INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **34** (2001) A15–A18 www.iop.org/Journals/jd PII: S0022-3727(01)21544-7

Structural transformations in low-temperature grown GaAs:Sb

D A Vasyukov[1], M V Baidakova[1], V V Chaldyshev[1], A A Suvorova[1], V V Preobrazhenskii[2], M A Putyato[2] and B R Semyagin[2]

[1] Ioffe Institute of Russian Academy of Sciences, Politechnicheskaya 26,
194021 St Petersburg, Russia
[2] Institute of Semiconductor Physics, Siberian Division of the Russian Academy of Science,
630090 Novosibirsk, Russia

E-mail: vasukov@pop.ioffe.rssi.ru

Received 13 September 2000

Abstract

Sb-doped and Sb-free GaAs films were grown by molecular beam epitaxy (MBE) at low temperature (LT) and were annealed in the MBE set-up at various temperatures within the range of 500–900 °C. The concentrations of arsenic antisites in as-grown samples obtained using near-infra-red optical absorption were found to be as high as 6×10^{19} and 7×10^{19} cm^{-3} in Sb-doped and Sb-free samples, respectively. Samples were studied by high-resolution x-ray diffractometry (HRXRD) and transmission electron microscopy (TEM). Despite the high concentration of intrinsic point defects, x-ray rocking curves demonstrated perfect crystalline quality in as-grown samples. After annealing at temperatures of 500–700 °C, the lattice mismatch decreased in both Sb-doped and Sb-free samples, but in Sb-doped samples the reduction was much higher than would be expected for the antisite defect concentration determined from optical measurements. The segregation of isovalent Sb impurity into the As clusters was suggested. Upon annealing at temperatures higher than 700 °C, Sb-doped samples manifested a strong broadening of the diffraction maximum related to the LT GaAs:Sb layer. The TEM and HRXRD studies revealed that high-temperature annealing resulted in formation of dislocation loops attached to the large As clusters.

1. Introduction

GaAs films grown by molecular beam epitaxy (MBE) at low temperature (LT) have attracted much attention due to high electrical resistivity and short carrier lifetime [1–5]. A distinctive feature of this material is a large quantity of As antisites (As_{Ga}) ($\sim 10^{20}$ cm^{-3}). The arsenic excess can be varied over a wide range by alteration of the growth temperature and As/Ga flux ratio. Arsenic excess can be enhanced by isovalent indium impurity doping or, alternatively, reduced by doping with Be acceptors and Si donors [6, 7]. Upon annealing, the excess As segregates in clusters, the size and concentration of which can be varied by altering annealing duration and temperature. It should be noted that formation of As clusters does not lead to deterioration of the crystalline structure of the LT GaAs matrices, either undoped or doped with In, Be or Si [6–8]. These impurities also do not influence the atomic structure of As clusters.

In this paper we show that in contrast to the other previously studied impurities, doping with Sb strongly affects the structural transformations in low-temperature grown GaAs films upon annealing.

2. Experimental procedure

The LT GaAs film doped with Sb ($\sim$1 at%) as well as conventional (Sb-free) samples were grown by MBE at (200 °C) on 2 inch GaAs (001) substrates. The thickness of samples was approximately 0.9 μm. Both samples were divided into ten parts; one part was maintained as grown, while the nine remaining parts were annealed in the MBE set-up under arsenic overpressure at 500, 555, 580, 620, 703, 750, 800, 850, or 880 °C, respectively. The samples were characterized by using near-infra-red optical absorption (NIRA) and high-resolution x-ray diffractometry (HRXRD) technique.

Table 1. Parameters of x-ray rocking curves for the Sb-free LT GaAs layers on (001) GaAs substrates.

T_{anneal} (°C)	$\Delta\theta$ (arcsec)	$\Delta a/a$ (10^{-4})	K_S (%)	FWHM$_S$ (arcsec)	FWHM$_L$ (arcsec)	T_L (μm)
As grown	−113	8.43	55[a]	13	22	0.90
500	−13	0.95	57	8	23	
555	−4	0.28	66	7	16	
580	−5	0.36	64	7	16	
620	−3	0.23	63	8	22	
703	5	−0.37	78	7	15	0.87
750	11	−0.87	65	11	13	0.90
800	3	−0.24	60	10	18	0.86
850	5	−0.40	80	7	15	0.88
885	3	−0.23	71	7	17	0.87

[a] The reflectivity factor of the layer in this sample $K_L = 21\%$.

