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Process of thermally activated decomposition of diluted magnetic semiconductors (DMS), namely $Ga_{1-x}Mn_xAs$, remains an important problem to be addressed in order to facilitate development of a DMS with room temperature ferromagnetism. X-ray absorption fine structure (XAFS) spectroscopy was combined with classical molecular dynamics (MD) simulations in order to study $Ga_{1-x}Mn_xAs$ (with x = 2.43 %) after medium temperature post growth annealing (250 – 450°C). To determine the changes of local atomic structure around Mn atoms XAFS spectra at Mn K-edge were gathered at about 90 K at BL22 beamline, ALBA synchrotron facility (Spain). With the aim to avoid unwanted artifacts on the absorption spectra (such as diffraction peaks from the substrate), the growth method was proposed and used to include an auxiliary layer that was later chemical etched to detach investigated layers from the substrate.

The annealed samples were separated into two groups based on modification of their X-ray absorption near edge structure (XANES) spectra profiles and dramatic decrease of the modulus of Fourier transforms amplitude, |FT(R)|, with annealing temperature increase. The first group was interpreted so that the Mn atoms are most likely to replace Ga in the GaAs matrix. Negligible amplitude reduction |FT(R)| of the sample annealed at 250°C may indicate interstitial manganese diffusion, Mn_I, in the GaAs matrix. The second group was associated with the beginning of formation of tiny Mn-rich inclusions in GaAs matrix. Considering this, various models with vacancies (Ga and/or As), Mn atoms in interstitial position with tetrahedral coordination and substitutional position (separately and in their various complexes) were studied using MD simulations to produce theoretical Extended X-ray Absorption Fine Structure (EXAFS) signals that were then directly compared to the experimental ones.

As expected, the complexity of the models used to describe effects caused by annealing rise with temperature increase. In case of the samples annealed higher than 300°C, the models do not represent anymore a diluted $Ga_{1-x}Mn_xAs$. Analysis of found in literature theoretical models that contain various complexes of Mn atoms allowed developing of a description of the local structure around Mn atoms in the samples annealed higher than 300°C. Thus, for such samples, the models that contain small Mn-rich clusters were confirmed. Moreover, it was identified that interstitial Mn with hexagonal coordination (Mn_{hex}) play crucial role in modification of the local structure around Mn atoms in the samples annealed at 300 - 450°C.

Besides XAFS spectroscopy, number of additional investigation techniques were used to characterize the studied samples. In the context of this work, all of them can be divided into supportive techniques (X-ray Diffraction (XRD), Energy Dispersive spectroscopy (EDX), Second Ion Mass spectroscopy (SIMS): those served to obtain additional information used for further calculations, such as Mn concentration, lattice constant, etc.) and verification techniques (Rutherford backscattering spectrometry (RBS) \ Particle Induced X-ray Emission/channeling spectroscopy (PIXE/c): that were used for verification/confirmation of the obtained MD-EXAFS results, namely, the type of Mn-contained complexes in GaAs).

Validation of the theoretical results by comparing them to the experiment allowed us to derive previously unknown details of local structure around Mn in GaAs matrix after annealing for the temperatures up to 450°C. This study demonstrates that MD simulations can accurately depict complex experimental systems in which one has control over high-level disorder, and shows the advantages of using a combined experimental/theoretical approach over standard EXAFS fitting methodologies.

The proposed models are in a good agreement with magnetic behavior of the samples, measured by Superconducting quantum interference device (SQUID) technique. The samples from the first group, for which manganese is inherent mainly in a substitute position, are ferromagnetic at low temperatures and paramagnetic at room temperature. On the contrary, the sample annealed at 450°C shows the presence of superparamagnetic phase at room temperature, which is indicative of the formation of tiny Mn-rich clusters.

The MD-EXAFS algorithm was researched, and the software code was developed for automation of routine procedures, data workflow control and final fitting/mixing procedure were developed using Python 3.5 programming language.

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