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Copper-related defects in $In_{0.53}Ga_{0.47}As$ grown by liquid-phase epitaxy

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High-purity $In_{0.53}Ga_{0.47}As$ lattice matched to InP was grown by liquid-phase epitaxy and used for the study of Cu-related defects. The samples had a free-electron carrier concentration of $n=5.0\times10^{14}$ cm^{-3} and an electron mobility of $\mu_{77\,K}=44\,000\ cm^2/V\,s$. A Cu-related acceptor level 25 meV above the valence-band edge was identified using photoluminescence measurements. Comparing the energy position of this shallow acceptor level with the $E_v+157.8$-meV Cu-acceptor level in GaAs supports the assumption of an internal energy reference level [J. M. Langer, C. Delerue, M. Lannoo, and H. Heinrich, Phys. Rev. B **38**, 7723 (1988)] common to GaAs and $In_xGa_{1-x}As$.

I. INTRODUCTION

The $In_xGa_{1-x}As_yP_{1-y}$ alloy system lattice matched to InP has received great interest in recent years, since it meets the demands on light-emitting devices and optical detectors for fiber communication systems.[1,2] In the field of microwave technology the quaternary $In_xGa_{1-x}As_yP_{1-y}$ alloys have shown very promising properties for the fabrication of high-frequency devices such as high electron mobility transistors (HEMT).[3,4] The ternary alloy $In_{0.53}Ga_{0.47}As$ lattice matched to InP, has been of particular interest owing to its high carrier mobility and a band-gap energy very close to the minimum dispersion energy ($E_{disp}=0.80$ eV) of common optical fibers.

Hence, the demands for high-purity and low dislocation density material as a basis for device fabrication are very high. It is, therefore, not surprising that a considerable number of studies have recently been focused on the epitaxy of $In_{0.53}Ga_{0.47}As$, with the main goal of improving the quality of high-purity material.[5–19] High-purity material of device quality is now attainable with different growth techniques such as liquid-phase epitaxy (LPE),[6] vapor-phase epitaxy (VPE),[7] metal-organic chemical-vapor deposition (MOCVD),[8] and molecular-beam epitaxy (MBE).[9]

The improved quality of $In_{0.53}Ga_{0.47}As$ is a good basis for further studies of how different intentional and unintentional dopants affect the electrical and optical properties of $In_{0.53}Ga_{0.47}As$ in order to improve device performances. In this respect, transition metals (TM) form an interesting class of impurities in III-V compounds, considering that, for example, semi-insulating (SI) InP is generally obtained by incorporating Fe atoms during crystal growth. Another example is chromium, which is used for the same purpose in GaAs. Whereas these impurities are intentionally introduced, there are others which are incorporated unintentionally and often cause disturbances. Copper is such an example of a TM impurity, which for most applications is an unwanted impurity in any III-V compound.[20,21]

Since the early sixties Cu is therefore one of the most studied defects in GaAs.[22–27] From electron paramagnetic resonance (EPR) (Ref. 28) and electron-nuclear double-resonance (ENDOR) (Ref. 29) measurements, it is known that transition metals occupy the Ga lattice sites in GaAs. This assignment has been further supported by studies of the random-alloy splitting of the Cu-related photoluminescence in $GaAs_{1-x}P_x$, clearly showing that Cu occupies the Ga lattice site.[30] Two acceptor levels at $E_v+157.8$ meV and $E_v+0.45$ eV are usually referred to as Cu-related defects in GaAs.[21] Detailed studies, using FIR (Fourier infrared)-absorption spectroscopy, have shown the $E_v+157.8$ meV level to be nearly substitutional Cu on Ga sites, i.e., slightly Jahn-Teller distorted in the [100] direction.[31] Indications have been put forth suggesting that this level is caused by a Cu complex,[26] but more recent work showed that the assignment of the so-called *C* photoluminescence line to the $E_v+157.8$ meV level is highly unlikely due to different symmetry and thermal annealing properties.[32] The origin of the other level is not certain. Several authors, however, attribute the $E_v+0.45$ eV level to a double ionized charge state of the single substitutional defect.[21,33]

Cu as an impurity defect has also been subject to studies in other III-V host materials, i.e., InP,[34–36] GaP,[37], GaSb,[38] and InSb.[39] At least two Cu-related[33] levels in InP, the substrate material employed for the crystal growth in this study, are fairly well established. One acceptor level at $E_v+0.127$ eV and another acceptor level at $E_v+0.34$ eV are identified as Cu-related centers.[34,35] A third acceptor level at $E_v+0.69$ eV has also been attributed to a Cu-related defect.[36] Up to now, no studies on Cu-related defects in $In_{0.53}Ga_{0.47}As$ have been performed.