The HRXRD study was carried out using a double-crystal diffractometer. In order to precisely evaluate the lattice mismatch and crystalline quality, the measurements were taken using an ω-scan method with wide-open detector. An asymmetrical germanium crystal was used as a monochromator, which provided a divergence of the initial x-ray beam of 1.0–1.2 arcsec for (400) reflection of Cu K$_{\alpha 1}$ radiation. X-ray rocking curves were recorded near (004) GaAs reflection.

Conventional transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM) were applied to investigate the structure of Sb-doped and Sb-free LT GaAs layers. A JEOL JEM 4000EX and Philips CM200 were used for the investigation. Cross-sectional and plan-view TEM specimens were prepared by conventional ion milling procedure [3].

3. Results and discussion

The concentration of As$_{Ga}$ in the samples was determined from the NIRA study using Martin's calibration [9]. It was found to be as high as 6×10^{19} and 7×10^{19} in Sb-doped and Sb-free samples, respectively.

Figure 1 shows x-ray rocking curves near (004) reflection of as-grown and annealed samples of (a) Sb-free LT GaAs and (b) Sb-doped LT GaAs. In these figures the right maximum corresponds to radiation reflected from the substrate and the left one corresponds to reflection from the LT GaAs film. The angle difference ($\Delta\theta = \theta - \theta_{Br}$) between the layer and substrate maxima corresponds to the average deformation value in the structure. This value originates from the high concentration of arsenic antisite defects in conventional LT GaAs films and also from the Sb content in LT GaAs:Sb samples. The most important parameters of x-ray rocking curves such as the angle difference between the layer and substrate ($\Delta\theta$), the reflectivity factors (K) and full widths at the half maximum (FWHM) of the layer (L) and the substrate (S) correspondingly, and calculated values of lattice mismatch ($\Delta a_{\perp}/a$) and layer thickness (T_L) for as-grown and annealed samples are shown in tables 1 and 2.

The lattice mismatch between the layer of as-grown conventional LT GaAs and the substrate was as high as $\Delta a_{\perp}/a = 8.4 \times 10^{-4}$. Taking into account the calibration by Liu *et al* [10], this value was found to be in remarkable agreement with the As$_{Ga}$ concentration of 7×10^{19} cm^{-3} obtained using NIRA data. Despite the high concentration of excess arsenic, the x-ray rocking curve confirmed the high crystalline quality of the as-grown film. The multiple interference fringes (see figure 1(a)) and narrow FWHM of the layer and the substrate (see table 1) prove this conclusion. After annealing, $\Delta a_{\perp}/a$ values were measurably reduced. This characteristic is the signature of transformation of As antisite defects to nanoscale As clusters. After annealing at $T_{anneal} = 620\,°\mathrm{C}$, $\Delta a_{\perp}/a$ was close to zero. When the annealing temperature was higher, the $\Delta a_{\perp}/a$ became negative and as low as -0.4×10^{-4}.

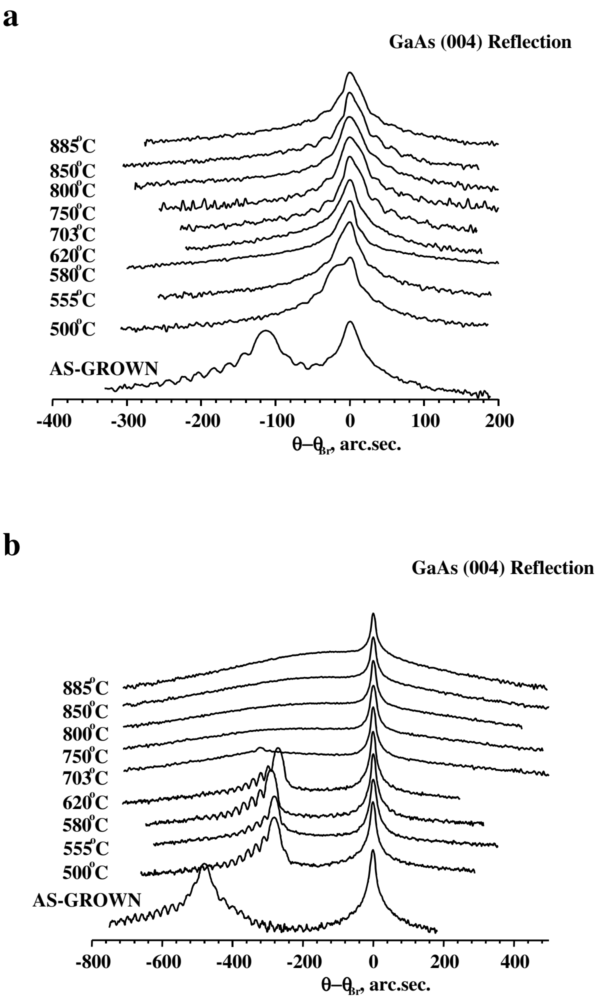

Figure 1. X-ray rocking curves for conventional (a) Sb-free and (b) Sb-doped LT GaAs films annealed at various temperatures. The annealing temperatures are shown on the curves.

