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Optical Properties of Low Temperature Grown GaAs: The Influence of a Hydrogen Plasma Treatment

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Defects generated during the growth process in low temperature grown GaAs are studied by infrared (IR) absorption and low temperature photoluminescence. The growth temperature and As₄-pressure during growth determine critically the density of antisite related defects. Annealing the layers well above the growth temperature reduces the defect density. Hydrogen plasma treatment has only a minor effect on the defect density. However, hydrogen plasma treatment at temperatures below the growth temperature of the layers reveal a new photoluminescence (PL) band which is tentatively assigned to a complex involving hydrogen and an intrinsic defect.

1. INTRODUCTION

Recently, GaAs grown by low-temperature (LT) molecular beam epitaxy (MBE) has attracted a great deal of technological interest^{1,2)}. In the as grown state, LT GaAs layers grown at 200°C are crystalline with a high concentration (up to 1% or more) of excess arsenic on interstitial lattice sites. Furthermore, large arsenic antisite defect concentrations ($\sim 10^{20}$ cm⁻³) as well as gallium vacancy concentrations ($\sim 10^{18}$ cm⁻³) seem to be characteristic of this material and could provide the basis for new device applications. Upon annealing the layers at 600°C under arsenic overpressure, the excess arsenic precipitates into nanometer-size clusters and the point defect concentration decreases by one or two orders of magnitude, giving rise to a change in resistivity. As-grown LT GaAs layers exhibit hopping conductivity which is drastically reduced after annealing.

In this study, we have investigated the annealing behavior of LT GaAs layers grown at 200°C or 300°C. We find that in addition to the substrate temperature, the As_4 pressure is a crucial parameter that strongly influences the optical properties of LT GaAs and which has to be taken into account when comparing experimental results from samples of different origins. Atomic hydrogen was introduced into the LT GaAs layers at temperatures well below the growth temperature to achieve deep defect passivation without the formation of As precipitates. No passivation of deep As_{Ga} defects was detected, but a new photoluminescence band at 0.90eV was generated under these annealing conditions.

2. EXPERIMENTAL

The samples used in this study consist of undoped GaAs-layers of 2µm thickness grown by MBE on 600µm thick semiinsulating GaAs-substrates. During growth, the substrate temperature (T_G) was held at 200°C or 300°C as measured with a thermocouple mounted below the substrate. For all samples the gallium-pressure was fixed at $8.5 \cdot 10^{-5}$ Torr and the As₄-pressure was varied for the different samples as indicated in Table I. Samples were exposed to a remote DC hydrogen plasma (1000V, 1mbar) for ≈20 hours at temperatures in the range of 180-500°C.

Absorption measurements were performed with a BOMEM DA3.01 FTIR spectrometer using a halogen lamp source and an InSb-detector. For the optical quenching experiments, the samples were cooled down to 10K in a continuous flow exchange gas cryostat in the dark and then absorption was measured with a light intensity so that quenching of the absorption during the measurement was small. Intentional quenching was performed by exposing the samples to white light of higher intensity for several minutes until the decrease in absorption saturated.

Photoluminescence was measured at 4.2K with 100mW Ar⁺ laser excitation at 514nm, using a liquid nitrogen cooled germanium detector.

3. RESULTS

3.1 Absorption

The concentration of As_{Ga} antisite defects in the LT GaAs layers was determined by optical absorption measurements in the photon energy range from 0.7 - $1.5eV^{3}$). The spectra of two representative samples are

shown in Fig. 1 in comparison to the much weaker absorption of the substrate material.



Fig. 1 Near bandgap absorption of two LT GaAs layers compared to the absorption of the substrate material. The full lines give the absorption directly after cooling the layers to 10K, the dashed lines give the absorption after optical quenching with a white light source.

For each layer, the quenchable and unquenchable part of the As_{Ga} absorption was determined. Low growth temperature and a high arsenic As_4 pressure lead to a smaller amount of quenchable As_{Ga} centers. (Table I lists the total As_{Ga} concentrations and the percentage of quenchable As_{Ga} centers.)

sample	growth temperture T _G	layer thickness	As ₄ -pressure (BEP=[As ₄]:[Ga])	arsenic antisite concentration
305	200°C	2μm	15-10 ⁻⁶ Torr (BEP=18)	15·10 ¹⁹ cm ⁻³ 7% quenchable
306	200°C	2µm	8-10-6 Torr (BEP=9)	11·10 ¹⁹ cm ⁻³ 8% quenchable
307	300°C	2µm	15·10 ⁻⁶ Torr (BEP=18)	6.4.10 ¹⁹ cm ⁻³ 46% quenchable
308	300°C	2µm	9.10 ⁻⁶ Torr (BEP=11)	6.2.10 ¹⁹ cm ⁻³ 50% quenchable
309	300°C	2µm	7.10 ⁻⁶ Torr (BEP=8)	4.8.10 ¹⁹ cm ⁻³ 56% quenchable

Table I Compilation of the growth parameters and As_{Ga} concentrations for the samples studied.

