Mn Occupations in $Ga_{1-x}Mn_xN$ Dilute Magnetic Semiconductors Probed by X-Ray Absorption Near-Edge Structure Spectroscopy

Shiqiang Wei,[1]* Wensheng Yan, [1] Zhihu Sun, [1] Qinghua Liu,[1] Wenjie Zhong,[1] Xinyi Zhang,[2] H. Oyanagi,[3] and Ziyu Wu[4]

[1]*National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China*
[2]*Department of Physics, Surface Physics Laboratory (National Key Laboratory), and Synchrotron Radiation Research Center, Fudan University, 220 Handan Road, Shanghai 200433*
[3]*Photonics Research Institute, National Institute of Advanced Industrial Science and Technology 1-1-1 Umezono Tsukuba, Ibaraki 305-8568, Japan*
[4]*Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China*

Abstract. X-ray absorption near-edge structure (XANES) is used to study the characteristics of different sites of Mn in the $Ga_{1-x}Mn_xN$ dilute magnetic semiconductor (DMS) with zinc-blende structure. The XANES spectra of representative Mn occupation sites (substitutional Mn_{Ga}, interstitial Mn_I, Mn_{Ga}-Mn_I dimer and Mn cluster) in GaN lattice are theoretically calculated and compared with experimental results. The substitutional Mn in GaN is characterized by a pre-edge peak at 2.0 eV and a post-edge multiple-scattering peak at 29.1 eV. The peaks shift in position and drop in intensity dramatically for the interstitial Mn_I and MnGa-Mn_I dimmer, and disappear completely for Mn clusters. We propose that the distinct characteristics of Mn K-edge XANES spectra for different Mn sites favor to discriminate Mn occupations in GaMnN DMS.

Keywords: XANES, dilute magnetic semiconductor, local and electronic structures
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INTRODUCTION

Since the discovery of (Ga, Mn)As dilute magnetic semiconductor (DMS) and the achievement on the coherence of optically injected spin-polarized carriers over nanosecond time scales [1], a comprehensive research interest has been devoted to experimental and theoretical studies on III-V DMSs recently. This is attributed to that the DMS spintronic devices combining the properties of electron's charge with spin make it capable of realizing the nonvolatility, the low electric power consumption, and the increased integration densities in future technological applications, compared with conventional semiconductor devices [2].

In device applications, the ideal ferromagnetic semiconductors would have Curie temperatures above room temperature and would be easy to dope with p-type and n-type impurities. A number of studies from the first principle calculations have suggested that the substitutional (Ga,Mn)N DMS with a Mn concentration lower than 5 at% is favored to form a ferromagnetic (Ga, Mn)N phase [3]. Recently, Chitta et al, Jeon et al and Thaler et al have reported p-type and n-type ferromagnetic (Ga,Mn)N DMS thin films with TC about 350 K. Practically, it is expected that ferromagnetism indeed arises from the Mn ions properly incorporated into the host semiconductors in spintronic devices, but it is quite possible that the ferromagnetism of the (Ga, Mn)N DMSs may come from the energetically favorable Mn compounds and/or clusters [4]. However, conventional characterization techniques are difficult to detect the small amount of Mn-Mn clusters or Mn precipitates in the III-V DMSs [5]. Therefore, to understand magnetic natures of DMS, it is essential to determine the structural information about the locations of the doping Mn impurities.

In this paper, XANES with the advantage of distinguishing the local coordination geometry and the electronic structure surrounding a kind of special atoms in condensed matter was performed to investigate local and electronic structures of zinc-blende p-type $Ga_{1-x}Mn_xN$ DMSs. The representative

structural models as shown in Figure 2 were used to calculate XANES spectra of $Ga_{1-x}Mn_xN$ DMS. Our purpose is to reveal electronic structural features of Mn K-edge XANES spectra for the substitutional Mn, the interstitial Mn, the Mn-Mn dimer and the Mn4 cluster in the $Ga_{1-x}Mn_xN$ DMSs.

EXPERIMENT

$Ga_{1-x}Mn_xN$ DMSs with a thickness of 300 nm and Mn content ranging from 1.0 to 10 at.%, were grown on semi-insulating GaAs(001) substrates at 680 °C using plasma-assisted molecular beam epitaxy. Hall-effect measurements unambiguously showed that the as-prepared $Ga_{1-x}Mn_xN$ samples have strong p-type conductivity with the hole density of about 10^{18} cm^{-3}. X-ray diffraction (XRD) studies demonstrated that the Mn-doped GaN thin films have cubic zin-blende structure [6]. The Mn K-edge XANES spectra of $Ga_{1-x}Mn_xN$ thin films and Ga K-edge XANES spectrum of crystalline GaN thin film were measured at the beamline 13B1 of Photon Factory (PF) of National High Energy Institute of Japan and the U7C beamline of National Synchrotron Radiation Laboratory (NSRL) of China. The electron beam energy of PF is 2.5 GeV and the maximum stored current was about 450 mA. The storage ring of NSRL was operated at 0.8 GeV with a maximum current of 300 mA. The monochromator is Si(111) plane double crystals.

