

Copper defects inside AlN:Cu nanorods – XANES and LAPW study

A A Guda¹, S P Lau², M A Soldatov¹, N Yu Smolentsev¹, V L Mazalova¹, X H Ji³
and A V Soldatov¹

¹ Southern Federal University, Zorge 5, Rostov-on-Don, 344090 Russia

² Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong (P.R. China)

³ Key Laboratory of Specially Functional Materials and Advanced Manufacturing Technology, South China University of Technology, Ministry of Education, Guangzhou 510640, China

E-mail: guda_sasha@mail.ru

Abstract. AlN ferromagnetic nanorods with 5 at.% of copper were studied by using x-ray absorption spectroscopy (XAFS) above the Cu K- and L3- edges. Theoretical simulations of XAFS spectra clearly identify a formation of small copper clusters inside AlN lattice. Average size of clusters was estimated to be 50-70 atoms from the analysis of both XANES (X-ray Absorption Near Edge Spectroscopy) and EXAFS (Extended X-ray Absorption Fine Structure) regions of spectra. Calculations of magnetic moments for different types of point copper defects in AlN lattice were made.

1. Introduction

Nanostructured AlN is a promising material for nanoelectronics. One can control semiconductor properties of this material and create new ferromagnetic properties by means of doping with transition metal atoms. There are reports on room-temperature ferromagnetism observed in AlN, doped by Fe, and Mn [1] and calculations for different impurities of AlN, doped by Cr, Mn, Ca and Mg [2]. But there are still debates about the nature of the ferromagnetism in diluted magnetic semiconductors [3]. The main problem is that it is not easy to obtain exact positions of doping atoms in a host lattice and determine precise local atomic structure around dopants. This information is crucial for understanding of semiconducting and ferromagnetic properties of the material. X-ray absorption spectroscopy is a unique tool for solving this problem. Advanced analysis of XANES [4] allows prediction of local atomic geometry around absorbing atom with high degree of accuracy. This work is devoted to the study of the copper dopants in the AlN:Cu ferromagnetic nanorods by means of theoretical analysis of XANES and EXAFS parts of spectra above copper K- and L3-edges.

2. Experiment

AlN:Cu nanorods were prepared in tube furnace on Si (100) substrate in the presence of CuCl₂ during reaction of heating as copper source [5]. The typical diameter and length of the nanorods, is around 20-50 nm and 1 μm respectively. The concentration of the Cu atoms in AlN:Cu nanorods is about 3-5%. The spontaneous magnetization and the coercivity of the AlN:Cu are about 0.38 emu·cm⁻³ and

100 Oe respectively. It is important to note that AlN:Cu material is highly resistive at room temperature ($>10^5 \Omega \text{ cm}$). Diffraction experiments prove the fact that AlN:Cu nanorod is a single AlN crystal with wurtzite structure, which has growth direction (0001).

The Cu L_{2,3} XANES spectra were recorded under UHV conditions at Russian-German beam line (RGLB) of BESSYII synchrotron. We used total electron yield (TEY) for the measurements. The Cu K-edge spectrum from the same sample was measured using RIGAKU R-XAS spectrometer at Southern Federal University. EXAFS measurements were performed at beamline U7C of National Synchrotron Radiation Laboratory (NSRL) of University of Science and Technology of China.

3. Methods of calculation

All x-ray absorption spectra above Cu K-edge were simulated using finite difference method beyond muffin-tin approach, implemented in an fdmnes2008 package [6]. Hedin-Lundquist exchange-correlation potential was used for estimating of electronic interactions. Magnetic properties of the point Cu defects in AlN host lattice were calculated using a full-potential linear augmented plane-wave (LAPW) approach, implemented in Wien2k-8.3 package [7]. The generalized gradient approximation in the scheme of Perdew–Burke–Ernzerhof (GGAPBE) was used for the exchange-correlation potential. Self-consistency is considered to be achieved when the total energy difference between succeeding iterations is less than 10^{-5} Ry per supercell unit. 2x2x2 supercell of w-AlN was used in order to simulate 5% concentration of copper defects in AlN lattice. Along with magnetic properties all x-ray absorption spectra above the Cu L-3 edge were calculated in the same formalism with assumption of ground state approximation.