The HRXRD measurements of as-grown Sb-doped LT GaAs (figure 1(b)) showed narrow FWHM, multiple interference fringes, and evidenced the high crystalline quality of the film characterized by lattice expansion at $\Delta a_{\perp}/a = 3.6 \times 10^{-3}$, exceeding the degree of expansion in the Sb-free sample. After annealing at temperatures of 500–700 °C, the lattice mismatch decreased to $\Delta a_{\perp}/a = 2 \times 10^{-3}$. The reduction was much higher than would be expected for the antisite defect concentration determined from optical measurements. We suggest that such a strong reduction could be due to segregation of isovalent Sb impurity into the As clusters. In the samples annealed at $T_{anneal} = 700$–$885\,°\mathrm{C}$, the

Table 2. Parameters of x-ray rocking curves for the Sb-doped LT GaAs layers on (001) GaAs substrates.

T_{anneal} (°C)	$\Delta\theta$ (arcsec)	$\Delta a/a$ (10^{-3})	K_S (%)	K_L (%)	FWHM$_S$ (arcsec)	FWHM$_L$ (arcsec)	T_L (μm)
as grown	−480	3.6	61	16	9	25	0.88
500	−281	2.1	65	14	10	20	0.86
555	−282	2.1	59	11	11	19	0.90
580	−290	2.2	70	15	10	22	0.86
620	−270	2.0	62	13	9	23	0.92
703	−320	2.4	68	1.3	10	85	
750	−254	1.9	55	0.8	13	328	
800	−208	1.5	63	1.0	11	390	
850	−175	1.3	63	1.3	11	295	
885	−144	1.1	64	1.5	11	254	

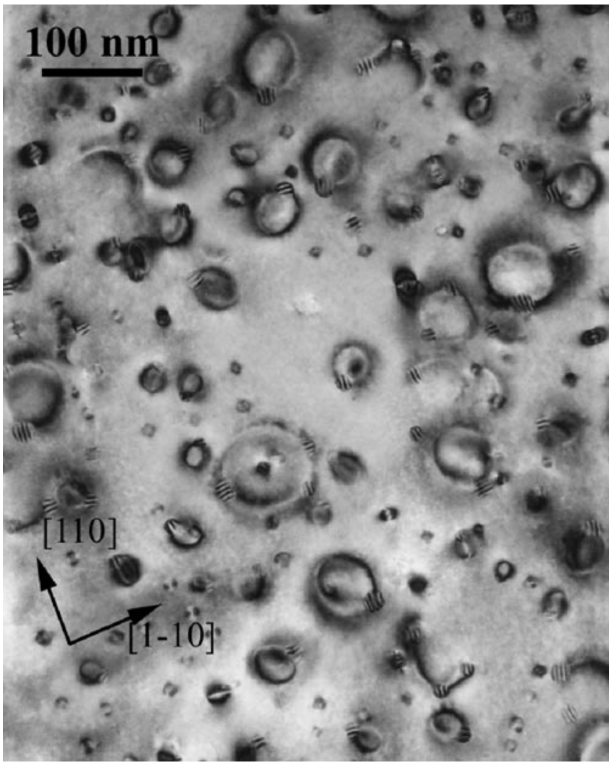

Figure 2. Bright-field TEM image along the [001] direction for Sb-doped LT GaAs film annealed at 703 °C.

HRXRD study revealed strong broadening of the layer maxima and decrease of their reflectivity (K_L). Reshaping of the x-ray rocking curves was inherent in the dramatically dislocated layers with a profusion of continuous defects. Therefore, we may conclude that Sb incorporation in As clusters induces violent strains in the surrounding matrix and heavily influences crystalline quality of GaAs.

