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Avoidance of surface-related defects in MOVPE-grown InGaP layers

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Abstract

Deep-level transient spectroscopy studies of n-type InGaP/GaAs structures revealed an electron trap E1 with a thermal activation energy of 0.75 eV. From the shape of the depth profiles for this deep level an extrinsic defect can be concluded, which moves from the air exposed InGaP surface via interstitial sites into empty substitutional sites of the InGaP lattice. By comparison of InGaP samples grown at 580 °C with different V/III input ratios as well as at 650 °C, it is suggested that the most probable candidate for the E1-related defect is oxygen on phosphorus site. It is shown that this defect is due to an extrinsic defect. The concentration of the E1-related defect depends on the concentration of phosphorus vacancies, which are due to thermal degradation of the growing InGaP layer surface as a result of insufficient stabilization. The in-diffusion of oxygen is promoted by particular intrinsic defects, probably antiphase boundaries, in the InGaP layer determined by the growth condition. With a sufficiently thick GaAs cap layer or by adequately chosen growth conditions for InGaP, the surface-related defect E1 can be avoided.

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1. Introduction

Layer structures containing InGaP on GaAs are widely used for heterojunction bipolar transistors and light emitting diodes. For the growth of such structures, metalorganic vapour phase epitaxy (MOVPE) is commonly used. Defect studies of n-type InGaP layers have revealed an electron trap with a thermal activation energy of 0.75 eV [1–4]. Since the presence of deep levels can affect the device operation [4,5], it is essential to avoid such traps by optimizing the growth procedure.

The dominant electron trap (labeled E1) has been correlated to the existence of oxygen in the InGaP layer resulting from indiffusion from the layer surface exposed to air [6]. Additionally, it has been suggested that the initial concentration of the deep-level defect E1 at the surface as well as its diffusion into the InGaP layer at room temperature are apparently promoted by intrinsic defects in the InGaP layer determined by its growth condition. This paper discusses the in-diffusion of E1 related defects into MOVPE-grown n-type InGaP layers from the free InGaP surface upon contact to air using deep-level transient spectroscopy (DLTS). We have investigated the effect of V/III input ratio and growth temperature during the growth of the InGaP layer on the subsequent defect in-diffusion. It is shown that the tendency for indiffusion is reduced with increased phosphorus supply to the InGaP surface during growth. These findings suggest that the intrinsic defects promoting the oxygen in-diffusion are phosphorus vacancies resulting from thermal degradation of the growing InGaP layer surface as a result of insufficient stabilization. Using adequately chosen growth conditions this surface-related defect can be avoided.

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,

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PH_3, and AsH_3 as precursors. InGaP was deposited at growth temperatures T_g of 580 and 650 °C with V/III input ratios of 70 and 140. The lattice mismatch of the layers determined by double-crystal X-ray diffraction was less than 5×10^{-4}. The growth rate was 2.5 μm/h. GaAs layers were grown with 1.2 μm/h and V/III input ratio of 20. The optical and structural properties were investigated by photoluminescence and high-resolution transmission electron microscopy [7]. 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. [8]). The samples for DLTS [9] were prepared by evaporating Au/Ge ohmic contacts on the n^+-GaAs substrates and Ti/Au-metal–semiconductor (MS) contacts on the InGaP or GaAs cap. Deep-level spectra were obtained under various bias as well as pulse conditions. The peak heights, which are related to the individual trap concentrations strongly depend on reverse bias, i.e., on depth. The deep-level concentration was determined from the DLTS peak heights according to the full corrections given in Ref. [10].

3. Results and discussion

We have previously reported [6] that towards the surface of a lattice-matched InGaP layer grown at 580 °C with a V/III ratio of 70, a dominant electron trap (labeled E1) about 0.75 eV below the conduction band edge E_C is found, if InGaP is not capped with a GaAs layer thicker than 50 nm. Fig. 1 shows typical depth profiles of the concentration N_T of this electron trap E1. Curve 1 in Fig. 1 has been measured with MS contacts prepared directly on the InGaP layer about 1 month after growth. The distribution is characterized by a high concentration at the surface and a rapidly decreasing concentration in the bulk. The maximum concentration at the surface is found to be about $1 \times 10^{15}\,cm^{-3}$. Curve 3 in Fig. 1 shows the E1 distribution in InGaP grown under the same conditions but capped with 50 nm GaAs. Remarkably less E1-related defects are formed, if the InGaP is protected by GaAs. For thicker GaAs cap layers, the electron trap E1 is no longer found, see also Ref. [8]. Curve 2 in Fig. 1 has been measured on the same layer but with contacts prepared about 1 month after wet-chemical removal of the 100 nm thick GaAs cap layer. Nearly the same E1 distribution is found after removal of the GaAs cap as for the uncapped InGaP layer. These findings indicate that contact to air gives rise to the formation of the E1-related defect in InGaP. The formation and the diffusion process of the E1-related defect start at the InGaP surface upon exposure to air. They are suppressed by a GaAs cap as long as this cap remains on the InGaP.