TM impurities are also of theoretical interest. Detailed models and calculation methods have been developed in recent years, to describe their electronic properties.[28,29,40–45] An interesting and debated feature of TM's in III-V compounds is the existence of an energy reference level, common to all members of the same isovalent semiconductor group. Early theoretical work suggested the binding energies of TM's within such a group to adjust to this constant energy reference level rather than to the actual band edges of the respective semiconductor.[41–45] This model has been used for predictions of band alignments for heterojunctions between different III-V and II-VI materials.[41–43] Recent work suggests the TM energy levels to be pinned to the average dangling-bond energy level,[42] rather than to the so-called "vacuum level."[41,44] This internal-reference rule has been thoroughly verified by comprehensive experimental studies on deep TM levels.[43,46]

In this paper we present data which have been obtained for an energetically shallow Cu-related defect in $In_{0.53}Ga_{0.47}As$. The starting material subjected to Cu diffusion was high-purity $In_{0.53}Ga_{0.47}As$, fabricated with an optimized LPE process. Our data suggest the energy internal-reference level model to be valid also for this TM level.

II. EXPERIMENTAL DETAILS

A. Epitaxial growth and sample preparation

The LPE growth was performed using a conventional horizontal sliding boat with multiple wells, fabricated from high-purity graphite, which is contained in a quartz tube. During growth, the quartz tube was flushed with Pd-diffused hydrogen.

As a solvent, In of 99.999 99% purity was used. The solutes were undoped polycrystalline InAs and GaAs with a net electron concentration $n \leq 10^{16}$ cm^{-3}. The InP (100) substrates, cut to 10×10-mm^2 pieces, were n type (Sn) or semi-insulating Fe doped and etched in $HF:H_2O$,1:5 and $HCl:CH_3OH$, 1:20 before entering the graphite boat. The InAs was etched in $KOH:H_2O$, 1:4 by weight, rinsed in 18-MΩ deionized water and finally etched in a 1% Br-methanol solution. For GaAs, an $H_2SO_4:H_2O_2:H_2O$, 5:1:1 etchant was used. The solvent In was delivered in pieces, specified to fit the graphite boat wells. Etching the In prior to weighing and loading was found not to affect the electron carrier concentration of the $In_{0.53}Ga_{0.47}As$ obtained.

The liquidus temperature T^{liq} of the solution, consisting of the solvent In and the solutes InAs and GaAs, was chosen to be 610 °C. Before deposition, a homogenization period of 1 h at a temperature of 615 °C was employed. Minimizing thermal damage of the substrate is of great importance for sample morphology. Therefore, the substrate was kept under a cover of InP. Step cooling of the solution to the growth temperature T^{g} prior to growth initiation was applied. This method was found to result in a more homogeneous composition, compared to ramp cooling during growth.[11] A supercooling of $T^{\mathrm{liq}} - T^{g} = 4$ °C gave layer thicknesses of 4–5 μm after 10 min of growth. The growth was terminated by sliding the substrate into a post-growth position and subsequently quenching in order to prevent As outdiffusion from the grown layer.

The liquid Ga and As atomic mole fractions, χ^{1}_{Ga} and χ^{1}_{As}, respectively, were experimentally determined by applying room-temperature photoluminescence (PL) to derive the layer composition.[18,47,48] $\chi^{1}_{\mathrm{Ga}} = 0.02161$ and $\chi^{1}_{\mathrm{As}} = 0.04225$ turned out to yield a good lattice match at the growth temperature, in accordance with the In-Ga-As phase diagram obtained by Treager, Kuphal, and Zschauer.[19]

Extensive baking of the growth solution was crucial for obtaining high-purity $In_{0.53}Ga_{0.47}As$ layers, as previously reported.[5–15] The optimum solution-baking scheme for our system and the source materials was found to be 50–60 h baking of the growth solution at 660–670 °C.

