Local Atomic and Electronic Structure of the Fe dopants in AlN:Fe Nanorods

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Abstract. Fe-doped AlN nanorods were studied by means of x-ray absorption spectroscopy above the Fe K- and L\textsubscript{2,3}- edges. Theoretical simulations of the x-ray absorption spectra show that Fe atoms mainly substitute Al. A minor fraction of Fe interstitials or Fe-Al-N ternary alloy can be identified as well. Bader’s AIM analysis predicts that neutral substitutional Fe Al defect is in 2\textsuperscript{+} charge state, though Al in pure AlN is in 3\textsuperscript{+} charge state. Fe L\textsubscript{2,3} absorption spectra and photoluminescence data indicate the coexistence of Fe\textsuperscript{2+}/Fe\textsuperscript{3+} in AlN:Fe nanorods so different charge states of substitutional Fe\textsubscript{Al} should co-exist.

1. Introduction
Nanostructured AlN doped with iron [1-4] attracts much interest due to its potential applications in spintronic devices, which offer unique opportunity to integrate conventional semiconductor and ferromagnetic technology. The main requirement for the materials in this area is the presence of ferromagnetic properties at room or higher temperatures. However, a full explanation of the magnetic properties of these materials has not been established yet. The first was a model of Zener [5]. It is based on the assumption that the magnetic atoms replace metal atoms in the crystal lattice of the semiconductor. However, in gallium arsenide, doped atoms often occupy interstitial position [6]. The formation of manganese clusters is shown in a number of papers [7]. Other authors, being based on the results of X-ray diffraction, observed a presence of the GaMn\textsubscript{3}N phase in GaN:Mn [8]. Other theories such as a model involving magnetic polarons [9] and some other approaches [10-12] have been developed to explain the magnetic properties of diluted magnetic semiconductors.
Nanostructured AlN is a wide band gap semiconductor. Controlling synthesis process of nanostructures from AlN it is possible to check demanded properties. However, understanding of the origin of the ferromagnetism in the Fe-doped AlN presents a challenge in the modern material sciences. There are several reports that Fe-doped AlN nanorods exhibited room temperature ferromagnetism with a saturated magnetic moment of 0.64\(\mu_B/Fe\) [13]. It notes that the magnetic moment of TM-doped AlN nanotubes reaches maximum for Fe-doped AlN nanotubes [14]. It is found that the Fe atoms substitute the Al atoms in the lattice when the iron concentration is smaller than 1.2%, while they are embedded into interstitial spaces of the lattice at larger Fe concentrations. A maximum of the saturation magnetization is found to be 2.81 emu/cm\(^3\) for 1.2% of Fe atoms in AlN:Fe film [15].

A careful analysis should be provided for the synthesized samples in order to rule out the presence of secondary phases that induce ferromagnetic properties [16]. This work is devoted to the study of the local atomic structure and charge state of Fe dopants in the AlN:Fe ferromagnetic nanorods. Both near edge and extended regions of x-ray absorption spectra above Fe K-edge are utilized. The multiplet structure of Fe L\(_{2,3}\) spectra is used as a fingerprint for the Fe charge state.

2. Methods

AlN:Fe nanorods were prepared in a horizontal tube furnace on Si (100) substrate in the presence of FeCl\(_3\) during reaction of heating as iron source [17]. The Fe L\(_{2,3}\) XANES spectra were recorded under UHV condition at the Russian-German beam line (RGBL) of BESSYII synchrotron in the total electron yield mode. The Fe K-edge spectrum was measured in the fluorescence mode at the Structural Materials Science beamline [18] of the Kurchatov Synchrotron Radiation Center with a Si avalanche photodiode as a fluorescence detector and an ionization chamber as an incident beam intensity monitor.

X-ray absorption spectra above the Fe K-edge were simulated using self-consistent real space multiple scattering approach, implemented in the Feff9.0 software [19]. Hedin-Lundquist exchange-correlation potential was used in the simulations. Relaxation of atomic positions for model defects in AlN was performed in the full-potential linear augmented plane-wave approximation (LAPW), implemented in the Wien2k program package [20]. The generalized gradient approximation in the scheme of Perdew–Burke–Ernzerhof (GGA-PBE) [21] was used for the treatment of exchange-correlation effects.

3. Results and discussion

The nanorods are 500 nm in length with a sharp tip 15-20 nm in diameter. The spontaneous saturated magnetization and the coercitivity of the AlN:Fe are about 0.64\(\mu_B/Fe\) and 116 Oe, respectively. Diffraction patterns show that AlN:Fe nanorod is a single wurtzite AlN crystal with the growth direction (0001) with no impurity phases within sensitivity of the method.

