Vol. **103** (2003) *ACTA PHYSICA POLONICA A* No. 6

Proceedings of the XXXII International School of Semiconducting Compounds, Jaszowiec 2003

Observation of Vacancies in $Ga_{1-x}Mn_xAs$ with Positron Annihilation Spectroscopy

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Positron annihilation spectroscopy can be used to determine the role of vacancy defects in semiconductors, by identification and quantification of the vacancies and their chemical surroundings. We have studied 0.5–0.8 μm thick low temperature MBE GaMnAs layers with Mn content 0.5–5% and different As_2 partial pressures at growth. The Doppler broadening results show that the Ga vacancy concentration in the layers decreases with increasing Mn content and decreasing As_2 partial pressure.

PACS numbers: 61.72.Ji, 75.50.Pp, 78.70.Bj

1. Introduction

The possibility to include magnetic impurities at relatively high concentrations in GaAs by means of low temperature molecular beam epitaxy (LT-MBE) has opened new exciting prospects of combining magnetic phenomena with high speed electronics and optoelectronics [1, 2]. The numerous investigations of $Ga_{1-x}Mn_xAs$ alloys that have been carried out so far have revealed interesting material properties, the most notable being carrier-induced ferromagnetism [3]. However, the question of self-compensation of the holes induced by Mn remains open.

The point defects in Be- and Si-doped as well as undoped LT GaAs have been previously studied by positron annihilation spectroscopy [4–9]. Ga vacancies have

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been found in both p- and n-type materials, complexed with either As antisites or Si impurities, respectively [6]. As vacancies have also been observed in highly Si doped LT GaAs [8]. It has been shown [9] that in Be-doped (i.e. p-type) LT GaAs, the Ga vacancy concentration is independent of the Be concentration.

We report on the incorporation of native point defects, specifically vacancies, in LT-MBE $Ga_{1-x}Mn_xAs$ layers with Mn content 0.5–5%. The vacancies were investigated by positron annihilation spectroscopy using a variable energy slow positron beam. We demonstrate that Ga vacancies are present in all the layers studied. Furthermore, the Ga vacancy concentration decreases with increasing Mn content, indicating that the Mn impurities have a significant influence on the formation of native point defects in LT-MBE GaAs.

2. Experimental

Positron annihilation studies were carried out using a variable energy (0–40 keV) positron beam. After implantation and rapid thermalization in the sample, the positrons can get trapped at neutral and negative vacancy defects, where the positive ion core is missing. Due to the reduced electron density at vacancies, the lifetime of the trapped positron increases compared to the lifetime of the positron in the defect-free lattice. Furthermore, the positron–electron pair momentum distribution becomes narrower, which can be observed as a narrowing of the Doppler broadened 511 keV annihilation line. Positrons can get localized also at the hydrogenic states of negative ion defects, even if these do not contain open volume. This trapping at shallow positron states can be used to obtain information on ionized acceptors such as negative antisites and impurities.

The electron–positron pair momentum distribution is measured by recording the Doppler broadening of the 511 keV annihilation line with a high-resolution Ge detector. The shape of the momentum distribution is described in terms of the low and high electron momentum parameters S and W, respectively [10]. The S parameter represents the fraction of positrons annihilating mainly with valence electrons with a longitudinal momentum component of $|p_L| < 3.1 \times 10^{-3} m_0 c$, where m_0 is the electron mass and c the speed of light. The W parameter is the fraction of annihilations with core electrons with a large momentum component of $11 \times 10^{-3} m_0 c < |p_L| < 28 \times 10^{-3} m_0 c$. The narrower momentum distribution caused by positron trapping at vacancies is seen as an increase in the S parameter and as a decrease in the W parameter.

The annihilation parameters S and W are characteristic of each material. The values recorded at a particular positron implantation energy E are linear superpositions of the parameter values characterizing annihilations at different positron states, weighted with the annihilation fractions $\eta_i(E)$ for the corresponding states

$$S(E) = \eta_{\text{surface}}(E) S_{\text{surface}} + \eta_{\text{layer}}(E) S_{\text{layer}} + \eta_{\text{substrate}}(E) S_{\text{substrate}}, \qquad (1)$$

$$W(E) = \eta_{\mathrm{surface}}(E)W_{\mathrm{surface}} + \eta_{\mathrm{layer}}(E)W_{\mathrm{layer}} + \eta_{\mathrm{substrate}}(E)W_{\mathrm{substrate}}. \quad (2)$$

In Eqs. (1)–(2) (S_{surface}, W_{surface}), (S_{layer}, W_{layer}) and ($S_{\mathrm{substrate}}$, $W_{\mathrm{substrate}}$) are the characteristic parameter values for positron annihilation at the sample surface, inside the LT-MBE GaAs layer, and in the substrate, respectively. The surface parameter is very sensitive to structural and chemical effects, e.g. to the contamination of the sample surface. The fractions $\eta_i(E)$ depend on the positron diffusion length, implantation depth and on the defect concentrations. When the implantation energy is high enough, no positrons can diffuse to the surface and $\eta_{\mathrm{surface}} = 0$.