RESULTS AND DISCUSSION

Figure 1(a) shows Mn K-edge XANES spectra of zinc-blende structural $Ga_{1-x}Mn_xN$ thin films and Ga K-edge XANES spectrum of crystalline GaN. It can be observed that there are three strong peaks of A (16.8 eV), B (30.3 eV), and C (64 eV) in the post-edge region of Mn K-edge for the $Ga_{0.99}Mn_{0.01}N$. The XANES spectrum of crystalline GaN also presents three strong peaks located at the similar positions as those of $Ga_{0.99}Mn_{0.01}N$. Moreover, a strong peak A1 (2.0 eV) in the edge region appears for $Ga_{0.99}Mn_{0.01}N$, but it is absent for GaN. These features will further be shown in Figure 1(b) from XANES calculation, and the peaks A1 and B are the main feature for the Mn atoms located in the substitutional sites of $Ga_{1-x}Mn_xN$ DMS. Increasing the Mn concentration of $Ga_{1-x}Mn_xN$ to 0.025, peak A1 is reduced in intensity and peak B is split into two small peaks B1 (29.1 eV) and B2 (36.3 eV). This implies that Mn atoms occupy some new sites with the increase of Mn doping concentration. At the higher Mn content of 0.10, no A1 and B peaks appear in the XANES spectrum of $Ga_{1-x}Mn_xN$.

In order to investigate the XANES spectra of zinc-blende structural $Ga_{1-x}Mn_xN$ DMS, we have attempted to model four representative $Ga_{1-x}Mn_xN$ clusters for the XANES calculations: the substitutional Mn_{Ga} for the Ga site in GaN, the tetrahedral interstitial Mn_I surrounded by four Ga atoms, the Mn_{Ga}-Mn_I dimer and the Mn_4 cluster precipitated in GaN lattice. The initial structural parameters of the $Ga_{1-x}Mn_xN$ cluster with 123 atoms based on the crystalline zinc-blende GaN and optimization of total energy are used to calculate the theoretical Mn K-edge XANES spectra of $Ga_{1-x}Mn_xN$ [7]. The XANES calculations were carried out using a self-consistent, fully relaxed core-hole potential. The Hedin-Lundqvist model of exchange potential with a 0.8 eV shift and additional broadening of 1.2 eV is used.

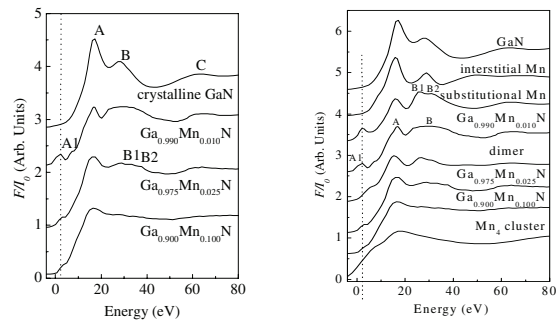

FIGURE 1. (a) The Mn *K*-edge XANES spectra of $Ga_{1-x}Mn_xN$ thin films and Ga K-edge XANES spectrum of crystalline GaN. **(b)** Comparison of the Mn K-edge XANES spectra from theoretical calculations for the models shown in Figure 2 and the experimental XANES spectra for $Ga_{1-x}Mn_xN$ with various Mn concentration *x*.

Figure 1(b) displays the Mn K-edge XANES spectra for the models as shown in Figure 2. It is evident that the XANES features for the Mn atoms locating at the substitutional (model 1) and interstitial (model 2) sites are quite different. For the substutional Mn in (Ga, Mn)N DMS, three peaks A1, A and B (B1 and B2) are obvious. Moreover, the peak B is the strongest in height. In contrast, for the interstitial Mn, the A1 peak in the pre-edge region disappears, instead a shoulder peak as indicated by an arrow appears, and the height of peak B is significantly lower than that of peak A. In the substitutional Mn sites, Mn atoms are coordinated by four N neighbors, while in the case of interstitial Mn the four nearest neighbors of Mn are Ga atoms. The difference between the substitutional and interstitial Mn sites in their nearest neighbors consequently produces the different multiple-scattering contributions that are attributed to the distinct features in their B peaks in the post-edge XANES spectra. The A1 pre-edge peak can be interpreted as the transition of Mn 1s core electron to hybridized orbital of Mn 3d and N 2p states. It can be observed that the calculated XANES spectrum of GaMnN with substitutional Mn almost reproduces the experimental spectrum of $Ga_{0.990}Mn_{0.010}N$. Hence, we can deduce that most of Mn atoms in $Ga_{0.990}Mn_{0.010}N$ with a low Mn dopant occupy the substitutional positions of the Ga sites in GaN. For the calculated XANES spectrum of the

