Thermally activated decomposition of (Ga,Mn)As thin layer at medium temperature post growth annealing

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Abstract. The redistribution of Mn atoms in Ga$_{1-x}$Mn$_x$As layer during medium-temperature annealing, 250-450 °C, by Mn K-edge X-ray absorption fine structure (XAFS) recorded at ALBA facility, was studied. For this purpose Ga$_{1-x}$Mn$_x$As thin layer with x=0.01 was grown on AlAs buffer layer deposited on GaAs(100) substrate by molecular beam epitaxy (MBE) followed by annealing. The examined layer was detached from the substrate using a “lift-off” procedure in order to eliminate elastic scattering in XAFS spectra. Fourier transform analysis of experimentally obtained EXAFS spectra allowed to propose a model which describes a redistribution/diffusion of Mn atoms in the host matrix. Theoretical XANES spectra, simulated using multiple scattering formalism (FEFF code) with the support of density functional theory (WIEN2k code), qualitatively describe the features observed in the experimental fine structure.

1. Introduction

A potential simultaneous use of the ferromagnetic and semiconductors properties in spintronics has attracted a great interest to diluted magnetic semiconductors (DMS) with the most studied material being (Ga,Mn)As. With the optimized MBE growth and post growth annealing procedures nowadays (Ga,Mn)As layers have achieved the Curie temperature, $T_C$, as high as about 200 K. This is remarkably high as for DMS, but still too low in view of potential application in spintronics devices. From physics point of view, an indirect coupling between localized spins mediated by charge carriers is of paramount importance for the possibility of magnetic ordering in DMS [1]. However, the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction mechanism, which is used to describe the properties of DMS systems, has limitations predicting an increase of $T_C$ with increasing concentration of Mn impurities, the situation which is not always experimentally observed. Further studies not only on the influence of microstructure and its inhomogeneities upon material’s properties but also on transformation processes (including formation and migration of point defects) which occur in (Ga,Mn)As during growth and post growth annealing should lead to an improved understanding of the microstructure evolution and could potentially lead to a further progress in reaching larger $T_C$ in (Ga,Mn)As.

The paper aims to check the effectiveness of x-ray absorption fine structure (XAFS) as a probe of thermally activated decomposition of DMS, namely, (Ga,Mn)As after medium temperature post growth annealing.
2. Sample Preparation and Experimental Details
The Ga$_{1-x}$Mn$_x$As layer was grown in a SVT Associates MBE system [2] on GaAs (100) substrate. The test measurements of the energy dependence of the X-ray absorption coefficient of Mn atoms embedded in a single GaAs crystal matrix on bulk GaAs substrate were disturbed by elastic scattering from the substrate. To overcome this problem, a possibility of a physical separation of the studied layers from the substrate was investigated. For this purpose, thin AlAs buffer layer was deposited on GaAs substrate prior to the Ga$_{1-x}$Mn$_x$As growth. Finally, about 1000 Å amorphous As capping layer was deposited on Ga$_{1-x}$Mn$_x$As. After removing from the MBE setup, the film was cleaved into four pieces: one piece was left intact to serve as a reference sample (referred further as “as-grown”) and the other three were annealed at temperatures 250 °C, 350 °C and 450 °C. The annealing temperature was calibrated by the temperature of desorption of As capping layer and by the thermocouple placed at the vicinity of the MBE substrate holder.

The content of Mn in the Ga$_{1-x}$Mn$_x$As layer was estimated to be at the level of 1 at. % by Energy-dispersive X-ray spectroscopy (EDX) using Auriga 40 FIB-SEM workstation. High resolution diffraction (HR-XRD) studies were performed using a Philips X’Pert-MRD diffractometer equipped with a parabolic x-ray mirror, a four-bounce Ga 220 monochromator at the incident beam, and a three-bounce Ge analyzer at the diffracted beam. After conventional initial analysis, all samples were subjected to the separation of the Ga$_{1-x}$Mn$_x$As layer from the GaAs substrate by chemical etching, a so-called “lift-off” procedure [3]. Its schematic representation is shown in Figure 1. The local atomic and electronic structure around Mn atoms was studied by XAFS spectroscopy with the spectra collected at the BL22 CLÆSS beamline at ALBA light source [4] at room temperature.

Figure 1. Schematic representation of the steps during the “lift-off” procedure.