When the layer under study contains defects that can trap positrons, the layer-specific S and W parameters can be written as

$$S_{\mathrm{layer}} = \eta_{\mathrm{bulk}}S_{\mathrm{bulk}} + \sum_i \eta_{\mathrm{defect},i}S_{\mathrm{defect},i}, \quad (3)$$

$$W_{\mathrm{layer}} = \eta_{\mathrm{bulk}}W_{\mathrm{bulk}} + \sum_i \eta_{\mathrm{defect},i}W_{\mathrm{defect},i}, \quad (4)$$

where (S_{bulk}, W_{bulk}) and ($S_{\mathrm{defect},i}$, $W_{\mathrm{defect},i}$) characterize the annihilations in the perfect lattice, and in the defect i, respectively. If only one type of defects that can trap positrons is present in the layer, the measured S and W are linear combinations of the values (S_{bulk}, W_{bulk}) and the values (S_{vacancy}, W_{vacancy}) characterizing the annihilations of the positrons trapped at vacancies. In the $W-S$ plane the measured (W, S) points fall on a straight line between the points (W_{bulk}, S_{bulk}) and (W_{vacancy}, S_{vacancy}), and the exact position is determined by the fraction of trapped positrons. The slope of the line is a defect-specific parameter and it can be used as a fingerprint to distinguish between different vacancies.

The vacancy-type defects in $\mathrm{Ga}_{1-x}\mathrm{Mn}_x\mathrm{As}$ were studied in 0.5–0.8 μm thick layers grown on semi-insulating (SI) GaAs substrates by LT-MBE with Mn content 0.5–5% (equivalent to 1×10^{20}–1×10^{21} cm^{-3}). An undoped LT-MBE GaAs and a p-type GaAs sample ([Zn] = 10^{19} cm^{-3}, known to be free of vacancy-type defects) were measured for reference. We studied the effect of increasing Mn content on

TABLE

Detailed growth data of the LT-MBE GaMnAs samples.

Mn content	Thickness	As$_2$ flux	Growth T [°C]	Additional information
0%	0.6 μm	low	210	
0.5%	0.8 μm	low	210	
0.5%	0.8 μm	low	210	annealed at 270°C for 1 h
1.5%	0.6 μm	low	230	
1.5%	0.5 μm	high	230	
2.5%	0.6μm	low	230	
2.5%	0.5 μm	high	240	
5.0%	0.5 μm	low	240	

the vacancy concentration in LT-MBE GaMnAs as well as the effect of increasing the As_2 partial pressure during growth with constant Mn content. Also the effect of post-growth annealing was studied. The details of the LT-MBE samples are collected in Table.

3. Results

The S and W parameters in all GaAs layers were measured at 300 K as a function of the positron beam energy E (typical S vs. E plots are presented in Fig. 1). The results are presented relative to the S and W parameters of the defect-free p-type GaAs reference, for which the parameters are thus defined as $(W_{\text{bulk}},\ S_{\text{bulk}}) = (1,\ 1)$. This enables the comparison of results obtained with different measurement systems, since the relative S and W parameters are rather independent of the energy windows and of the small variations in the energy resolutions of different Ge detectors. The implantation profile (a derivative of a Gaussian) of the monoenergetic positrons into GaAs is such that even though the positrons penetrate to a mean depth of 0.3 μm at 10 keV beam energy, a significant fraction stops deeper than 0.5 μm. Thus, in Fig. 1, only the data below 15 keV is shown, and depending on thickness of the layer, the data from 6–10 keV upwards is affected by the data coming from the substrate SI GaAs, which appears to be defect-free.

