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Defect study of MOVPE-grown InGaP layers on GaAs

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Abstract

MOVPE-grown n-type GaAs/InGaP/GaAs structures with different GaAs cap layer thicknesses were studied by deep-level transient spectroscopy. An electron trap E1 with a thermal activation energy of 0.75 eV is formed in lattice matched InGaP after the MOVPE growth, if is not capped by sufficiently thick GaAs. The lattice mismatch of the InGaP layer influences the thermal activation energy of the deep defect, but not its occurrence or concentration. The starting surface concentration of the deep level defect as well as its diffusion at room temperature into the InGaP are apparently promoted by intrinsic defects in the InGaP layer determined by its growth condition. The shape of the depth profiles suggests that an extrinsic defect moves via interstitial sites into empty substitutional sites of the InGaP lattice. Oxygen atoms on phosphorus sites are probable candidates for the E1-related defects.

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1. Introduction

Structures using InGaP on GaAs substrates find applications in heterojunction bipolar transistors, lasers or light-emitting diodes. It was shown that deep levels can affect the device operation and reliability by increasing leakage current or inducing point-defect reactions [1,2]. Depending on the epitaxial growth technique, several deep-level defects in InGaP layers were reported. In MOVPE-grown n-type material, only one electron trap was found with a thermal activation energy of 0.8 ± 0.1 eV [2–6]. The same defect was also observed in MBE-grown InGaP [7–9]. Until now, this dominant electron trap is considered as a typical bulk level in InGaP layers [2–9] or related

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to interfacial states generated by heat treatment in Au/InGaP Schottky diodes (LPE-grown InGaP) [10].

We have previously shown [11] that towards the as-grown InGaP surface, the In mole fraction increases due to parasitic indium deposited from the horizontal reactor during cooling after growth. This process is accompanied by compressive strain, which may lead to the formation of deep-level defects near the surface of InGaP layers as it was seen by Huang in InGaP with an In-concentration higher than 53.2% [6]. In the following, it is shown that the formation of the dominant electron trap (labeled E1) at about 0.75 eV below the conduction band edge E_C depends on the growth conditions, but not on the strain. Additionally, it will be demonstrated that the E1-related defect is not generated during growth, but after growth starting from the InGaP surface, if the InGaP layer is not covered by a sufficiently thick GaAs layer.

2. Experimental procedure

The investigated (GaAs)/InGaP/GaAs structures were grown in a horizontal MOVPE reactor (Aix 200) at 70 hPa on (0 0 1) n^+-GaAs substrates using TMGa, TMIn, Si_2H_6, PH_3, and AsH_3 as precursors. Weakly {1 1 0}-ordered InGaP alloys were grown at 580 °C [12]. {1 1 1}B-ordered (double-variant ordered) InGaP layers [13] were realized at a growth temperature T_g of 650 °C. A V/III input ratio of 70 and growth rates of 2.5 μm/h were used. GaAs was grown with 1.2 μm/h and V/III input ratios of 20. The lattice mismatch of the layers determined by double-crystal X-ray diffraction was normally less than 5×10^{-4}, but for some samples intentionally varied from -5 to 16×10^{-4}. In order to determine the electronic properties the layer structures were Si-doped with carrier concentrations in the $10^{17}\,cm^{-3}$ range (cf. Ref. [14]). Deep levels were investigated by deep-level transient spectroscopy (DLTS) [15]. The DLTS samples were made by evaporating Au/Ge ohmic contacts on the n^+-GaAs substrates and Ti/Au-metal-semiconductor (MS) contacts on the InGaP-or GaAs-cap epilayer.

3. Results and discussion

We have previously reported [11] that towards the surface of an InGaP layer grown at 580 °C a dominant electron trap (labeled E1) about 0.75 eV below the conduction band edge E_C is found. Huang [6] has found this trap in compressively strained InGaP. To test the influence of strain we varied the lattice mismatch $\Delta a_\perp/a_o$ of the grown InGaP layers between -5×10^{-4} and $+16 \times 10^{-4}$. The DLTS peak temperature T_{max} for the related deep level is shown in Fig. 1. T_{max} shifts from 410 to 330 K in correlation to the misfit. This corresponds to a shift of the activation energy from 0.8 to 0.5 eV. For lattice matched InGaP the energy of E1 defect is found to be 0.75 eV. The free carrier concentration in the investigated InGaP layers was kept constant at about $1 \times 10^{17}\,cm^{-3}$ by intentional doping. This value was always checked by capacitance vs. DC-bias method. Thus, an influence of the Poole–Frenkel effect as discussed by Dekker [7] can be excluded. While the energetic position of the E1 trap depends on the composition and strain, its concentration is the same for the differently strained samples grown with the same growth procedure and measured after the same storage time. Thus, the interpretation given by Huang [6] does not hold for our samples.

