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Poster

Microdefects and nonstoichiometry level in GaAs:Si/GaAs films grown by liquid-phase epitaxy method

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Abstract

GaAs:Si/GaAs films heavily doped with Si were investigated by complex methods including X-ray diffractometrical measurement of diffraction maximum integral intensity for a quasi-forbidden reflection of the continuous spectrum wavelengths permitting determination of defect structure parameters, i.e. mean radius and concentration of precipitates and chemical composition violation (level of nonstoichiometry), as well as second ion mass spectroscopy (SIMS), measurements of electrophysical parameters. The level of nonstoichiometry was shown to depend on parameters of defect structure. The conclusion was drawn about interaction on point defects with precipitates enriched with silicon atoms. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Point defects, i.e. impurity atoms, interstitials or vacancies are well known [1] to interact with various structure defects in crystals. They can form, for example, the Cottrell atmospheres around dislocations. The microdefects of so-called Coulomb deformation centres with quadratic law of atomic displacement variations from a centre of defect (dislocation loops or spherical precipitates) can also act as a sink for point defects. This property of dislocations as well as microdefects is usually used for cleaning of crystal bulk from undesirable impurities (getter effect in solid-state devices technology). Dependence of stoichiometrical defects in binary semiconductor compounds on dislocation density was shown by Fujimoto [2] in GaAs crystals. The GaAs crystals heavily doped with Si were shown [3] to have little or no dislocations. The authors of this paper dealt with the etch pits counting method, and reported that these crystals also had no precipitates.

Being one of the most important problems in semiconductor binary materials, nonstoichiometry should be studied by various methods. One of them is X-ray diffraction investigations which can determine not only the concentration of compositional defects but also their situation in every sublattice of a binary crystal [2]. The physical base of this method is the integral intensity (II) of a diffraction maximum for so-called quasi-forbidden reflections (QFR) which structure factors F_{QFR}, depend on the difference of atomic form factars ($F_{\mathrm{QFR}} = C_A f_A - C_B f_B$) of both sublattices, were C_A and C_B is the concentration of components A and B. In the case of the GaAs the II is very sensitive to little changes of C_i because $f_{\mathrm{Ga}} \sim f_{\mathrm{As}}$. The important problem of structure perfection effect on the II for the QFR is solved by various methods [2–4]. The last method (4), based on the measuring of the II of the QFR for different wavelengths situated between two absorption K-edges and comprising them with calculated value, permit to determine not only the parameter of non-stoichiometry, $\Delta = (C_{\mathrm{Ga}} - C_{\mathrm{As}})$, in GaAs crystals but the parameters of defects structure (average radius, $\bar{r}$, and concentration n of microdefects).

The aim of this paper consisted in elucidation of real defects structure of GaAs films heavily doped with silicon, determination of its main parameters as well as in discov-

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ering possible interactions of it with point defects of nonstoichiometrical nature. The auxiliary methods, i.e. the measurements of electrophysical parameters of films (majority carrier concentration and their mobility), the secondary ion mass spectrometry (SIMS) were also planned for use for characterisation of the material under investigation.

2. Sample characteristics and peculiarities of experimental methods

The GaAs:Si/GaAs were grown at the Institute of Physics Polish AS (Warsaw) by the LPE method. They were heavily doped (up to 10^{21} cm^{-3}) with Si during the growth process. Their physical characteristics are given in Table 1. The samples can be conventionally divided into two groups: the thin samples (thickness 4–8 μm) and thick ones (13–15 μm). General quantity of Si atoms, N_{Si} in films was determined by the second ion mass spectrometry (SIMS). Also the concentration of majority carriers (holes) was measured. Because the quantity of acceptors was lower compared with N_{Si} the films were suggested to have much Si atoms in electrically passive state (in interstitial position or coagulated in microprecipitates). The mobility of carriers was measured too (see Table 1).