Mn_{Ga}-Mn_I dimer (model 3), the peak A1 in the pre-edge region is absent and the peak B is obviously reduced in height. A pre-edge shoulder peak as indicated by an arrow can also be observed. Although the shape of the B peak for the XANES spectrum of $Ga_{0.975}Mn_{0.025}N$ looks slightly similar to the calculated XANES spectrum of GaMnN with substitutional Mn, the intensity of B peak in $Ga_{0.975}Mn_{0.025}N$ is close to the calculated XANES spectrum of MnGa-MnI dimer. This suggests that a substantial part of Mn atoms, besides the substitutional Mn, may exist in the form of MnGa-MnI dimer (or small cluster of MnGa compound) in the $Ga_{0.975}Mn_{0.025}N$. In fact, the Mn-Mn distance (1.93 Å) in Mn-Mn dimer is equal to the Mn-N bond length (1.93 Å) in the substitutional GaMnN. Both the Mn-Mn and Mn-N coordinations give rise to the nearest peaks at almost the same position in R-space. These two overlapped peaks make the EXAFS analysis not sensitive enough to exclude the existence of minority of Mn in the form of dimer. In contrast, the minority of Mn-Mn dimer in $Ga_{0.975}Mn_{0.025}N$ can be easily detected by XANES owing to its sensitivity to the electronic structure. For the XANES spectrum of Mn4 cluster embedded in the GaN matrix (model 4, the first neighbor distance of Mn-Mn coordination shell is 2.63 Å), only very broad peaks appear in the post-edge region. This feature looks like that of the heavily Mn-doped sample $Ga_{0.900}Mn_{0.100}N$, implying the prominent existence of Mn clusters in $Ga_{0.900}Mn_{0.100}N$. It is consistent with our previous work on the same sample by using EXAFS method [6].

From our calculations of the model structures, it is clear that the XANES spectra of GaMnN with different Mn sites in GaN lattice have distinct characteristics and can discriminate Mn forms in GaN. In fact, several authors have used XANES to identify the existing form and valence of Mn in GaMnN DMS. By comparing the position of the absorption edge of GaMnN with those of the reference compounds, the average valence state of Mn in GaMnN was determined [8]. However, discrepancy exists in interpreting the origin of the pre-edge peak, and accordingly, the valence of Mn. In Ref. 8, the pre-edge peak (6539 eV) in the Ga1-xMnxN XANES spectra was attributed to the existence of Mn clusters since this peak occurs close to that of metallic Mn K edge. In Ref. 9 a pre-edge double-peak structure (6539, 6542 eV) is observed in both experimental and theoretical spectra, which is ascribed to the co-existence of Mn ions with valencies of +2 and +3. Oxidation state mapping has also been performed by Martinez-Criado et al [10] to study in the micrometer scale the distribution and partitioning of Mn atoms in specific valence states. A homogeneous distribution of Mn^{2+} and Mn^{3+} was observed at low Mn concentrations, while a strong spatial-dependent metallic Mn cluster and Mn^{2+} distribution was detected at high Mn content. Our experimental XANES spectrum of $Ga_{0.990}Mn_{0.010}N$ coincides with those in Ref. 8; however, as our calculations have shown, the pre-edge peak A1 does not originate from the Mn clusters, but comes from the substitutional MnGa sites. Following Titov et al, [9] such a single-peak behavior in the pre-edge XANES indicates the +2 valency (d5 configuration) of Mn in the substitutional sites. This suggests that the doped Mn acts as an acceptor, in agreement with the p-type conductivity of the GaMnN.

CONCLUSION

The theoretical XANES spectra of representative structure models of Mn in GaN lattice, i.e., substitutional MnGa, the interstitial Mn_I, the MnGa-Mn_I dimer and Mn cluster, demonstrated that the Mn K-edge XANES spectra of different Mn sites have distinct characteristics and can be regarded as a discrimination of Mn occupations in GaN. The comparison between the experimental and the theoretical XANES spectra indicates that that majority of Mn atoms locate at Ga substitutional sites in $Ga_{1-x}Mn_xN$ with the lowest Mn content (0.010). Upon increasing the Mn content in to 0.025, a significant fraction of Mn dopants form dimers. At the highest Mn doping concentration (0.100), a secondary phase (Mn cluster) is precipitated.

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