The source of room temperature ferromagnetism in granular GaMnAs layers with zinc blende clusters

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Granular GaAs∶(Mn,Ga)As films were prepared by annealing the $Ga_{0.985}Mn_{0.015}As$/GaAs layers at 500 °C or 600 °C. It is commonly accepted that this processing should result in the formation of cubic or hexagonal MnAs clusters, respectively. We demonstrate that such a priori assumption is not justified. If in the as grown sample there are not many defects with the interstitial Mn atoms, only small cubic clusters can be formed even after annealing at 600 °C. Moreover, in a sample containing solely cubic GaMnAs clusters, the Mn ions are ferro-magnetically coupled at room temperature. This fact was explained by the existence of GaMnAs solid solution in the clusters, with content of Mn close to 20% (higher than ever found in the layers) as was confirmed by experiment and theory. Extended X-ray absorption spectroscopy studies excluded the possibility of formation of the hypothetic zinc blende MnAs clusters. Not more than one Mn atom was detected in the second shell around central Mn atom.

1 Introduction The interest in granular materials composed of semiconductor matrix with nanoinclusions of magnetic materials is rapidly growing due to the demonstration of their usefulness in the construction of prototype electronic devices [1]. Large scale applicability of ferromagnetic semiconductors is limited by the Curie temperature, which for GaMnAs layer is below 200 K. In this material the ferromagnetic precipitates are easily produced, yielding multi-phase granular materials as an effect of high temperature annealing at 400–700 °C of the GaMnAs layers [2, 3] or the Mn-implanted GaAs crystals [4]. It is now commonly accepted that annealing the low temperature grown epilayer at the temperature around 500 °C produces small cubic clusters of zinc-blende type (ZB) but annealing starting from 600 °C and higher, results in formation of larger NiAs-type MnAs nanoclusters [2, 3]. Therefore, in many studies, without checking this experimentally, it is a priori assumed that appropriate inclusions have been formed [5]. In this Letter we report the results of studies on the formation of nanoclusters in GaAs/GaMnAs layers in commonly accepted post-annealing conditions and correlate their structure with the ferromagnetism which exists up to room temperature. We also prove that depending on the quality of the as grown layer merely small cubic (Ga,Mn)As clusters can be formed even after annealing at 600 °C.

2 Results and discussion $Ga_{0.985}Mn_{0.015}As$ layer was grown by molecular beam epitaxy (MBE) on the (001)-oriented GaAs substrate at the temperature of 230 °C. The nominal thickness of the layer was 0.8 μm. After deposition, the sample was cut into three pieces: one of them was left untreated, the remaining pieces were reintroduced into the MBE growth chamber and an-

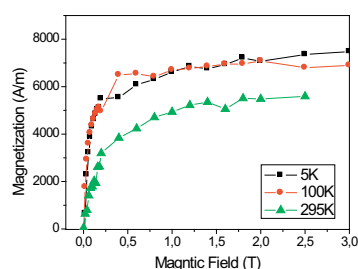**Figure 1** (online colour at: www.pss-rapid.com) Magnetization of $Ga_{0.985}Mn_{0.015}As$ annealed at 600 °C as a function of magnetic field measured at 5 K, 100 K and 295 K.

Figure 3 (online colour at: www.pss-rapid.com) Histograms of $Ga_{0.985}Mn_{0.015}As$ sample annealed at 500 °C (left) and 600 °C (right).

nealed under As_2 flux for 30 min at $T = 500$ °C and at $T = 600$ °C.

Magnetization measurements were performed using superconducting quantum interference device (SQUID) magnetometer as a function of temperature (5–325 K) at constant magnetic fields and at chosen temperatures in the magnetic field from 0 T to 3.0 T. Magnetic field was applied in-plane of the sample surface. Magnetization data were corrected for the diamagnetic contribution of the GaAs substrate. For annealed samples the magnetization was observed at all temperatures and also at room temperature. The results obtained for the sample annealed at 600 °C are presented in Fig. 1. One can notice that from 5 K to 100 K the magnetization did not change reaching the saturation at about 1 T. To find the source of the observed room temperature ferromagnetism in the samples a detailed characterization of the sample structure was performed.

