Journal of Alloys and Compounds 725 (2017) 632–638

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Polarization-dependent XAFS and density functional theory investigations of the quality of the epitaxial GaMnN structure

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ARTICLE INFO

Article history:
Received 14 March 2017
Received in revised form
27 June 2017
Accepted 17 July 2017
Available online 20 July 2017

Keywords:
GaMnN
MBE
XAS
Ferromagnetic
Synchrotron radiation
Polarization

ABSTRACT

Ferromagnetic GaMnN in which manganese substitutes randomly gallium, can constitute a major technological advance, especially due to the already dominating role of group III nitrides in photonics and high power electronics. However, obtained till now results concerning the nature of magnetism of (Ga,Mn)N, can be often related to defects as the main factors determining the properties of the material. Non-polarization and polarization-dependent EXAFS analysis have been used in order to investigate the local structure of homogenous GaMnN. The analysis points on nitrogen defects such as vacancies (V_N) as well as on additional N atoms in the first coordination shell in the GaMnN structure. Moreover, the presence of oxygen atoms in bulk samples with 5 and 7% Mn was confirmed. Inclusions of metallic Mn and oxygen atoms on the $Ga_{0.9}Mn_{0.1}N$ surface were detected. The theoretical reconstruction of the XANES spectra using density functional theory (DFT) affirms the presence of the nitrogen defects.

1. Introduction

The discovery of ferromagnetism in semiconductor materials creates prospect for the emergence of new electronic technologies that use both the intrinsic spin of the electron and its associated magnetic moment. The new electronic components can be applied for the construction of quantum computers, sensors and memories. Promising materials for that purpose are II–VI compounds like CdTe, ZnTe, ZnO as well as III–V's (GaAs, InAs, GaN) semiconductor materials doped with transition metal Mn ions [1–3]. But only for two of these materials ferromagnetism above room temperature is predicted [2]. These are GaN and ZnO. In the latter case, significant p-doping has not been achieved yet. The record Curie temperature (T_C) observed for GaMnAs approached only 200 K while the high T_C (940 K) reported for GaMnN results from the coexistence of ferromagnetic and paramagnetic inclusions [4,5] and cannot be treated as a bulk material property.

Group-III nitrides are the material for short-wavelength optoelectronics including energy saving white light sources. Nitrides also become more and more important for high temperature and high voltage electronics [6]. The optical and physical properties of pure binary GaN materials are basically well known as well as their dependence on many different impurities and defect states. Various models describe the observed ferromagnetism in diluted magnetic III–V semiconductors (DMS). Some of them are based on a carrier-mediated exchange interaction, which enables the modification of magnetic behavior through charge manipulation [7–9].

A recent development of molecular beam epitaxy (MBE)-growth technique enables to fabricate high-quality GaMnN structures [10]. The samples investigated in this paper are part of a series which showed highly consistent magnetic properties over a wide range of Mn concentrations. Their magnetic properties are high in comparison to other GaMnN samples as well as in relation to other dilute magnetic semiconductor materials [10]. Its Curie temperatures also show a clear trend in relation to Mn concentration [11]. The structural properties were investigated by high-resolution x-ray diffraction. Rocking curves of the GaMnN layers show the same or even slightly lower peak width as the substrate they are fabricated on (to be publish). This observation indicates a similar or slightly lower number of threading dislocations in the GaMnN layer compared to the GaN template. The fabrication of low defects density GaN structures is still a challenge. Threading dislocation density can easily exceed $10^9 cm^{-2}$ on foreign substrates such as sapphire and device structures have not less than 10^6 cm^{-2}

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http://dx.doi.org/10.1016/j.jallcom.2017.07.174
0925-8388/© 2017 Published by Elsevier B.V.

extended defects even on the best ammono-thermally fabricated GaN substrates available with about 10^3 cm^{-2} [12,13].

Several defect types are present in the GaN structure, namely intrinsic defects such as nitrogen (V_N) or gallium (V_{Ga}) vacancies, self-interstitials, and antisite defects. Almost all as-grown GaN structures exhibit unintentional n-type conductivity previously thought as being a consequence of the formation of Ga vacancies. Now it is assumed that impurity atoms are responsible for that [14,15]. Mainly oxygen but also silicon are discussed widely as a sort of a growth contamination. There is strong evidence that nitrogen vacancies cannot be responsible for it due to their high formation energy under n-conductivity. On the other hand, nitrogen vacancies have a low formation energy in p-type GaN and therefore can act as compensating centers for acceptor doping [14,15]. The p-type doping in GaN with Mg is sufficient for light-emitting devices [16,17]. In the ferromagnetic GaMnN compound, Mn ions are a source of deep acceptors but they are not able to efficiently mediate the ferromagnetic ordering of Mn spins [2]. The observed increase of the Curie temperatures (T_C) with Mn concentration in magnetic GaMnN epitaxial layer was interpreted using the super-exchange model [9]. On the other hand, first-principle-based calculations indicate double-exchange as the dominant interaction in magnetic GaMnN [18]. A consistent and definitive knowledge about GaMnN compounds is missing despite a huge number of theoretical and experimental investigations. A comprehensive description of this system has not been developed yet. Various parameters influence the origin of ferromagnetism in diluted magnetic semiconductors. Several technical and physical questions have to be solved for a thorough DMS investigation. Relevant question may be whether defects are an impediment for obtaining ferromagnetism? Which defects may break the ferromagnetic order in the GaMnN system and why?