3. Results and Discussion
Figure 2(a) shows the ω/2θ scans obtained for the symmetric (004) reflection for all samples. The “as-grown” and 250 °C annealed samples revealed high crystalline perfection of the Ga$_{1-x}$Mn$_x$As layer. A satellite peak close to the dominant GaAs (004) peak is present in the XRD data for both samples. These satellite peaks are centered at lower angle with respect to the GaAs (004) with slight moving to lower angles when the annealing temperature is increased to 250 °C. A substantial change in the satellite peak position occurs when the annealing temperature is increased to 350 °C (generally, peak is not visible), where, according to literature data, the remanent magnetization and Curie temperature are appreciably lower than in the “as-grown” sample. After annealing at 450 °C, the satellite peak is dramatically shifted towards the GaAs (004) peak (revealed as a shoulder) accompanied, according to literature reports, by the total disappearance of remanent magnetization. Consequently, the lattice constant of the investigated layer decreases with the increasing annealing temperature reaching, or even exceeding, the lattice constant of the GaAs substrate. This decrease in itself is an indicator that some sort of reorganization occurs, possibly a formation of other Mn-containing phases, e.g., a precursor phase for Mn-rich (Ga,Mn)As clusters.

In order to determine the local atomic and electronic structure around Mn atoms the XAFS spectra at the K-edge of Mn were collected at room temperature on samples detached from the substrate (success in elimination of the elastic scattering is shown in Figure 2(b)). Figure 3(a) presents normalized XANES spectra around Mn K edge, whereas, an inset shows modulus of Fourier transforms, |FT(R)|, of the EXAFS function for all samples.
The analysis of XANES spectrum of the “as-grown” sample indicates that Mn atoms most likely substitute Ga in the GaAs matrix, which is also supported by our own \textit{ab initio} simulation results. The behavior of "as grown" sample is consistent with a small amount of structural disorder of the cubic structure of GaAs. An increase of annealing temperature to 350 \degree C leads to the slow broadening and suppression of main feature around 6549 eV along with increase of electronic states around 6544 eV of the absorption profiles (see Figure 3 (a)). With an increase of annealing temperature to 450 \degree C, the XANES spectrum is transformed into a featureless profile. This behavior is consistent with the loss of long-range periodicity of Mn atoms into investigated layer what is supported by HR-XRD observations.

Analysis of the modulus of Fourier transforms, \(|\text{FT}(R)|\), of the EXAFS function show a dramatic decrease of the \(|\text{FT}(R)|\) amplitude with increase of the annealing temperature: decrease by a factor of two is observed (see inset of Figure 3 (a)). Generally, such decrease can be modeled either via (i) an increase of the Debye-Waller factor (which corresponds to high structural disorder around Mn atoms) and/or (ii) a decrease of neighboring atoms number around Mn (which is a result of structural
transformation caused by Mn atoms migration in GaAs matrix before formation of Mn-rich inclusions in GaAs matrix). The latter can take place only when As/Ga vacancies are considered as well.

If the second possibility is considered, the following working hypothesis can be proposed: starting from the randomly distributed substitutional Mn (referred as monomers) and point defects like As/Ga vacancies formation of non-regular distributed areas of “N-mers” (dimer, trimer and so on combined through As) could occur. Theoretical support of this working hypothesis comes from our own *ab initio* calculations performed by WIEN2k code. In order to determine the possibility to form a specific type of point defect including, for instance, As vacancy, substitutional Mn, and their combination, their formation energies were calculated by introducing these defects within the structure and by relaxing the entire structure to minimize the forces on the atoms. The defect formation energy is then calculated as the difference between the total energy of the non-defected structure and the relaxed defected structure at constant volume. It was found that despite the fact that creation of As vacancy itself is unfavorable to the system, the lowest energy formation is developed when one (or more) substitutional Mn and one (or more) As vacancy are placed close to each other. Theoretical study by Raebiger *et al.* [5] also confirms the preference of Mn atoms to form “N-mers” (As vacancy/ies were not considered in this case, however). In addition to that, the quantitative analysis of the XANES spectra of annealed samples by FEFF 8 code (where models were formed based on results of EXAFS fitting, combined with structure optimization performed by WIEN2k) shows that the signal is a combination of signals coming from both Mn monomers and “N-mers” (see Figure 3(b)).

The proposed working hypothesis is further supported, though indirectly, if one considers annealing at high enough temperatures (up to about 600 °C): such annealing eventually leads to formation of the separated secondary phases consisting of Mn-rich phase and voids [6]. Annealing at much higher temperatures (above 650 °C) or for longer times will eventually lead to formation of separated hexagonal MnAs clusters [7].

4. Conclusions
The redistribution of substitutional Mn in Ga$_{1-x}$Mn$_x$As thin layer with $x=0.01$ during medium-temperature annealing, 250-450 °C, was studied using XAFS measurements at Mn K-edge. Analysis of experimental spectra allowed to propose a theoretical model where substitutional Mn and point defects like As/Ga vacancies form non-regular distributed areas of “N-mers”. Theoretical XANES spectra, simulated using multiple scattering formalism (FEFF code) with the support of density functional theory (WIEN2k code), qualitatively describe the features observed in the experimental spectra. To test the proposed model positron annihilation measurements are planned as this technique directly probes vacancies in sample and may identify a presence, type and amount of vacancies.

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