4. Results and discussion

Figure 1 shows the scanning electron microscopy images of AlN and AlN:Cu nanorod's massives on Si substrate (panels (a) and (b) respectively). Results of x-ray diffraction experiments prove the fact that nanorods grow preferentially along c-axis of AlN wurtzite structure. HRTEM images of AlN:Cu nanorods [8] reveal the areas with lattice distortions and the possibility of cluster's formation.

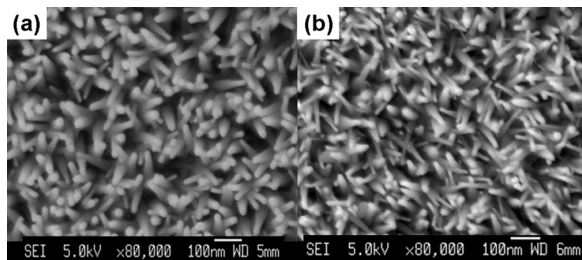


Figure 1. Scanning electron microscopy image of massive of AlN (a) and AlN:Cu (b) nanorods on Si(100) substrate.

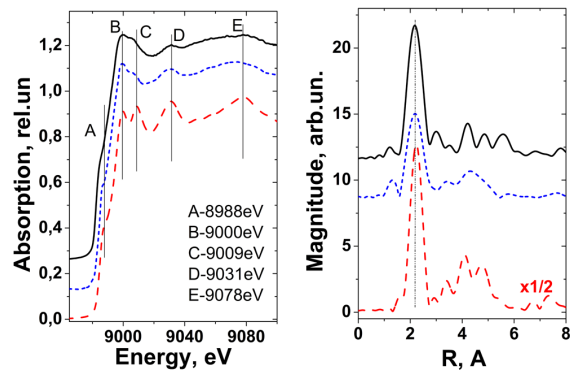


Figure 2. (Color online) Experimental XANES data (left panel) and magnitude of the Fourier transforms of $\chi(k)$ data (right panel) above Cu K-edge. Up to down: data for AlN:Cu nanorods (solid curve) copper clusters, grown during radiolysis in water solution of CuCl_2 (short dashes) and metallic copper (dashes).

Experimental XAS spectra above the Cu K-edge for AlN:Cu and reference samples are shown in Figure 2. Left panel represents XANES region of spectra while right panel is a magnitude of the Fourier transforms of $\chi(k)$ data, obtained from EXAFS part of spectra. Energy positions of peaks A, B, C, D and E are chosen to correspond the main maxima of bulk copper spectrum. Middle curve on the

graphs corresponds to data for small copper clusters, grown during radiolysis (spectrum 3 from [9]). One can notice good agreement between this curve and spectrum of AlN:Cu sample. This fact reveals the possibility of copper clusters presence in AlN lattice. Analysis of EXAFS data provide estimation [10] of the first shell coordination number for copper atoms in AlN lattice to be $N_1=8$ atoms, depending on the exact value of Debye-Waller factor. This gives estimation [11] of average size of cluster to be equal to 50-70 atoms, depending on the exact geometry of cluster.

Figure 3 shows theoretical simulations of the XANES spectra above the Cu K-edge. Upper curve is experimental XANES spectrum for AlN:Cu nanorods above the copper K-edge. We have verified several models for copper defects inside AlN lattice, made geometry optimization for each one and choose those with lowest energy of formation. They are: copper in Al site (1), copper in octahedral interstitial (2), copper clusters of different size (3) and (4), bulk copper (5). Calculations were done for different free copper clusters – from 3 atoms up to 200 atoms (only results for 13 and 55 atomic clusters are shown). Geometry structure for copper clusters was generated by Birmingham Cluster Genetic Algorithm (BGGGA) code [12].