X-ray absorption spectroscopy (XAS) is a practical tool for structural characterization because it provides information about the atomic number, distance between atoms and structural disorder. The structural parameters information give also information about defects in the structure. GaMnN crystallizes in a wurtzite structure where two kinds of first-neighbor bonds can be distinguished, namely a single bond length along the c-axis and three bonds slightly inclined to the c-plane. The linear polarization of the synchrotron radiation (SR) allows a separation of crystallographic-direction-dependent contributions from various chemical bonds. The bond length and the number of the nearest-neighbor atoms contribute to the particular chemical bond, i.e. the distribution of electron density in the given direction. In grazing geometry, the electric field ($\vec{e}$) of the SR inclines in a small angle in respect with the c-axis (p_z direction) such that only the bond along the c-axis contributes to XAS spectra. Three planar equivalent bonds mainly contribute to the spectra in normal incidence of the primary beam (electric field ($\vec{e}$) of the SR is almost parallel to the c-axis (p_{xy} direction), electronic transition are excited in the c-plane).

Our previous analysis suggests the presence of N vacancies (V_N) [19]. In that study average polarizations, i.e. randomly oriented samples, have been discussed. By measuring the polarization-dependent x-ray absorption spectra, in particular, Extended X-ray Absorption Fine Structure (EXAFS), one can determine the orientation of the bond with respect to the electric field vector of the synchrotron radiation and the coordination number N along this direction, which depends on the X-ray incident angle θ:

$$N(\theta) = \sum_{j=1}^{N} 3cos^2\theta j, \qquad (1)$$

where N is the effective coordination number, and θ_j is the angle between the electric field vector ($\vec{e}$) of the synchrotron radiation and the bond direction (distance *r*) of the given element (absorber) and *j*-th scatter pair [20].

Moreover, the experimental X-ray Absorption Near Edge Structure (XANES) spectra can be the interpreted regarding the density of unoccupied states (conduction band) since photon absorption is associated with an optical transition between electronic states of the atom in the sample. These unusual features of XAS technique enable to study the local and electronic crystal structure and theirs anisotropy.

In the GaN structure a single (π) bond length is around 1% shorter than σ bonds and they are equal 1.94 and 1.95 Å, respectively [21]. In the presented paper, we will focus on the polarization-dependent x-ray absorption spectroscopy analysis and density functional theory (DFT) of the Mn K absorption edge in order to check whether the anisotropy of the formed bond length is preserved in the first coordination shell of the GaMnN structure; and also to investigate the local and electronic structure in the ferromagnetic epitaxial GaMnN layers for chosen sample orientation.

2. Experimental

XAS experiments were carried out at the beamline C, Synchrotron DESY in Hamburg, Germany. The SR beam was monochromated using a Si(111) monochromator. The K Mn (6539 eV) absorption spectra were acquired for all $Ga_{1-x}Mn_xN$, $x = 5, 7, 10\%$, samples at room temperature in fluorescence mode. The XAS data were collected for a $Ga_{1-x}Mn_xN$, $x = 10\%$, for two different sample orientations with respect to the vector of the electric field ($\vec{e}$) of the SR. Orientations were chosen close to the *x, y* plane (so called *c*-plane, normal incidence or p_{xy} direction) and along *z* growth direction (called: *c*-axis or grazing incidence or p_z direction).

The spectra for $Ga_{1-x}Mn_xN$ with $x = 5$ *and 7%*, respectively, were acquired only for a standard orientation of the sample, i.e. 45° between sample and vector of the electric field ($\vec{e}$) of the SR. The standard orientation gives an average information along all bond directions. In order to simplify the reading of the paper we introduce the following terminology: 1) the sample with 10% Mn concentration measured in i) grazing incidence (p_z direction)- will be called **1a**; ii) normal incidence (p_{xy} direction)- **1b**; sample with 7% Mn- **2**, sample with 5% of Mn- **3**.

The samples were prepared in an EPI 930 (VEECO) molecular beam epitaxy chamber equipped with a radio-frequency plasma source. Single-side polished, [0001]-oriented sapphire substrates with about 2 μm thick GaN layers were used as template layers; the GaN layers were deposited by metal-organic vapor-phase epitaxy. Prior to growth the samples were cleaned in an ultrasonic bath and degassed in the vacuum system at temperatures of up to 800 °C. Substrate temperatures in the range of 730 °C–760 °C were used for the layer deposition. The growth time was chosen to be 60 min, which results in samples thicknesses between 170 nm and 240 nm. Detailed sample growth conditions and quality have been published elsewhere [10].

The extraction of the EXAFS oscillations from raw data was preceded by subtracting the pre-edge background; ii) normalizing to the experimental edge step; iii) and subtracting a smooth atomic background from normalized absorption data using the Athena program [22]. Next, the EXAFS oscillations were analyzed using the Artemis program [22]. Ga atoms were substituted by Mn atoms in the GaN host matrix with lattice parameters of a = 3.180 Å and c = 5.166 Å, respectively, in order to compute the theoretical scattering amplitudes for Mn-N and Mn-Ga pairs in GaMnN structure. The theoretical scattering amplitudes for Mn—O and Mn—Mn pairs were obtained from the MnO compound (a = 3.37 Å, c = 5.38 Å) and metallic Mn (a = 6.32 Å), respectively. All scattering