The figure 1 shows a magnitude of the Fourier transforms (FT) of \(k^3\chi(k)\) data, obtained from EXAFS part of spectra. From the data on the left panel it is clear that no iron clusters or bulk iron phase were created in AlN:Fe nanorods. The best fit of the FT data shown on the right panel was obtained with three contributions, which correspond to Fe-N, Fe-Al, Fe-Al bonds with distances equal to 1.93Å, 2.37Å, 3.01Å, correspondingly. The first and the third contributions can be attributed to the coordination spheres around substitution Fe\(_{Al}\) defects, while the second one probably corresponds to the octahedral interstitial position of Fe in AlN lattice.
Figure 1. Left panel shows the experimental Fourier transform of Fe K-edge EXAFS spectra for AlN:Fe nanorods and bulk Fe. Right panel shows a simulated and experimental FT with three contributions at different distances Fe-N, Fe-Al and Fe-Al.

Fe K-edge XANES region was used to further verify the structural models proposed by EXAFS. Left panel of the figure 2 shows the results of simulations for the substitutional \( \text{Fe}_\text{Al} \) defect and octahedral interstitial. The following AlN lattice parameters were used in the simulations: \( a=b=3.112 \), \( c=4.982 \), \( \alpha=\beta=90 \), \( \gamma=120 \), space group \( \text{P6}_{3}\text{mc} \), Al \((1/3, 2/3, 0)\), N \((1/3, 2/3, 0.382)\) [22]. The relaxation of AlN lattice around defects was performed within LAPW simulations for a \( 2 \times 2 \times 2 \) supercell containing the one point defect.

Figure 2. Left panel shows the experimental XANES spectrum for AlN:Fe nanorods above the Fe K-edge and theoretical spectra for the substitutional \( \text{Fe}_\text{Al} \) defect and octahedral interstitial \( \text{Fe}_{\text{int}} \) defect. Dashed line is a superposition of 30% interstitial and 70% substitutional positions of Fe atoms. Right panel shows Fe L\(_{2,3}\) XANES for AlN:Fe nanorods and series of reference compounds. Data for Fe-oxides are taken from [12].

The simulation for \( \text{Fe}_\text{Al} \) substitutional model reproduces well the shape of experimental Fe K-edge spectrum of AlN:Fe nanorods. However, the maxima on the experimental spectrum are broadened especially in the region marked as B and C. This indicates a significant structural disorder in the sample and co-existence of other structural defects in addition to the substitutional ones. A better agreement with the experiment was obtained with a combination of 30% Fe in the octahedral interstitial positions and 70% substitutional defects as shown by the dashed line. However, Fe-Al-N
ternary alloys can exist in Fe doped AlN as was shown in the work [23]. Additional experimental analysis should be carried out in order to unambiguously identify the complementary phase to the substitutional FeAl.

In the table 1 we show the results of Bader’s AIM analysis [24] for different compounds. As one can see from the table Al atoms in AlN have a formal charge 3+. One could expect that Fe in Al site should be in the same charge state. However Bader’s AIM analysis performed for the FeAl defect and reference compounds FeN and FeO shows that without any additional defect charge state of Fe in Al site is closer to 2+.

|       | AlN | FeN | FeO | FeAl in AlN |
|-------|-----|-----|-----|-------------|
| Al    | +2.45 | -   | -   | -           |
| N     | -2.45 | -1.10 | -2.19 | -2.19 |
| Fe    | -    | +1.10 | +1.31 | +1.40 |
| O     | -    | -    | -1.31 | -    |

The L$_{2,3}$ spectra of transition metals are more sensitive to the charge state rather than to the local atomic structure. Right panel of the Figure 2 shows the Fe L$_{2,3}$ XANES spectra for AlN:Fe nanorods and series of reference compounds. In contrast to the expected charge state Fe$^{2+}$ from the Bader’s analysis, Fe in AlN:Fe nanorods shows a multiplet structure which is closed to the Fe$^{3+}$ or a mixture of Fe$^{3+}$/Fe$^{2+}$ as in Fe$_3$O$_4$. Since neutral FeAl defect results in Fe$^{2+}$ charge state one can conclude that singly charged substitutional FeAl defect is more energetically favorable. The photoluminescence study of the AlN:Fe nanorods [25] also reveals the fact of the coexistence of Fe$^{2+}$/Fe$^{3+}$ charge states.

4. Conclusions
Theoretical analysis of X-ray absorption experiments above the Fe K-edges of AlN:Fe nanorods showed that more than 70% of Fe atoms substituted Al ones. Other 30% can be attributed to the octahedral interstitials or Fe-Al-N ternary alloy. The Fe L$_{2,3}$ XANES spectra show that Fe charge state in AlN is a mixture of Fe$^{2+}$/Fe$^{3+}$.

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