerno, and J.V. Gormley, Solid State Commun. **54**, 103 (1985); J. Lee, E.S. Koteles, M.O. Vassel, and J.P. Salerno, J. Lumin. **34**, 63 (1985).

[16]T. Steiner, M.L.W. Thewalt, E.S. Koteles, and J.P. Salerno, Phys. Rev. B **34**, 1006 (1986).

[17]J.P. Salerno, E.S. Koteles, J.V. Gormley, B.J. Sowell, E.M. Brody, J.Y. Chi, and R.P. Holmstrom, J. Vac. Sci. Technol. B **3**, 618 (1985).

[18]V. Heim and P. Hiesinger, Phys. Status Solidi B **66**, 461 (1974).

[19]B. Sermage and M. Voos, Phys. Rev. B **15**, 3935 (1977).

[20]K. Aoki, K. Kinugasa, and K. Yamamoto, Phys. Lett. **72A**, 63 (1979).

[21]A. Amore Bonapasta, B. Bonanni, M. Capizzi, L. Cherubini, V. Emiliani, A. Frova, and F. Sarto, in *Defect Engineering in Semiconductor Growth, Processing and Device Technology*, edited by S. Ashok, J. Chevallier, K. Sumino, and E. Weber, MRS Symposia Proceedings No. 263 (Materials Research Society, Pittsburgh, 1992), p. 467.

[22]M. Capizzi, C. Coluzza, P. Frankl, A. Frova, M. Colocci, M. Gurioli, A. Vinattieri, and R.N. Sacks, Physica B **170**, 561 (1991).

[23]Z. Sobiesierski (unpublished).

[24]Y.L. Chang, A. Frova, and J.L. Merz (unpublished).

[25]B. Clerjaud, F. Gendron, M. Krause, and W. Ulrici, Phys. Rev. Lett. **65**, 1800 (1990).

[26]B. Clerjaud, D. Cote, W.-S. Hahn, D. Wasik, and W. Ulrici, Appl. Phys. Lett. **60**, 2374 (1992).

[27]D.F. Blossey, Phys. Rev. B **2**, 3976 (1970).