Cu doping of the $In_{0.53}Ga_{0.47}As$ material was performed by evaporating Cu (99.999% purity) onto the substrate or the epitaxial side of the sample and subsequently heating the sample in a vacuum-sealed quartz ampule together with undoped InAs and GaAs, thus supplying a saturated atmosphere of the ternary material constituents.[49–51]

Samples from LPE layers grown on SI substrates were prepared for Hall measurements according to the van der Pauw configuration.[52] The diode structure required for space-charge measurements was achieved by Cd diffusion into the as-grown layer, performed in a closed quartz ampoule thus forming a $p^{+}n$ structure. The p source consisted of high-purity Cd:Ga:As, 38:5:57 by mole fractions.[53] The epitaxial layers used for diode fabrication were grown on Sn-doped InP (100). Diffusion temperatures of 600 °C during 100 min resulted in a junction depth of 1 μm. Standard photolitography and a $H_2SO_3:H_2O_2:H_2O$, 5:1:1 etchant was used to form a mesa diode structure which is obtained by removing the entire $In_{0.53}Ga_{0.47}As$ layer area except the island or mesa at each junction site in order to limit the leakage current.

B. Characterization techniques

The free-electron carrier concentration n and mobility μ_H of the obtained layers were determined by Hall measurements at room temperature and at 77 K. The Hall factor was assumed to be close to unity at the measurement temperatures according to previous data obtained by Rode[54] for GaAs and InAs. The highest magnetic field applied was $B = 0.3$ T. The magnetic field was calibrated using a nuclear magnetic-resonance probe and regarded as well below the low-field limit[55] ($B^2\mu^2 \ll 1$, where μ denotes the electron mobility). Deep-level transient spectroscopy (DLTS) measurements were applied in the temperature range between 35 and 350 K, using a standard correlation technique.[56] Minority-carrier injection pulse mode as well as normal pulse mode were applied in order to monitor both the upper and lower half of the band gap.

Photoluminescence samples, mounted in a He-flow cryostate were optically excited by the 514.5-nm emission of an Ar^{+} laser. The sample temperature measured by a calibrated Si diode could be varied between 5 and 350 K. The emitted light was collected by a mirror arrangement, dispersed by an 0.5-m grating monochromator and lock-in detected by a liquid-nitrogen-cooled Ge pin diode or an InAs diode. The spectral resolution was about 0.5 meV. With the addition of a W halogen and a globar light source, the same optical and cryogenic system was used for photoconductivity and photocapacitance measurements of Hall samples and diode structures, respectively.

III. RESULTS

A. High-purity reference samples

By applying the purification steps previously mentioned to our LPE process, we obtained a net electron concentration as low as $n=5.0\times10^{14}$ cm^{14} cm^{-3} and a mobility of μ_{77} K$=44\,000$ cm^2/V s. Low-temperature photoluminescence spectra from a representative sample is shown in Fig. 1(a). The main peak at 0.81 eV, labeled Exc. (*X*) in Fig. 1(a), originates from free and bound exciton recombinations. Alloy broadening of the luminescence peaks makes it difficult to resolve the different kinds of exciton recombinations since the binding energy of the bound exciton is very small (2–3 meV).[57,58] However, our experimental linewidth of the high-energy peak [FWHM (full width at half maximum) $=3.7$ meV] from the sample in Fig. 1(a) is among the smallest reported in the literature.[47,57–59] The broad peak of low intensity at the low-energy side in Fig. 1(a), labeled *D*-*A*, will be shown to be due to donor-acceptor recombination (*D*-*A*), according to the dependence of the peak energy position and peak intensity on the excitation density. The energy position of the *D*-*A* peak (0.789 meV) makes Zn the most probable candidate for the acceptor source in this sample.[57,58]