Fig. 2 shows typical depth profiles of the concentration N_T of the electron trap E1 for

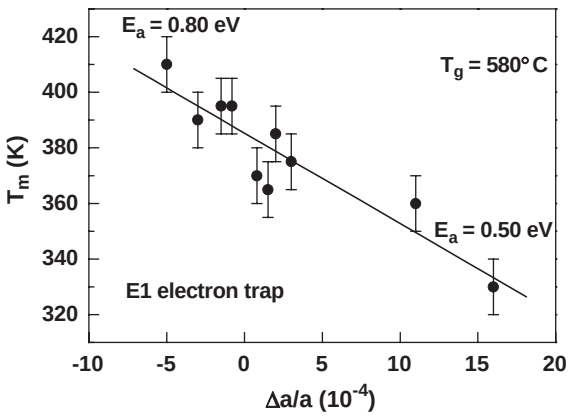

Fig. 1. Dependence of E1 electron trap peak temperature T_m (measured with a time constant of 0.46 s) on lattice mismatch $\Delta a_\perp/a_o$ of the n-type InGaP layer (uncapped).

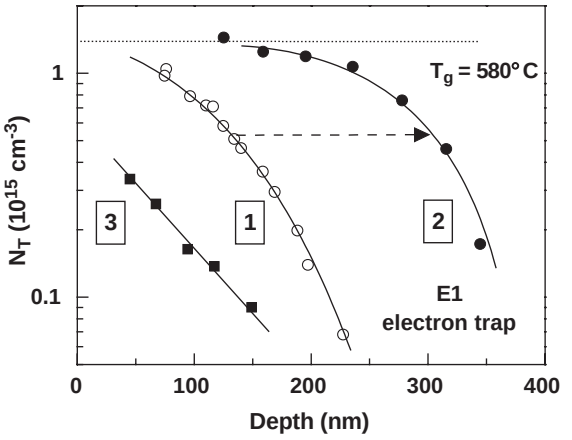

Fig. 2. Typical depth profiles of the concentration N_T of the electron trap E1 in 450 nm thick InGaP layers grown at 580 °C. Curves 1 and 2—measured with MS contacts directly on InGaP, curve 3—with MS contacts on 50 nm GaAs cap layer. Curves 1 and 2—measured 1 and 40 months after growth of the InGaP layer, respectively. Dotted line—saturation concentration at surface.

lattice matched $In_{0.52}Ga_{0.48}P$ layers grown at 580 °C with thicknesses above 450 nm. The distributions are characterized by a roughly constant concentration at the surface and a rapidly decreasing concentration in the bulk. The maximum concentration at the surface depends on the growth temperature and is found to be about 2×10^{15} for layers grown at 580 °C (cf. Fig. 2) and below 3×10^{13} cm^{-3} for InGaP grown at 650 °C. This shows that the preparation of the rectifying MS contacts is not the main reason for the occurrence of E1 close to the InGaP surface as found by Chae [10]. Curves 1 and 2 in Fig. 2 have been measured with MS contacts prepared directly on the same InGaP layer about 1 and 40 months after growth, respectively. The E1 distribution apparently shifts at room temperature into the epitaxial layer (see the arrow in Fig. 2), whereas the saturation density at the surface remains constant (dotted line in Fig. 2).

Curve 3 in Fig. 2 shows the E1 distribution in InGaP grown at 580 °C and capped with 50 nm GaAs. Remarkably less E1-related defects are formed, if the InGaP is covered by a GaAs layer. For thicker GaAs cap layers, the electron trap E1 is no longer found, see also Ref. [14]. If the GaAs layer is however removed, we find the deep level in these InGaP layers, too, as can be seen in Fig. 3. The curves in Fig. 3 were measured about one month after recess etch. Fig. 3 demonstrates that practically the same E1 distribution for all different samples is found after removal of the GaAs cap (100 nm thick in all cases) as for the uncapped InGaP layers (star symbols in Fig. 3). These findings indicate that contact to air promotes the formation of the E1 defect in InGaP. The formation and the diffusion process of the E1-related defect start at the surface after growth. Because the saturation density at the surface remains constant (dotted line in Fig. 2), the diffusion is associated with a constant source of defects at the surface.