The TEM study of the annealed LT GaAs samples revealed As precipitates dispersed over the film bulk. The cluster size strongly depended on the annealing temperature. For identical annealing conditions the clusters were found to be bigger in Sb-doped films than in Sb-free samples. This observation is consistent with an enhanced precipitation phenomenon previously reported by Bert *et al* [11] for Sb-doped LT GaAs films.

Figure 2 shows a bright-field plane-view TEM micrograph for the Sb-doped LT GaAs sample annealed at 703 °C. One can see the system of clusters with characteristic Moiré fringes and a large number of dislocation loops attached to these clusters. While the cluster microstructure in Sb-doped LT GaAs is similar to that in conventional LT GaAs, it should be noted that the dislocation loops have never been observed in Sb-free samples [3, 6]. The formation of the dislocation loops may originate from strong local strains induced by the clusters in the surrounding matrix. The strains may result from incorporation of Sb atoms in the clusters. This suggestion is consistent with the enhanced lattice relaxation revealed by our HRXRD study.

The dislocation loops begin to form when the cluster size in Sb-doped LT GaAs exceeds 8 nm. The loops grow with increasing cluster size, i.e. with increasing annealing temperature. This is probably the reason for the drastic deterioration of coherent x-ray rocking curves after high-temperature annealing of Sb-doped LT GaAs samples.

4. Conclusion

HRXRD study of the Sb-doped and Sb-free LT GaAs grown by MBE at 200 °C proved the perfection of the as-grown structures, displaying narrow FWHM and multiple interference fringes at x-ray rocking curves. High-temperature annealing of the Sb-free sample resulted in transformation of arsenic antisites to As clusters and to absolute diminution of deformity in the layer resulting from the presence of excess arsenic. The annealing of the Sb-doped sample at 500–700 °C yielded a strong decrease of the lattice mismatch, which cannot be explained solely by As cluster formation. We suggest that such a strong relaxation could be due to segregation of isovalent Sb impurity within the As clusters.

Another structural transformation was detected by HRXRD when the Sb-doped samples were annealed at temperatures higher than 700 °C. There was strong broadening of the diffraction maximum related to the LT GaAs:Sb layer. The TEM study demonstrated that the high-temperature annealing results in formation of dislocation loops attached to the large As clusters.

Acknowledgments

This work has been supported by Grant Nos RFBR 98-02-17617 and INTAS 97-30930. The research was carried out under the programmes 'Physics of Solid State Nanostructures' and 'Fullerenes and Atomic Clusters' by the Ministry of Sciences and Technological Policy of Russia. The authors are thankful to A E Kunitsyn for the optical measurements and N A Cherkashin for the TEM study.

References

[1] Smith F W, Calawa A R, Chen C L, Manfra M J and Mahoney L I 1988 *IEEE Electron Device Lett.* **9** 77

[2] Kaminska M, Liliental-Weber Z, Weber E R, George T, Kortright J B, Smith F W, Tsaur B Y and Calawa A R 1989 *Appl. Phys. Lett.* **54** 1831

[3] Bert N A *et al* 1993 *Solid State Phys.* **35** 1289–97

[4] Melloch M R, Otsuka N, Woodall J M, Warren A C and Freeouf J L 1990 *Appl. Phys. Lett.* **57** 1531

[5] Gupta S, Frankel M Y, Valdmanis J A, Wittaker J F, Mouron G A, Smith F W and Calawa A R 1991 *Appl. Phys. Lett.* **59** 3276

[6] Bert N A, Chaldyshev V V, Kunitsyn A E, Musikhin Yu G, Faleev N N, Tretyakov V V, Preobrazhenskii V V, Putyato M A and Semyagin B R 1997 *Appl. Phys. Lett.* **70** 3146–8

[7] Chaldyshev V V, Kunitsyn A E, Tretyakov V V, Faleev N N, Preobrazhenskii V V, Putyato M A and Semyagin B R 1998 *Semiconductors* **32** 692–5

[8] Faleev N N, Chaldyshev V V, Kunitsyn A E, Preobrazhenskii V V, Putyato M A, Semyagin B R and Tretyakov V V 1998 *Semiconductors* **32** 19–25

[9] Martin G M 1981 *Appl. Phys. Lett.* **39** 747

[10] Liu X, Prasad A, Nishio J, Weber E R, Liliental-Weber Z and Walukievich W 1995 *Appl. Phys. Lett.* **67** 279–81

[11] Bert N A, Chaldyshev V V, Suvorova A A, Preobrazhenskii V V, Putyato M A and Semyagin B R 1999 *Appl. Phys. Lett.* **74** 1588–90