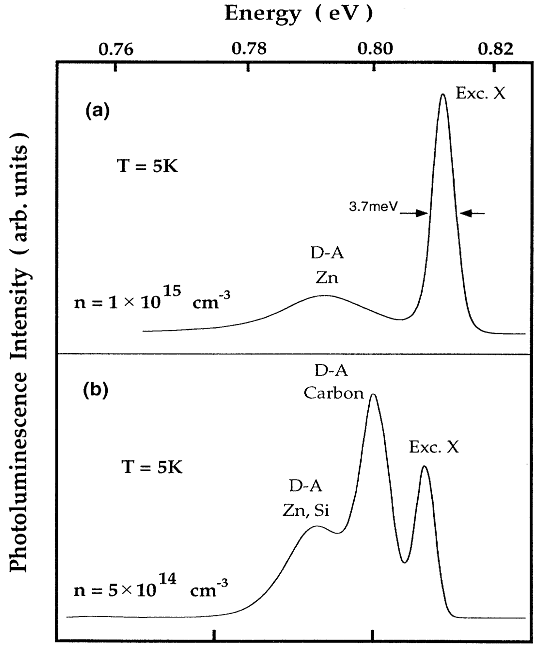

FIG. 1. (a) Photoluminescence spectra of a sample with a net electron concentration of $n=1.0\times10^{15}$ cm^{-3} and a mobility of $\mu_{77\,\mathrm{K}}=44\,000$ cm^2/V s. (b) Photoluminescence spectrum of a sample with a net electron concentration of 5×10^{14} cm^{-3} and a compensation ratio of $(N_D+N_A)/n=8$. The rather high compensation ratio is mainly due to carbon acceptors as seen from the high-intensity donor-acceptor emission (*D*-*A* carbon) at 0.80 eV.

Electron Hall mobilities μ_H as a function of electron carrier concentrations are presented in Fig. 2 together with theoretical curves (solid lines) computed by Takeda[55] and based on iterative solutions of the Boltzmann transport equation. A comparison of our sample with the lowest free-electron concentration with theory suggests a compensation ratio of $(N_D+N_A)/n=8$, where N_D and N_A denote the total donor and acceptor concentrations, respectively. Photoluminescence measurements of this sample [Fig. 1(b)] show a peak whose energy position correlates with that of the *D*-*A* recombination peak of carbon acceptors in MOCVD samples.[57] Further sources for the compensation and the low-energy *D*-*A* recombination peak of Fig. 1(b) are probably Zn- and Si-related acceptors, as suggested by the peak energy position.

B. Cu-doped samples

Hall measurements of samples which were Cu doped from a Cu film evaporated on the epitaxial side of the sample revealed a strong compensation of the original free-electron concentration. Samples subjected to Cu diffusion at 500 °C even turned out to be *p* type with a hole concentration exceeding 5×10^{14} cm^{-3} at room temperature.

Photoluminescence spectra of a reference sample as well as epi-side and substrate-side Cu-diffused samples are shown in Fig. 3. The reference spectrum shows in addition to the dominant exciton peak at 0.809 eV (labeled *X*), a peak at 0.793 eV (labeled *D*-*A* Zn). This peak is due to a *D*-*A* recombination process most probably involving Zn acceptors.[57,58]

A very intense peak, labeled *D*-*A* Cu in Fig. 3, can be seen at the low-energy side (20 meV lower than the exciton peak) of the spectrum originating from a substrate-side-diffusion sample. The intensity of the Cu-related emission (*D*-*A* Cu) is five times higher than the exciton peak (*X*) of the same sample and the exciton peak of the reference sample. Furthermore, the higher recombina-

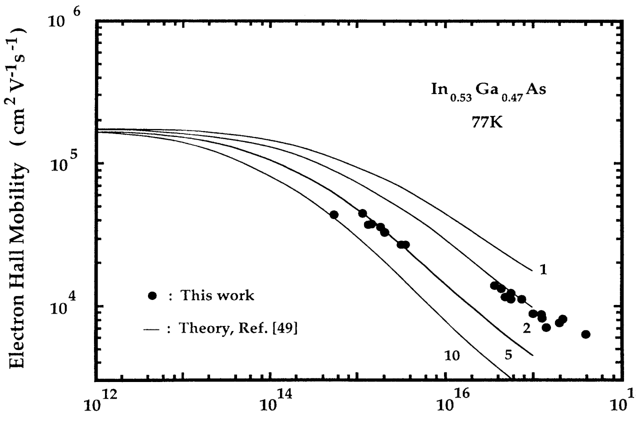

FIG. 2. Calculated (solid lines) electron Hall mobility μ_H at 77 K as a function of free-electron concentration for different compensation ratios $(N_D+N_A)/n$ (Ref. 55) together with experimental results.