Because the generation of this bulk defect can be prevented, when InGaP is grown at 650 °C, its occurrence and diffusion is apparently promoted by intrinsic defects in the InGaP layer, which are generated during growth or by the in-diffusion of an extrinsic defect.

To study the influence of the InGaP surface status on the E_1 formation, samples with different cooling-down processes were investigated (Fig. 4). The growth of the InGaP layers is usually finished by cooling-down the samples under stabilizing PH_3 flux to prevent thermal degradation of the

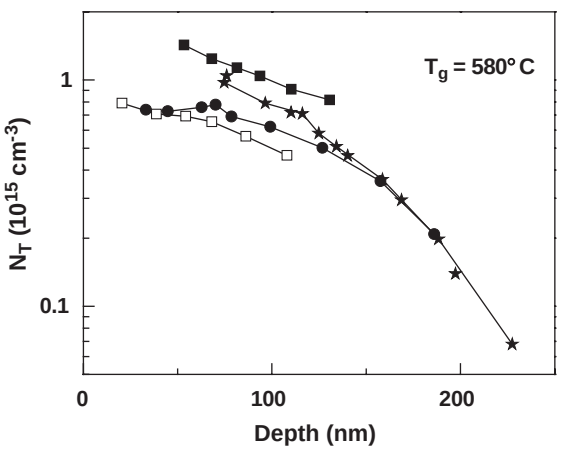

Fig. 3. Depth profiles of the E1 concentration N_T in various InGaP layers. Stars—InGaP layer grown without GaAs cap (curve 1 in Fig. 2); squares and circles—measured with MS contacts on InGaP after removal of 100 nm thick GaAs-cap layer. All measured 1 month after GaAs recess etch.

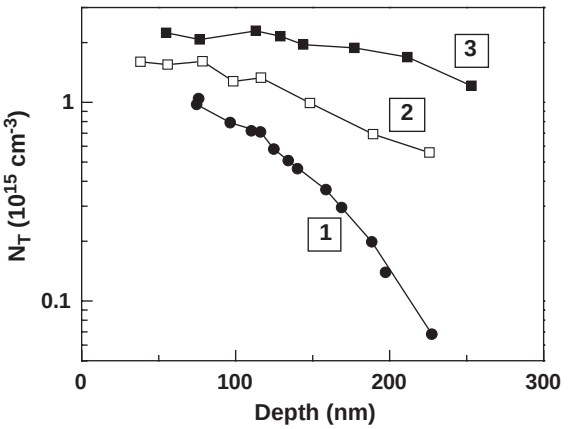

Fig. 4. Depth profiles of the electron trap E1 concentration N_T in thick InGaP layers grown at 580 °C without GaAs cap layer, but with different surface stabilization during cooling-down: curve 1—under PH_3, curve 2 and 3—under AsH_3. Curve 3—InGaP capped by GaP-monolayer. All measured 1 month after InGaP growth.

surface. When a flux of AsH_3 is used instead of PH_3, the depth profiles of the E1 concentration exhibit roughly the same shape. Fig. 4 compares the E1 distributions of structures grown at the same temperature of 580 °C and cooled-down with PH_3 (curve 1) or AsH_3 (curves 2 and 3) fluxes. The saturation density of the E1 concentration at the surface becomes apparently higher for samples cooled-down under AsH_3 flux. If the surface of InGaP was modified before cooling-down by capping with a GaP-monolayer, the E1 concentration is further enhanced (curve 3). Although curves 1–3 were measured at about the same time (1 month) after growth, the diffusion of the E1-related defect is accelerated in samples, which were cooled down under AsH_3 flux. In these samples the near surface region is thermally more degraded, indicating the importance of an intrinsic defect (probably, phosphorus vacancies) for the formation and in-diffusion of the E1 defect after the contact of the InGaP surface to air.