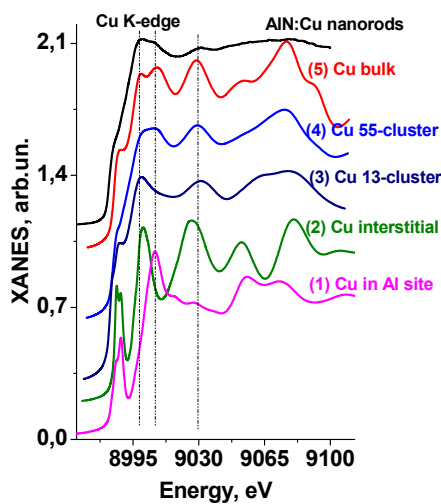


Figure 3. Experimental XANES spectrum for AlN:Cu nanorods above copper K-edge (upper curve) and calculations for different theoretical models.

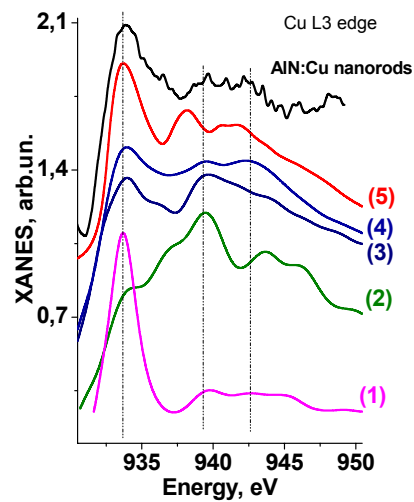


Figure 4. Experimental XANES spectrum for AlN:Cu nanorods above copper L3-edge (upper curve) and calculations for different theoretical models. Numeration is the same as in Figure 3.

Figure 3 clearly identifies the main type of copper defects inside AlN – clusters with average size of 50 atoms. Concentration of point copper defects should be less than 5% in order to reproduce well experimental spectrum for AlN:Cu nanorods. Though clusters inside AlN lattice have different environment than free ones, but this will not have significant effect on the Cu K-edge XANES for large enough clusters (more than 4 coordination spheres around central atom). We have verified this idea by means of calculations of copper clusters having different shells, consisting of aluminum and nitrogen atoms. The effect of environment of copper clusters inside AlN lattice results in small difference in the cluster size values estimated separately from analysis of XANES and EXAFS regions of Cu K-edge spectra.

Figure 4 is an analogue of Figure 3 but utilize the copper L3-edge XANES spectra. Energy positions of marked peaks were chose to represent maxima of smoothed experimental spectrum for nanorods (upper curve). Information from the copper L3 edge prove the fact of copper clusters presence in the AlN:Cu nanorods. But one can notice that proper linear combination of theoretical spectra for point defects on the left panel can also reproduce well experimental spectrum. This was the main

reason for using complementary information from Cu K-edge absorption spectrum in order to make univocal predictions.

Spin-polarized band-structure calculations were made for estimations of magnetic properties for different types of point defects. Experimental value $0.38 \text{ emu} \cdot \text{cm}^{-3}$ of spontaneous magnetization of the AlN:Cu means that one copper defect induces a magnetic moment which is equal to 0.012 Bohr magneton μ_B . Calculations predict that the largest value of magnetic moment $2\mu_B$ per supercell arise when Cu is placed in Al site. This result is in agreement with previous calculations for this type of defect [13]. For the present sample the concentration of this type of defect should be very small. Cu atom in octahedral and tetrahedral interstitial produce 0.65 and 0.83 μ_B correspondingly. But these defects are prohibited by the analysis of XAS experiments above Cu K and L3 edges. These calculations indirect indicate the possibility of magnetization of the surface atoms of small copper clusters inside AlN lattice. But this argument is needed to be rigorously proved by means of appropriate calculations.

5. Conclusions

Theoretical analysis of x-ray absorption experiments above the Cu K- and Cu L3- edges of AlN:Cu nanorods showed the direct evidence for copper cluster presence in the nanorods. Average size of clusters was estimated from simulations of XANES and EXAFS data above Cu K-edge and is of order 50 – 70 atoms (or 5-6 angstrom in radius). We have estimated that the largest magnetic moment will arise on copper atoms when they settle in Al site (2 Bohr magnetons in AlN lattice per one copper substitutional defect). Octahedral and tetrahedral interstitial positions of copper give the values of spin magnetic moment, equal to 0.65 and 0.83 Bohr magnetons correspondingly.

Acknowledgements

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