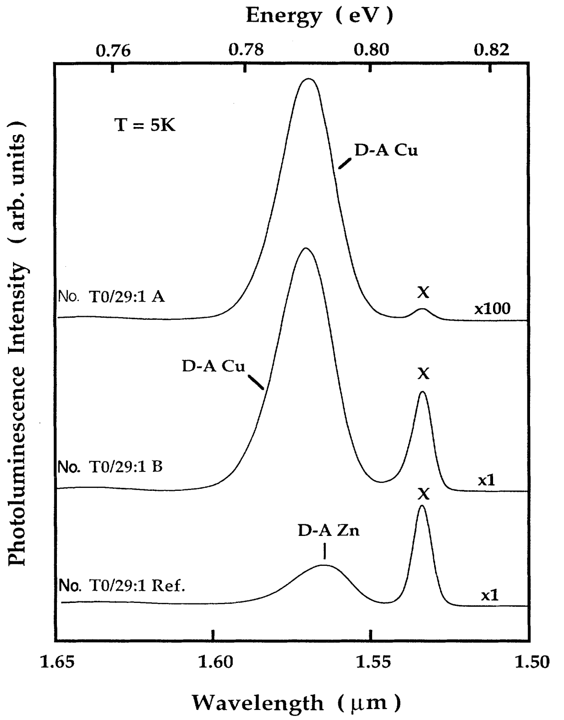

FIG. 3. Photoluminescence spectra of two Cu-doped samples and one reference sample. The Cu-doped samples were exposed to Cu diffusion from a Cu film, evaporated either on the front side or on the substrate side. The diffusion was performed at 500 °C during 4 h.

tion rate of the D-A Cu emission, compared to the D-A Zn emission, indicates a higher acceptor concentration for the Cu-doped sample.

The integrated luminescence intensity as a function of excitation density is shown in Fig. 4 for the Cu-doped sample and for the reference sample. The typical saturation behavior of the low-energy-side peaks, normally obtained for D-A recombinations, compared to the linear increase of the exciton recombination peaks, should be noted.[57,60,61] Further information on the nature of the recombination mechanism of the Cu peak is obtained from the energy position versus excitation density plot shown in Fig. 5(a). For a donor-acceptor recombination it is expected that, when increasing the excitation density J, distant pair transitions will be saturated first due to their longer lifetime. As a result, the peak energy $h\nu^{\text{peak}}$ of the D-A transition moves toward higher energy as the excitation density J increases.[60,61] This effect is clearly seen in Fig. 5(b). A quantitative expression describing the relation between excitation density J and D-A peak energy position $h\nu^{\text{peak}}$ of a shallow hydrogenlike state and a deeper state was derived by Zachs and Halperin:[61]

$$J = D[(\Delta E)^3/(E_D - 2\Delta E)]\exp(-2E_D/\Delta E)\ , \tag{1a}$$

with

$$\Delta E = h\nu^{\text{peak}} + E_A + E_D - E_g\ . \tag{1b}$$

Here, D is a proportionality factor and E_A and E_D are

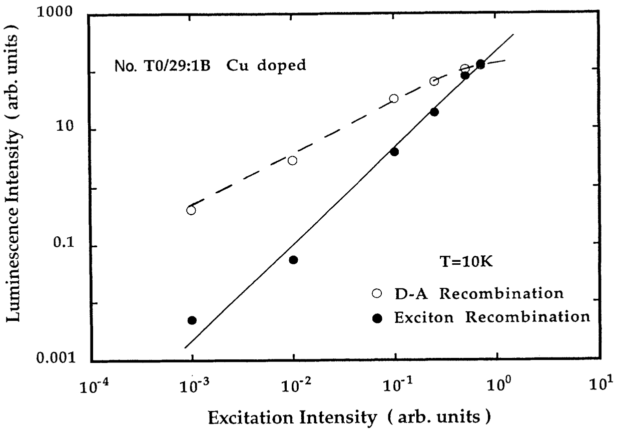

FIG. 4. Integrated luminescence intensity as a function of laser excitation density for the donor-acceptor recombination (D-A) and exciton (X) emission of Fig. 4.