In Fig. 2, the influence of the storage time of the uncapped InGaP surface in contact to air on the E1 distribution is demonstrated. The 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, whereas the saturation density at the surface remains constant (dotted line). As the saturation density at the surface remains constant, the diffusion is associated with a constant source of defects at the surface. Since the shape of the depth profiles in Figs. 1 and 2 is similar to distributions found for substitutional-interstitial diffusion processes [11], 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).

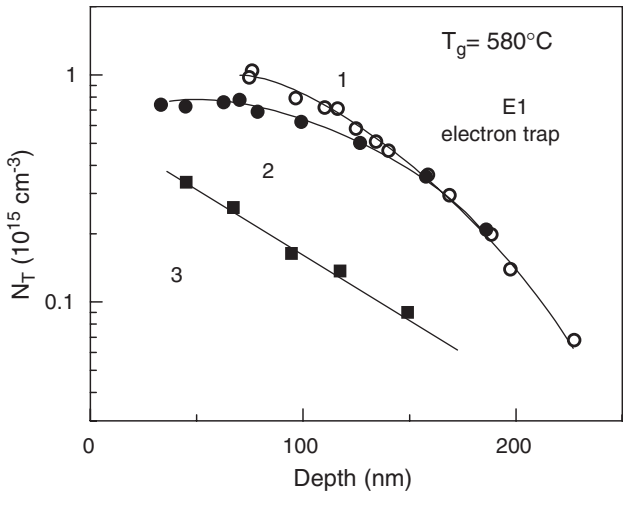

Fig. 1. Typical depth profiles of the concentration N_T of the electron trap E1 in 450 nm thick InGaP layers grown at 580 °C, V/III input ratio = 70. Curves 1 and 2 measured with MS contacts directly on InGaP, curve 3—with MS contacts on 50 nm GaAs cap layer. Curve 1—InGaP layer grown without GaAs cap, measured 1 month after growth; Curve 2—after removal of a 100 nm thick GaAs cap layer, measured 1 month after GaAs recess etch.

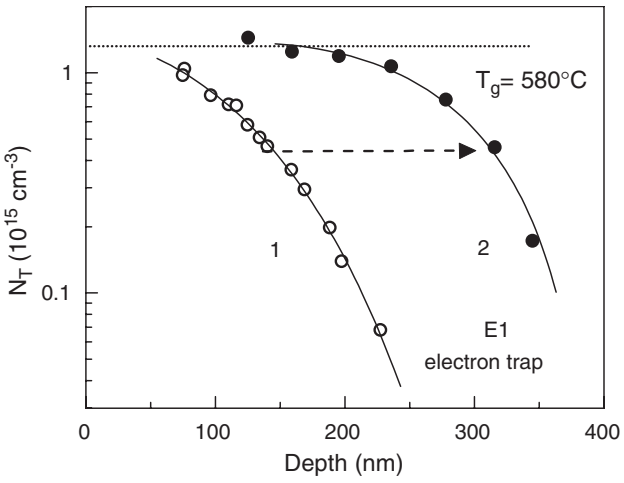

Fig. 2. Depth profiles of the E1 concentration N_T in a 450 nm thick InGaP layer grown at 580 °C, V/III input ratio = 70. All measured with MS contacts directly on InGaP. Curves 1 and 2—measured 1 and 40 months after growth of the InGaP layer, respectively. Dotted line—saturation concentration at surface.

As we do not detect any traps by DLTS when the InGaP surface has no contact to air, the necessary defect for the in-diffusion should either not cause a defect level in the gap or have a level below 0.15 eV (not measured here). Such defects could be connected with the antiphase boundaries dividing stacked domains of different ordering variants in the InGaP. In this case, the change of the crystal structure connected with different kinds of ordering in InGaP should influence the extrinsic defect in-diffusion. It is well known that the ordering can be changed by varying the growth temperature. We have previously shown [7] that the microstructure of InGaP layers grown at 580 °C is characterized by {1 1 0} ordering with a high number of domains with small dimensions and a low degree of ordering, i.e. many irregular stacking sequences exist. In contrast, two-variant {1 1 1} CuPt-B type ordering occurs in InGaP grown at 650 °C. The domain sizes and ordering degree are much larger than at 580 °C. To check the assumption that a lower number of antiphase boundaries produces less intrinsic defects and leads to a reduced defect diffusion via interstitial sites, InGaP was grown at 650 °C with the same V/III ratio of 70 as for the samples shown in Fig. 1 curve 1 and measured by DLTS. The concentration N_T of the electron trap is found to be below the detection limit of $3 \times 10^{13}\,cm^{-3}$, i.e., the in-diffusion of the E1-related defect is suppressed. Since the generation of the E1-related trap can be prevented when InGaP is grown at 650 °C, the formation of phosphorus vacancies near the surface during the contact preparation is not the cause for the formation of the E1 trap. Its occurrence and diffusion are apparently promoted by intrinsic defects in the InGaP layer, which are generated during the growth or by the in-diffusion of an extrinsic defect.