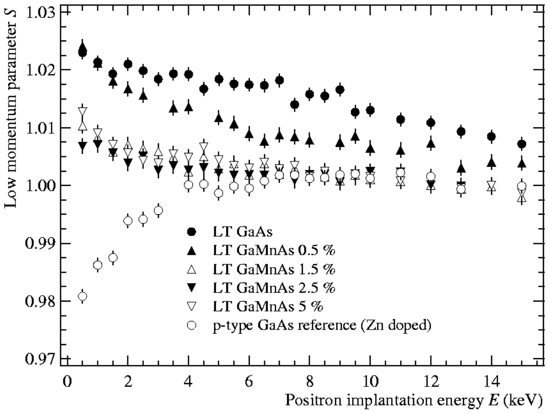

Fig. 1. Typical S vs. E curves measured from the LT GaMnAs samples.

The effect of the positrons diffusing to the surface of the sample is clearly seen in Fig. 1. It also shows that the diffusion length of the positrons in the GaMnAs layers is so short that positrons implanted with an energy of 3 keV no longer diffuse to the surface. Thus the data between 4–6 keV can be taken as coming purely from the layer under study. The S parameter of the GaMnAs layer is clearly a function of the Mn content in the layer, and decreases with increasing concentration of Mn.

A better understanding of the situation can be obtained by looking at Fig. 2, where the S and W parameters measured from all the LT-MBE GaMnAs layers and the reference sample are presented in the (W, S) plane. The measured points fall on a straight line, indicating that only one type of defect is detected. The line goes through the reference point, i.e. the bulk values of S and W. Since the slope of the line is characteristic of the defect, it also goes through the S and W parameters specific to the defect in question. Previous studies on GaAs [4, 7] give for the specific ($W_{V_{Ga}}$, $S_{V_{Ga}}$) parameters of the Ga monovacancy (0.73(1), 1.021(3)). This value fits very nicely on the extension of the line in Fig. 2, and it can thus be concluded that the defect present in the GaMnAs layers is the Ga monovacancy V_{Ga}.

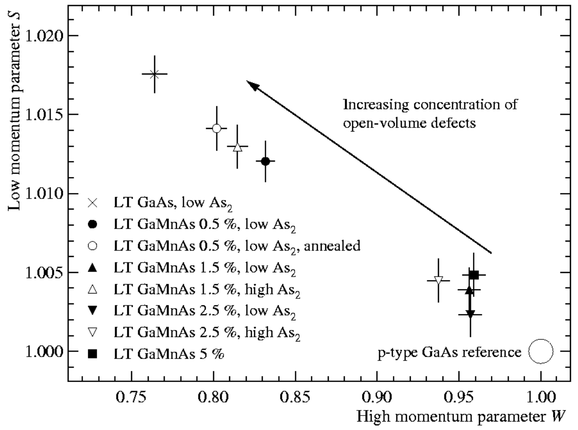

Fig. 2. The $S(W)$ plot showing the dependence of the vacancy concentration on the Mn content in the GaAs layers.

The identification of the observed defect as a Ga vacancy is supported by the fact that the amount of vacancies decreases with increasing Mn content. This is expected for a cation vacancy, since its formation energy increases as the material becomes more and more p-type. The increase in the As_2 partial pressure during growth increases the amount of defects in the layers, which also supports the identification. The richer the As conditions, the more Ga vacancies are formed. The thermal annealing at 270°C also seems to increase the Ga vacancy concentration.

The Ga vacancy concentrations in the GaMnAs layers can be calculated from the positions of the (W, S) points on the line between the bulk and Ga vacancy parameter values [10]. The concentrations vary from $\approx 10^{18}$ cm^{-3} in the LT-MBE GaAs layer and $\approx 10^{17}$ cm^{-3} in the low Mn content (0.5%) layers to $\approx 10^{16}$ cm^{-3} in the high Mn content (1.5% and up) layers. The negative Mn ions can act as shallow traps for positrons also at room temperature, which results in less annihilations in the vacancies. Thus, with the present measurement data, the concentrations stated above should be viewed as lower limits.

4. Conclusions

We performed positron annihilation experiments to study native defects in LT-MBE GaAs and $Ga_{1-x}Mn_xAs$ where the Mn content and the stoichiometry were varied during growth. Ga vacancies were identified in all samples. The concentration of Ga vacancies was shown to decrease with increasing Mn content. This behavior is different from Be-doped LT-MBE GaAs, where the Ga vacancy concentration was observed to be independent of the Be concentration [9], though smaller than in undoped LT-MBE GaAs. Thus it can be concluded that Mn has a significant influence on the incorporation of point defects in LT-MBE GaAs layers.

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