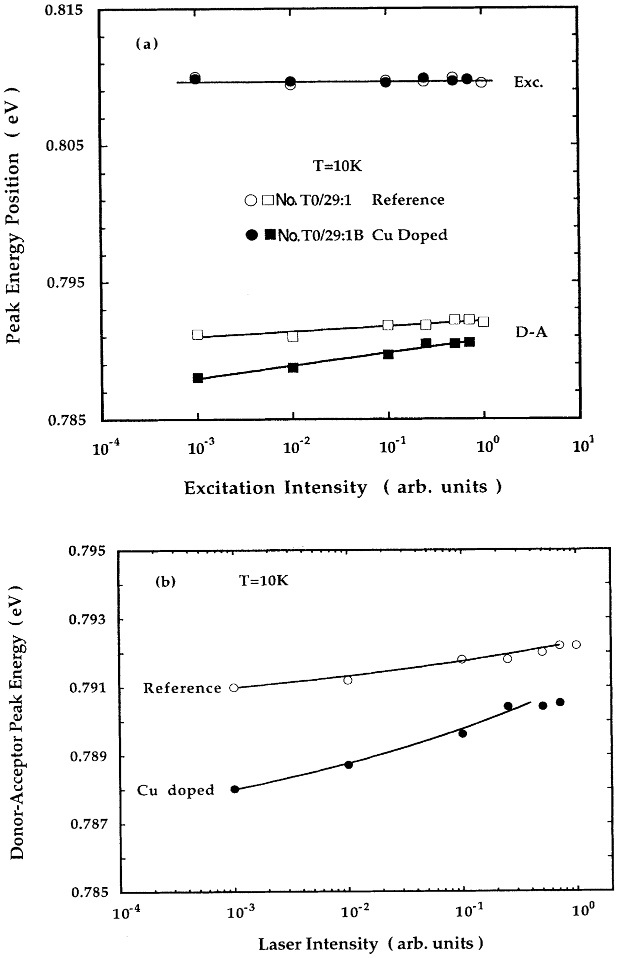

FIG. 5. (a) Peak energy position as a function of excitation density, measured at 10 K for the D-A and exciton emission of a copper-doped sample and a reference sample. (b) Using Eq. (1), the experimental data shown in Fig. 7(a) for the D-A emissions are fitted with the acceptor ionization energies E_{acc} as free parameters (solid lines).

the acceptor and the shallow hydrogenlike donor ionization energies, respectively. The band-gap energy E_g, determined from the exciton peak position, is 0.812 eV. The hydrogenlike donor ionization energy E_D is known to be 3 meV.[57] Fits of Eqs. (1a) and (1b) with D and E_A as free parameters are shown as solid lines in Fig. 5(b), giving an acceptor ionization energy of $E_a^{\mathrm{Cu}}=25$ meV for the Cu-related peak and $E_a^{\mathrm{ZN}}=21$ meV for the reference sample as well as a value of $D=2\times10^7$.

From temperature-dependent photoluminescence investigations of Cu-doped samples and reference samples (Fig. 6), and by adjusting the parameters of the expression[62]

$$I_T/I_0=[1+C_1\exp(-E_1^{\mathrm{act}}/k_BT)+C_2\exp(-E_2^{\mathrm{act}}/k_BT)]^{-1} \quad (2)$$

to our experimental points, we obtained a thermal activation energy of $E_{\mathrm{Cu}}^{\mathrm{act}}=19$ meV for the exciton recombination of Cu-doped samples, [Ex. (X) in Fig. 3]. Here, the parameters C_1 and C_2 are temperature-independent constants. The integrated intensity at the lowest temperature is denoted by I_0 and the integrated intensity at the actual temperature by I_T. The activation energy obtained should be compared with $E_{\mathrm{Ref}}^{\mathrm{act}}=16$ meV for the exciton recombination of the reference sample, which shows that the exciton peak of the Cu-doped sample is an exciton bound to an acceptor in this temperature interval. In shallow hydrogenlike systems the thermal activation energy E^{act}, which is required for a hole in the ground state to reach the first excited state, is only $\frac{3}{4}$ of the local ionization energy E_A.[57] Hence, the binding energies obtained from the temperature dependence of the emissions are $E_A^{\mathrm{Cu}}=25$ meV and $E_A^{\mathrm{Ref}}=21$ meV, respectively. These values are in good agreement with the values obtained from the spectral peak positions confirming the different origins of the luminescence of the Cu-doped samples and the reference samples.