Figure 2 summarizes the annealing behavior of all layers. Thermal annealing for 20 min. in a hydrogen plasma leads to a reduction of the As_{Ga} concentration only for temperatures well above the growth temperature. The passivation of deep level defects by hydrogen under the plasma conditions can be excluded, because the same reduction of antisite centers is found by annealing the layers at the same temperature in argon atmosphere.



Fig.2 Decrease of the total As_{Ga} concentration with



3.2 Photoluminescence of the as-grown LT GaAs layers

The low temperature PL spectra of the LT GaAs layers are distinctively different for samples grown at 200°C and 300°C. (Two typical spectra are given in Fig. 3.)



Fig. 3 Low temperature (T=4.2K) photoluminescence of LT GaAs layers grown at 200°C and 300°C.

Layers grown at $T_G=200^{\circ}C$ exhibit only a PL-band with maximum at 1.13eV (1100nm). The intensity of the PL band increases with As₄ pressure. Layers grown at $T_G=300^{\circ}C$ show in addition a band at 1.05eV (1180nm), which is superimposed on the low energy side of the 1.13eV band. The PL-band at 1.05eV seems to be independent of As₄ pressure in the pressure range studied. In addition, the layers grown at 300°C show the pronounced PL of the EL2 at 0.68eV (1800nm)⁴). The onset of this PL can already be detected at 1600nm by the Ge-detector. The EL2 PL increases with increasing As₄ pressure.

3.3 Photoluminescence of annealed LT GaAs layers.

Heat treatment of LT GaAs above the growth temperature leads to an increase in PL intensity. Figure 4 depicts two spectra which exhibit the 1.13eV band after hydrogen plasma treatment with the layers heated to 500°C. We find a reduction of the 1.05eV band in the layers grown at $T_G=300$ °C as well as a decrease in the EL2 PL. To rule out effects of the atomic hydrogen, reference layers were annealed under the same conditions in argon atmosphere and no difference in the spectra could be detected.



Fig. 4 Influence of annealing in a hydrogen plasma with the LT GaAs layers at a temperature above the growth temperature of the layers.

For layers grown at T_G =300°C, hydrogen treatment below the growth temperature under identical conditions gives different PL spectra.



Fig. 5 Photoluminescence of a LT GaAs layer ($T_G=300^{\circ}C$) after annealing at T=180°C in Ar atmosphere or in a H-plasma. For comparison, the PL spectra of the as-grown sample is given.

As shown in Fig. 5, we detect an increase in PL intensity after annealing in Ar atmosphere at 180°C for 20h but no change in the PL spectrum. Hydrogen-plasma treatment under identical conditions leads, however, to the formation of a strong PL band at 0.90eV.

4. DISCUSSION

Several groups have studied the optical properties of LT GaAs. However, in most cases the as-grown lavers were annealed at higher temperatures before measurement. Excitonic recombination at an axial pair defect was found for growth temperatures in the narrow temperature range from 325°C - 400°C⁵⁾. Annealing of LT GaAs above 400°C leads to a broad band at 0.8eV which was assigned to the recombination at an As_i - V_{Ga} pair^{5,6)}. Recently, Yu *et al.* detect two PL-bands at 0.68eV and 1.1eV in LT GaAs grown at 200°C - 300°C. The 1.1eV-band presumably corresponds to our two bands at 1.13eV and 1.05eV and was interpreted as an VGa-related emission. According to our measurements, at least two different complexes are responsible for the broad feature around 1.1eV. The band at ~1.13eV shows no dependence on As4 pressure, whereas the intensity of the band at 1.05eV is increasing with As4 pressure.

Annealing of the LT GaAs samples above the growth temperature leads to a reduction of the As_{Ga} concentration. In particular, the number of quenchable As_{Ga} defects increases with annealing temperature. The penetration depth of the hydrogen is apparently far too small to passivate a significant portion of these defects. Hydrogen plasma treatment below the growth temperature $T_G=300^{\circ}C$ leads however to a strong PL at 0.9eV of unknown origin. This band is however very similar to the one found in bulk GaAs samples after extended hydrogen exposure⁷). We tentatively assign the band to recombination at a complex consisting of hydrogen and an intrinsic defect.

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5. REFERENCES

- ^{*}Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastr. 72, D-79108 Freiburg, Germany
- 1) D.C. Look, Thin Solid Films 231 (1993) 61.
- 2) G.L. Witt, Mater. Sci. Eng. B <u>22</u> (1993) 9.
- P. Silverberg, P. Omling and L. Samuelson, Appl. Phys. Lett. 52 (1988) 1689.
- 4) M.K. Nissen, T. Steiner, D.J.S. Beckett, M.L.W. Thewalt, Phys. Rev. B <u>65</u> (1990) 2282.
- P.W. Yu, D.N. Talwar, C.E. Stutz, Appl. Phys. Lett. <u>62</u> (1993) 2608.
- P.W. Yu, G.D. Robinson, J.R. Sizelove and C.E. Stutz, Phys. Rev. B <u>49</u> (1994) 4689.
- J. Weber, F. Bantien, S.J. Pearton and W.C. Dautremont-Smith, Mater. Sci. Forum <u>10-12</u> (1986) 579.