The peculiarities of the integral reflectivity (IR) measurements for the wide region of wavelengths situated between the As and Ga absorption K-edges were published elsewhere [5]. To determine the average radius R_0 and concentration of microdefects (precipitates) n the fitting procedure of the calculated IR, R_i^T, by the statistical dynamical theory of X-ray scattering for a real crystal [6] to experimental data $R_i^{\exp}$ was used for the QFR, 200, and fundamental, 400 reflections. The essence of such a procedure consisted in the minimisation of the functional

$$\Phi = \sum_{i=1}^{N} \left[R_i^{\exp}(\lambda)_i - R_i^T(\lambda)_i \right]^2 / \sigma_i^2 \tag{1}$$

where the σ_i^2 is the statistical error of calculation.

The experimental dependences 1 and 2 of the $R_i^{\exp}(\lambda)$ are given, respectively, for samples 5–5 and 5–8, for example, in Fig. 1. The solid lines show the results of the fitting procedure. The fitting reliability parameter R is equal to 2.3 and 1.5%, respectively, for samples 5–8 and 5–5. So the results of this procedure can be considered as satisfactory ones. The parameters R_0, n and Δ are given in Table 1.

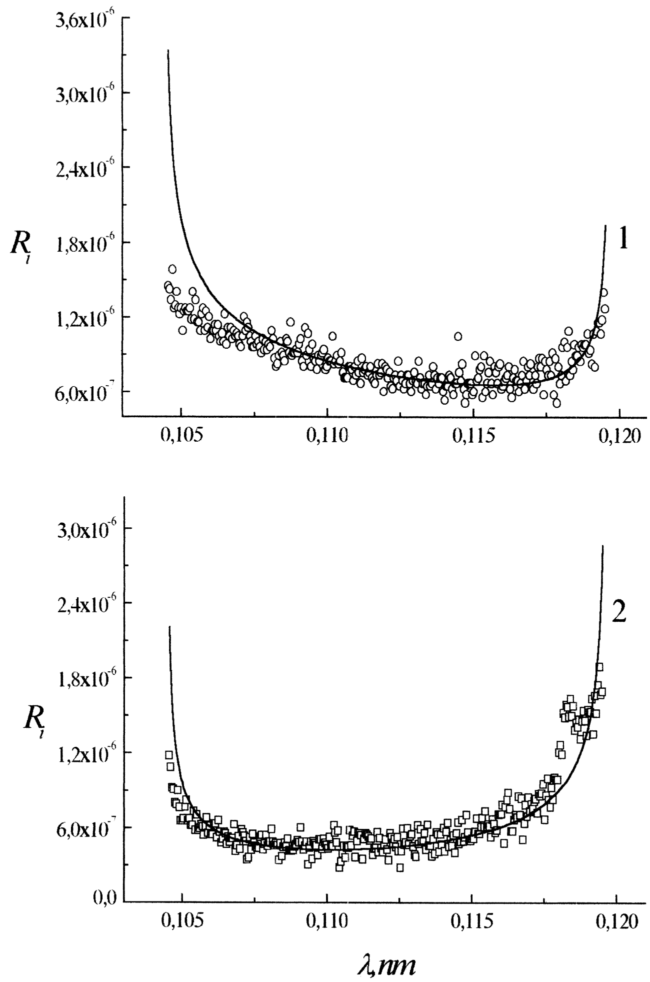

Fig. 1. Spectral dependences of the reflectivity, $R_i^{\exp}(\lambda)$, for the samples 5–5 (1) and 5–8 (2). The experimental and theoretical values are shown by markers and solid lines, respectively. Parameter Δ is equal to 0.047 and 0.008 for curves 1 and 2, respectively (Ga excess).

Table 1
Parameters of films and precipitates

Sample number	Film thickness (μm)	Carrier mobility (cm^2/Vs)	Si conc. (SIMS) (cm^{-3})	Carriers conc. p (cm^{-3})	$\Delta = C_{Ga} - C_{As}$	Precipitate parameters	
						R_0 (μm)	n (cm^{-3})
6–2	4	13	1.6×10^{19}	4.3×10^{19}	−0.009	5.0	9×10^{6}
6–4	7.8	5.8	3.9×10^{19}	6.8×10^{19}	+0.001	4.6	1×10^{7}
8–3	4.8	20	1.4×10^{21}	1.7×10^{19}	+0.011	3	6.5×10^{6}
5–8	13.4	20	2.5×10^{19}	5.4×10^{18}	+0.047	1	2.5×10^{6}
5–7	14.6	30	8.3×10^{19}	2.4×10^{18}	+0.025	1.9	5×10^{6}
5–5	15.3	30	1.6×10^{20}	2.3×10^{18}	+0.008	1.8	3×10^{7}