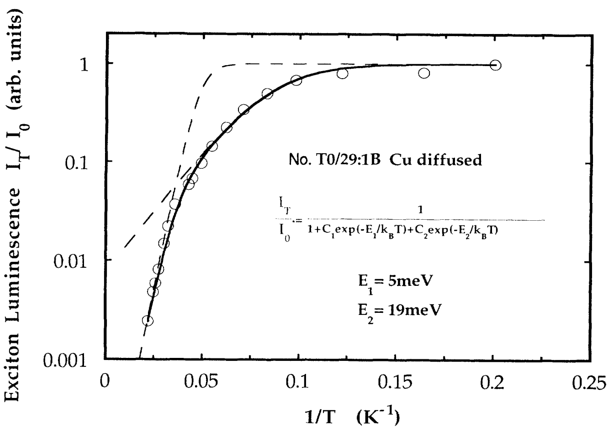

FIG. 6. Temperature dependence of the integrated relative intensity of the excitonic emission (X) of a Cu-doped sample. Equation (2), involving two thermal activation energies, is fitted to the experimental data (solid line). The smallest activation energy $E_1=5$ meV is interpreted as the thermal dissociation energy of the exciton bound to a Cu acceptor. The second thermal activation energy $E_2=19$ meV is required for the ionization of the neutral Cu acceptor.

The valence and conduction energy band variations of $In_xGa_{1-x}As$ relative to a fixed internal-reference energy level as a function of x is shown in Fig. 7.[63] It has been suggested that the ground-state energy of transition metals in unstrained III-V semiconductors is approximately constant relative to this internal-reference level for varying compositions or lattice constants.[41-45] Following this model and extrapolating the energy position of the Cu-related energy level in GaAs through the whole composition range to InAs, the lower Cu level is found about 20 meV above the valence band at the composition corresponding to $In_{0.53}Ga_{0.47}As$, in good agreement with our luminescence results. Based upon these arguments, we

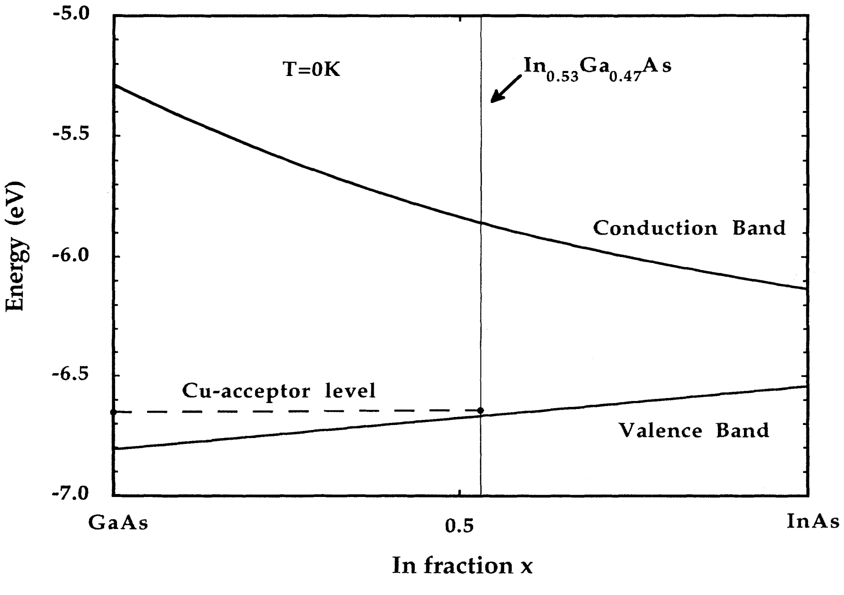

FIG. 7. Conduction- and valence-band positions relative to an internal-reference energy level as a function of the In content of the $In_xGa_{1-x}As$ alloy system. The Cu-related 157.8-meV acceptor level in GaAs (Ref. 24) is extrapolated to $x=0.53$, corresponding to $In_{0.53}Ga_{0.47}As$, giving an energy position of 20 meV above the valence-band edge.