Since the shape of the depth profiles in Figs. 2 and 3 is similar to distributions found for substitutional—interstitial diffusion processes [16], we believe that an extrinsic defect moves via interstitial sites into empty substitutional sites of the InGaP lattice. The diffusion coefficient for such a process strongly depends on the local defect concentration and gives therefore rise to the rather sharp diffusion front of the E1 distribution (cf. Fig. 2). When InGaP is grown at temperatures of 650 °C, the E1 density is strongly reduced, because there are less lattice sites available for the diffusing defect. Oxygen atoms on phosphorus sites are the most probable candidates for the E1-related defects. It would correlate to findings of Xiang [9], where an oxygen-related defect at 0.63–0.82 eV was found. Because the phosphorus vacancy, V_P, is not mobile enough at room temperature to cause the observed diffusion profile we think that diffusing oxygen atoms create and use phosphorus vacancies in the bulk. Such a reaction of extrinsic and intrinsic defects is well known, for example, for Zn diffusion in GaP [16]. We can therefore conclude that, when InGaP is not covered by GaAs, its properties may degrade at room temperature due to the in-diffusion of impurities from the open surface.

The reason for the much lower E1 concentration in the InGaP grown at 650 °C remains unclear. The InGaP layers were grown with nominally the same input flows of precursors, but at 650 °C the thermal dissociation of phosphine is higher. This can result in a lower concentration of phosphorus vacancies. On the other hand, the crystal structure connected with ordering in the InGaP layers grown at 580 and 650 °C is different. The domain sizes in the 650 °C grown InGaP are much larger. The lower number of antiphase boundaries, which are connected with that, offers less intrinsic defects which might lead to a reduced defect diffusion via interstitial sites. Further investigation are needed to understand the difference between these materials responsible for the defect formation and diffusion.

Since the stabilization of the InGaP surface under phosphine and also under arsine for switching to GaAs-based layers is important for the growth of device structures containing InGaP layers, the influence of such InGaP growth interruptions at 580 °C on the in-diffusion of the electron trap E1 was studied. The depth profile of the concentration N_T is plotted in Fig. 5 for a structure with InGaP growth-interruptions for 60 s under PH_3 stabilization. This introduced 20 nm

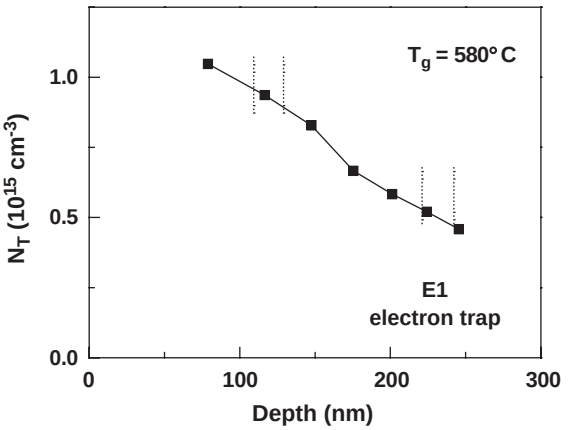

Fig. 5. Depth profile of the trap concentration N_T in InGaP with introduced 20 nm thick InGaP intralayers introduced during growth interruptions (dotted vertical lines). Measured 1 month after InGaP growth.

thick interlayers (dotted lines 1 in Fig. 5) with higher ordering degrees (see Ref. [17]). The formation of E1 is not affected by the different ordering degree and the polarization charges of the interlayer. When an $In_{0.50}Ga_{0.50}As_{0.07}P_{0.93}$ interlayer is formed by growth interruptions under AsH_3 flux [17], the E1 trap density is also not modified (not shown). This means that this defect is only related to the free GaInP surface, but not to interfaces if they are undisturbed.

4. Conclusion

Depth profiling of deep levels in GaAs/InGaP/GaAs structures grown with different thicknesses of a GaAs cap layer shows that the well-known dominant electron trap E1 with an activation energy of 0.75 eV is not formed during the MOVPE growth. The trap is formed after the growth starting from the surface, if free-standing InGaP has contact to air. The thermal activation energy of E1 largely depends on the lattice mismatch of the (In,Ga)P layer to the GaAs substrate. We do not find any influence of the technique to prepare the Schottky contacts. The starting surface concentration of the deep-level defect as well as its diffusion at room temperature into the InGaP are apparently governed by reactions between intrinsic and extrinsic defects in the InGaP layer. The concentration of intrinsic defects is determined by the growth conditions of the bulk InGaP layer and/or its near surface region. The diffusion is associated with a constant source of defects at the surface. From the shape of the depth profile we believe that an extrinsic defect moves via interstitial sites into empty substitutional sites of the InGaP lattice. Oxygen atoms on phosphorus sites are probable candidates for the E1-related defects. The E1 density is strongly reduced by InGaP growth at temperatures of 650 °C. The generation of the E1 defect is entirely prevented, if the InGaP layer is sealed, e.g., by a sufficiently thick GaAs cap layer.

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