3. Results and discussion

Let us note in the first place that the shapes of both graphs in Fig. 1 for samples 5–8 (1) and 5–5 (2) differ slightly. Really, both plots have some $R_i(\lambda)$ minima situated in their left or right regions. These minima are connected with wave points where the real part of the structure factor F_{rh} for the 200 reflections goes to zero due to the influence of the Ga or As excess in the films. We have calculated this effect of nonstoichiometry parameter Δ on the integral reflectivity. Results of these calculations of $R_i(\lambda)$ are shown in Fig. 2 in the case of $\Delta = C_{Ga} - C_{As} = 0.05$ (Ga excess, (2)) and $\Delta = -0.05$ (As excess, (3)) as compared with the stoichiometrical composition graph (1). So one can judge sometimes the sign of nonstoichiometry in a crystal even qualitatively when analysing the shape of a graph. The values of the Ga excess (As vacancies) were equal to 0.047 and 0.008 for samples 5–8 and 5–5, respectively. It can mean that silicon in the first sample (relatively low concentration of Si ($N_{Si} = 2.5 \times 10^{19}$ cm^{-3})) occupies preferentially the As vacancies as compared with the case of the 5–5 film (large concentration of Si ($N_{Si} = 1.6 \times 10^{20}$ cm^{-3})). So the quantity of As_{Si} acceptors in the 5–8 sample ($p = 5.4 \times 10^{18}$ cm^{-3}) is 2.8 times larger than that in the 5–5 film ($p = 5.4 \times 10^{18}$ cm^{-3}) because some Ga atoms in it can also be replaced with silicon (donor action of Ga_{Si} at higher level of Si doping).

Behaviour of acceptor concentration p and parameter Δ as a function of the Si doping level N_{Si} is shown in Fig. 3a,b for the thin and thick films. Carrier concentration p diminutions with growth of N_{Si} are similar in both groups of samples. This result may be connected, in our opinion, with some compensation effect due to partial replacement of Ga atoms with silicon by their higher concentration because Si_{Ga} is a donor. The Δ parameter behaviour is, however, different in thin and thick films contrary to the regularities of acceptor variations. In thin films an enhancement of nonstoichiometry takes place (from -0.009 (sample 6–2) to 0.011 (film 8–3)). An opposite effect is observed in thick films. Δ parameter (As vacancy excess)

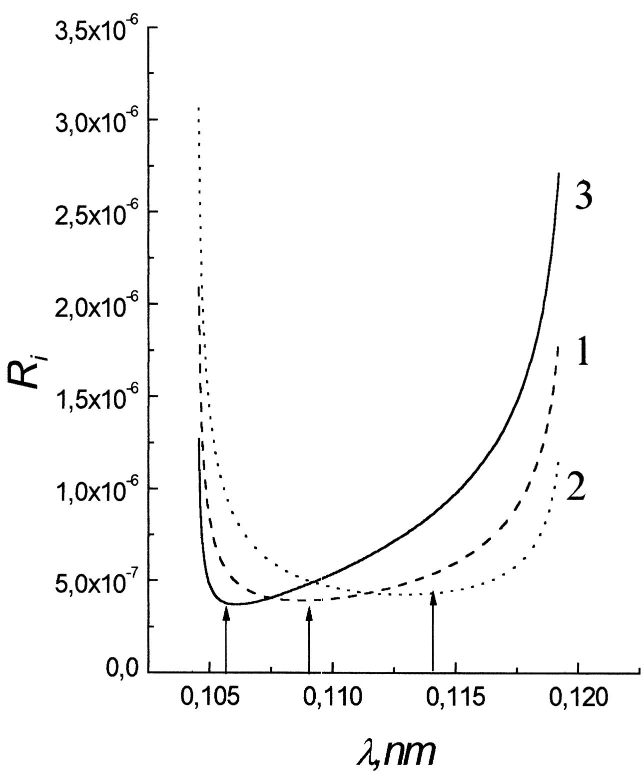

Fig. 2. Influence of the deviation parameter Δ of a structure nonstoichiometrical composition on the minimum position (pointer) of the reflectivity $R_i^{calc}(\lambda)$. Stoichiometrical composition (1). Ga excess ($C_{Ga} - C_{As} = 0.05$) (2). As excess ($C_{Ga} - C_{As} = -0.05$) (3).