Transmission electron microscopy (TEM) studies were performed using a JEOL 2000EX instrument operating at 200 kV accelerating voltage. To get information about the size distribution of clusters the histograms of nanoclusters were acquired from the high-resolution images obtained in $\langle 011 \rangle$ projection. It was found that small clusters with cubic ZB structure and sizes less than 10 nm are present in both samples. In Fig. 2 the example of a TEM image for the sample annealed at 600 °C is presented together with the related diffraction pattern.

Histograms of the size distribution of clusters are presented in Fig. 3. One can notice that thermal processing at higher temperature does not produce clusters with dimension larger than 7 nm.
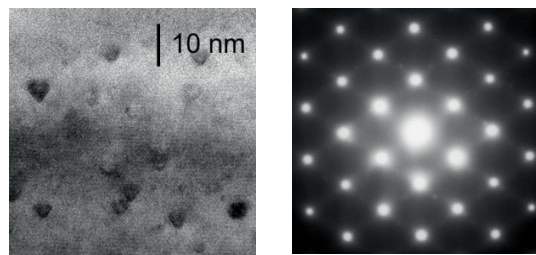
To examine the local atomic order around Mn atoms and to confirm the formation of MnAs ZB clusters only, the X-ray absorption spectroscopy (XAS) was applied.

XAS measurements were performed at liquid nitrogen temperature, at the A1 experimental station in DESY-Hasylab using a double crystal Si(111) monochromator. The Mn K-edge spectra were registered using a seven-element fluorescence Si detector. The XAS spectra were analyzed using the IFEFFIT package [7]. The data were analyzed from $k_{min} = 1.9$ Å^{-1} to $k_{max} = 12.5$ Å^{-1}. The fitting was performed in R space. The data were weighted by k^3 to enhance the oscillations for high k.

As a starting model of ZB clusters it was assumed that the distance of the first coordination sphere is equal to 2.55 Å [6]. This value was then refined in the fitting procedure. According to the atomic order in hypothetical ZB MnAs, widely discussed in the literature, Mn atoms should have 4 As atoms in the first shell and in the next shells 12 Mn and 12 As atoms. Surprisingly, for none of the investigated samples 12 Mn atoms can be found in the second coordination sphere. Only Ga atoms in the second sphere provided physical parameters of the fit. The amplitude and phase of scattering photoelectrons remarkably differ for Mn and Ga atoms and can be easily distinguished during the EXAFS analysis. Moreover, in the MnAs of the NiAs-type 6 As atoms are present in the first shell followed by 2 Mn and 6 Mn atoms, therefore the existence of such clusters would will be easily discovered in EXAFS analysis.

Concluding, we can rule out the existence of hypothetic pure MnAs nanoclusters in the investigated samples.

Figure 2 Cross-sectional bright-field TEM image (left) and electron diffraction pattern (right) of granular layer obtained after annealing at 600 °C.
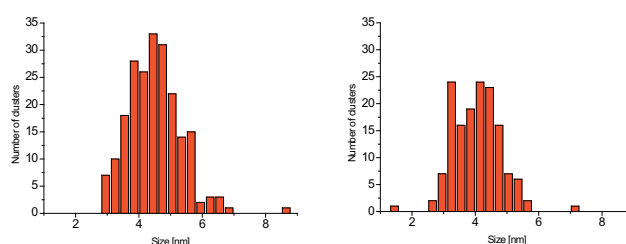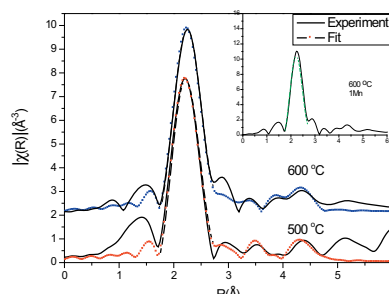

Figure 4 (online colour at: www.pss-rapid.com) $Ga_{0.985}Mn_{0.015}As$ annealed at 500 °C and 600 °C. Model of (Mn,Ga)As ZB inclusions with 12 Ga in second shell. Inset: Model with 1 Mn and 11 Ga in second shell. Fourier Transform of the EXAFS (full line) and the result of fitting (squares).