Since we believe that an extrinsic defect moves via interstitial sites into empty substitutional sites of the InGaP lattice, a probable candidate for the E1-related defect is oxygen on phosphorus site. This is in line with the findings of Xiang et al. [12], who report on an oxygen-related trap at 0.63–0.82 eV activation energy. The concentration of free phosphorus sites, i.e., phosphorus vacancies in the InGaP bulk should influence the concentration of the E1 defect.

To clarify the influence of phosphorus supply on the trap concentration of E1, we increased the V/III input ratio from 70, curves 1 and 2 in Fig. 3, to 140, curve 3, using a higher phosphine flow during InGaP growth at 580 °C. The curves in Fig. 3 have been measured with MS contacts prepared directly on the InGaP layer about 1 month after growth. The InGaP layer grown with the higher V/III ratio, curve 3, shows a factor of up to five lower trap concentration than the other samples. We showed previously that with the higher V/III input ratio during the InGaP growth, the type of ordering remains unchanged [7] and that a small increase in the ordering degree did not affect the formation of the E1-related defect [6]. Thus the main reason for the lower E1 trap concentration with higher V/III ratio has to be a lower concentration of an intrinsic defect. When InGaP is grown with a higher phosphorus supply, the E1 trap concentration is obviously reduced, because there are less lattice sites available for the diffusing defect. This is further evidence that the possible empty substitutional sites of the InGaP lattice are the phosphorus sites. For InGaP growth at 650 °C with the same low V/III ratio of 70, the thermal decomposition efficiency of phosphine is doubled to nearly 40% in comparison to 20% at 580 °C growth temperature. Therefore, the phosphorus supply to the InGaP surface is for 650 °C similar to the case when at 580 °C growth temperature the V/III input ratio is increased from 70 to 140. However, since in InGaP grown at 650 °C the E1-related defect is not detected, also the crystal structure plays a role in the in-diffusion process, as it is known for substitutional-interstitial diffusion processes. A higher number of domain boundaries in layers grown at 580 °C seems to facilitate diffusion.

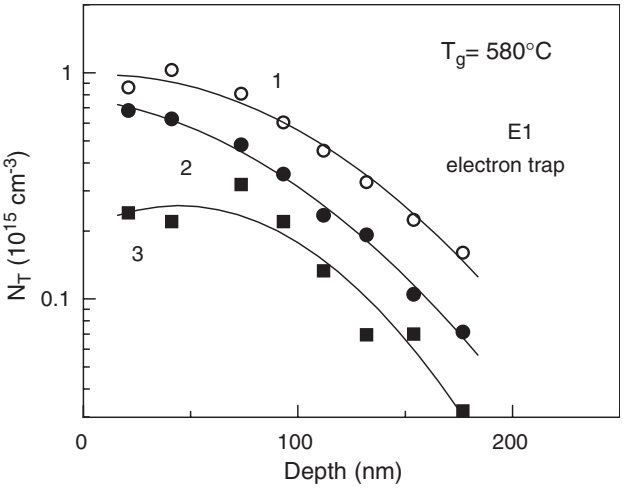

Fig. 3. Depth profiles of the electron trap E1 concentration N_T in thick InGaP layers grown at 580 °C with V/III input ratios of 70, curve 1 and 2, and 140 (with increased PH_3 flow), curve 3. All measured with MS contacts directly on InGaP and 1 month after air contact. Curve 1—InGaP layer grown without GaAs cap; Curve 2 and 3—after removal of a 100 nm thick GaAs cap layer.

As the phosphorus vacancy V_P is not mobile enough at room temperature to cause the observed diffusion profiles, we think that oxygen atoms diffusing via the antiphase boundaries 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 (see e.g., Ref. [11]). The degradation of the open InGaP surface at room temperature due to the in-diffusion of impurities can be obviously avoided by the proper choice of growth condition.

4. Conclusion

Depth profiling of deep levels in GaAs/InGaP/GaAs structures grown with different thicknesses of a GaAs cap layer shows that the dominant electron trap E1 with an

activation energy of 0.75 eV is formed after the growth starting from the surface, if free standing InGaP has contact to air. The E1 density is strongly reduced by a higher phosphorus supply to the surface during the growth, i.e. with higher V/III input ratios at 580 °C or higher decomposition rates of phosphine at elevated growth temperatures and moderate phosphorus desorption rates. The generation of the E1 defect is also entirely prevented, if the InGaP layer is sealed, e.g., by a sufficiently thick GaAs cap layer.

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