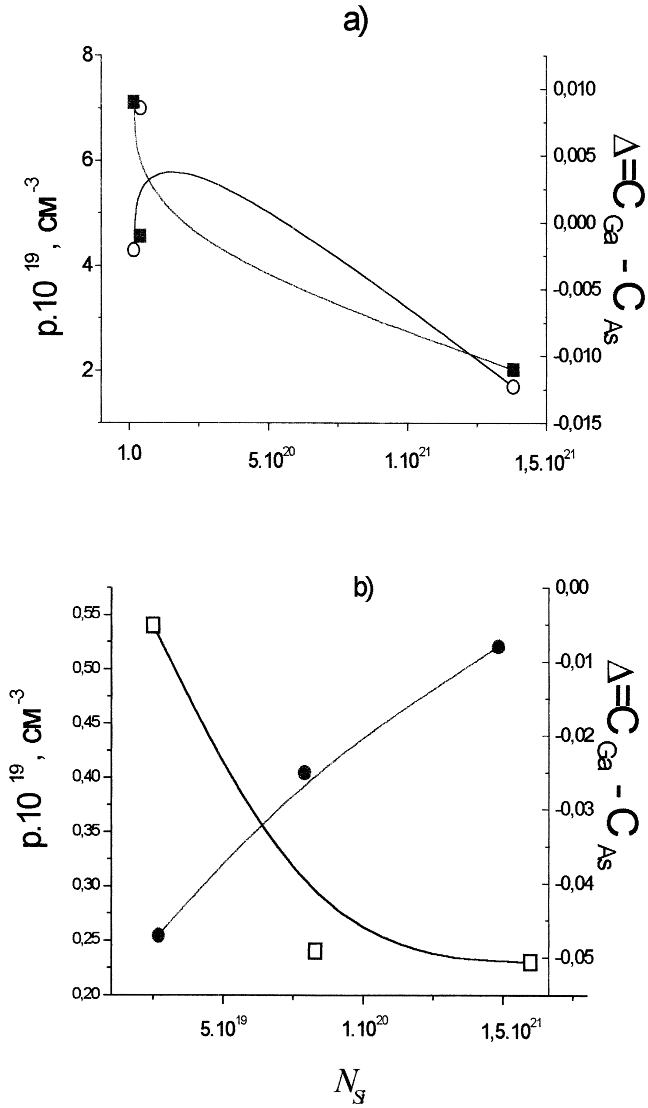

Fig. 3. Dependences of the acceptor concentrations p and nonstoichiometry parameter Δ on the concentration of silicon atoms as determined by the SIMS method. The case of (a) thin film, and (b) thick films (see Table 1).

drops here from 0.047 to 0.008. Therefore the 5–5 film tends to stoichiometric composition.

These peculiarities of p and Δ variations with N_{Si} can be perhaps understood taking into account the character of precipitate parameter variations in both of the film groups (Fig. 4a,b). The average radius R_0 and concentration n of precipitates as determined by the mentioned fitting procedure for the X-ray reflectivities $R_i(\lambda)$) at high levels of Si doping grow in thick films or decrease in thin samples, respectively, for high level of doping.