Table 1 Numerical values of EXAFS fitting procedure. σ^2 denotes disorder factor, R the distance of shells in Å.

sample	4 As: R_{As}, σ^2	12 Ga: R_{Ga}, σ^2	12 As: R_{As}, σ^2
500 °C	2.557(2), 0.0055(6)	4.06(4), 0.025(6)	4.73(3), 0.018(4)
600 °C	2.577(4), 0.0049(2)	4.23(4), 0.025(7)	4.68(2), 0.017(3)

To the authors' knowledge the existence of cubic inclusions with 12 Mn in the second shell was reported in none of the published EXAFS results (see [8] and references therein). The results of EXAFS analysis for samples annealed at 500 °C and 600 °C are presented in Fig. 4 and numerical results in Table 1.

One can notice the increase of the subsequent shells distance from Mn atoms in the sample annealed at 600 °C. The considerable disorder in the Ga shell indicates that Mn atoms can be present in this shell. The best fit achieved under assumption of one Mn atom located in the second shell is presented in the inset of Fig. 4 for the sample annealed at 600 °C. Such model is within the accuracy of EXAFS method providing slightly worse agreement with the experimental data and a quite large error in the parameters of the appropriate scattering path. This scattering path is located at the distance 4.43(16) Å with disorder factor $\sigma^2 = 0.007(6)$. The presence of 1 Mn atom in a second shell gives in a 6 nm cluster the concentration of Mn close to 20%. The characteristic feature of the investigated sample was that in the as grown layer 90% of Mn atoms occupied the substitutional position as was reported in Ref. [9] from a study performed for the same sample. It implies that the substitutional position of Mn atoms is stable and for producing hexagonal MnAs inclusions in such a layer an annealing temperature higher than 600 °C is necessary.

In Fig. 5, the Curie temperatures as a function of Mn concentration in ZB GaMnAs solid solution were calculated by using the hybrid method [10]. Effective exchange interactions between Mn atoms were estimated from first-principles and Curie temperatures were calculated by performing Monte Carlo simulations.

The LDA + U method was employed to describe the electronic structure of GaMnAs correctly [10]. The agreement between the theoretical predictions and available ex-
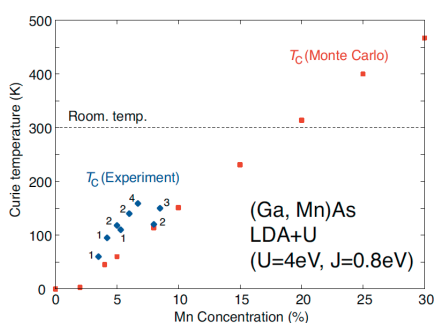
perimental Curie temperatures is good, knowing that the experimental determination of Mn content is difficult. One can notice that the content of Mn close to 20% is sufficient to increase the Curie temperature to 300 K. Observation of ferromagnetic-like behavior at temperatures as high as 295 K suggests that at least some clusters must contain about 20% of Mn. There are probably also clusters with lower Mn content, which are paramagnetic at 295 K, but are ferromagnetic at lower temperatures (e.g. clusters with 6−7% of Mn are ferromagnetic below about 150 K, see Fig. 5). These clusters may be responsible for increase of the saturation value of magnetization at low temperatures, where all clusters (both with low and high Mn content) contribute to saturated magnetization. We estimated that about 80% of Mn ions enter highly concentrated (~20% Mn) clusters.

Concluding, the presently reported studies revealed that the source of room temperature ferromagnetism in granular layers with cubic (Mn,Ga)As clusters embedded in GaAs matrix are small (from 3 nm to 6 nm) ZB inclusions. These inclusions are composed not of ZB MnAs but of GaMnAs solid solution with content of Mn much higher than reported in the literature for layers so far.

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Figure 5 (online colour at: www.pss-rapid.com) Dependence of Curie temperature on the content of Mn in GaMnAs solid solution as result from calculation (squares). Available experimental values [11] are plotted by diamonds.