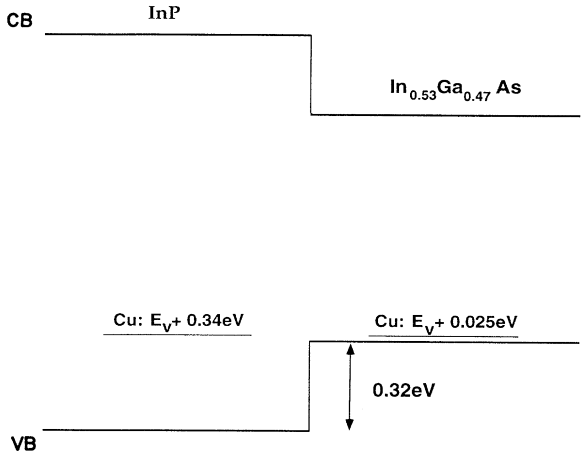

FIG. 8. Conduction- and valence-band positions of InP and $In_{0.53}Ga_{0.47}As$, relative to an internal reference level, as determined from the energy position of the $E_v+0.025$ eV acceptor level in $In_{0.53}Ga_{0.47}As$ obtained in this study and the $E_v+0.34$ eV acceptor level in InP (Ref. 34).

tentatively attribute the Cu-related defect in our samples to the substitutional metal-site defect configuration, i.e., the same configuration as for the Cu defect at $E_v+157.8$ meV in GaAs. Assuming a common energy reference level implies that a valence-band offset between InP and $In_{0.53}Ga_{0.47}As$ of 0.32 eV is obtained using an energy position of $E_v+0.34$ eV for the Cu level in InP (Ref. 34) and $E_v+0.025$ eV for the acceptor level in $In_{0.53}Ga_{0.47}As$ obtained in this study (see Fig. 8). This result is in good agreement with the theoretical valence-band offset of 0.33 eV obtained by Van de Walle,[63] and with the value of 0.35 eV deduced from a least-squares fit of available data, compiled by Langer *et al.*[43]

DLTS measurements were employed to further determine the nature of the Cu-related defects. In the temperature range between 40 and 300 K no peaks were detected. The reasons for the absence of DLTS peaks could be (1) an unfavorable combination of capture and emission rates, making the defect impossible to be detected in injection mode applied to our p^+n diodes; or (2) an ionization energy of the induced acceptor level which is comparable to the ionization energy of the shallow *p*-doping (Cd acceptors). Alternative (2) would imply that the diode is frozen out in the temperature region where DLTS peaks are expected and is therefore in agreement with what one would expect for a sample with a level about 25 meV above the valence-band edge, considering that the binding energy of the Cd acceptor is about 20 meV. Nevertheless, it should be noted that the lack of DLTS peaks further demonstrates the high purity of our samples.

IV. CONCLUSIONS

High-purity $In_{0.53}Ga_{0.47}As$ was grown lattice matched to InP (100) using LPE. The purity of the resulting layers is among the best reported in the literature, which provided excellent conditions for investigating different dopants in $In_{0.53}Ga_{0.47}As$.

Doping of the LPE layers with Cu at 500 °C produced an acceptor level 25 meV above the valence band. The assignment of this level to a Cu-related defect is supported by the fact that a similar energy position is obtained when extrapolating the $E_v+157.8$ meV Cu level in GaAs to the composition of $In_{0.53}Ga_{0.47}As$ and assuming a fixed internal-reference level.[41–44] Further, a valence-band offset of 0.32 eV between InP and $In_{0.53}Ga_{0.47}As$, estimated from our data and previous investigations of Cu-related defects in InP,[34–36] agrees both with theoretical band-offset calculations[63] and experimental values.[43]

Our experimental data are not in disagreement with theoretical assessments of TM behavior in III-V alloys[41,42,44,45] and band-lineup calculations.[63] Our data also provide a possible explanation for the lack of experimental data on Cu-related defects in InAs, since an extrapolation of our data would place the substitutional acceptor level well below the valence-band edge of InAs.

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