One can suppose the nonstoichiometric point defects can interact with the Coulomb deformation centres (precipitates) appearing during the LPE growth process of GaAs: Si/GaAs films. As a result of this interaction, a large

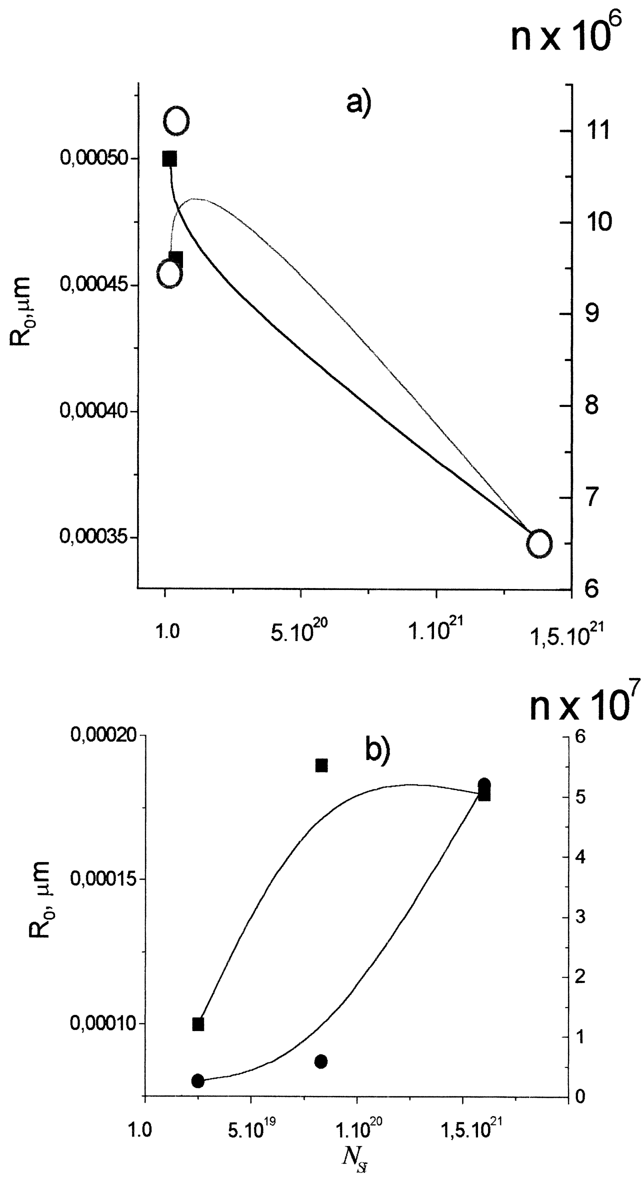

Fig. 4. Dependences of the radius R_0 and concentration n of precipitates on the SIMS determined concentration of Si atoms: (a) and (b) correspond to thin and thick film cases, respectively.

quantity of Si atoms is attracted to the mentioned microdefects. So the excess of silicon atoms which are in electrical passive state, especially in thick films (large values of radius and concentration of precipitates), takes part mainly in the formation of precipitates. Only a small part of silicon in these conditions has the possibility to replace the Ga atoms creating Ga_{Si} donors. As a result of this process the level of nonstoichiometry and the quantity of acceptors in thick films are decreased.

Similar processes of point defect interactions with microdefects take place perhaps in thin films too. But the concentration of silicon-enriched precipitates now is not so high as in the formerly discussed group of samples because of comparatively lower volume of molten material of GaAs. Excess of Ga atoms in GaAs lattice at the expense of As vacancies formation leads to enhancement of nonstoichiometry degree, Δ, as well as to an increase of As_{Si} acceptors concentration p due to replacement of these vacancies by silicon. Formation of As vacancies may be better in thin films, where the process of As atom evaporation plays a larger role. One can also note the correlation between the radius R_0 of microprecipitates and the majority of carrier mobility in thin films. The last value grows with decreasing microprecipitate radius.

4. Conclusion

The precipitates enriched by silicon as well as nonstoichiometrical defects were discovered in the LPE grown GaAs:Si/GaAs films using an X-ray diffraction method based on the spectral dependence of reflectivity for the QFR of continuous spectrum. So the previous conclusion that microprecipitates are not present in GaAs crystals heavily doped with silicon obtained by means of the etch pit counting method is not correct. Application of the SIMS data as well as measurements of electrophysical parameters gave the possibility to draw the conclusion in this paper about the interaction of point defects connected with chemical composition violation with the mentioned microdefects in a bulk of films.

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