Copper-oxide metalorganic nanocomposite: morphological and X-ray spectroscopy studies

G Yalovega¹, A Funik¹, T Myasoedova¹ and M Brzhezinskaya²

¹ Southern Federal University, Faculty of Physics, Rostov-on-Don, Russia
² Helmholtz Zentrum Berlin fur Materialien und Energie, Berlin, Germany

E-mail: yalovega1968@mail.ru

Abstract. Oxidation state, local and electronic structure as well as the surface morphology of a CuOₙ nanocomposites were investigated. The research is focused on studying the relationships between surface morphology and structure of the inorganic component of the nanocomposites. The physico-chemical mechanisms of change in local and electronic structure, oxidation state and the surface morphology of nanocomposites in the interaction of metal oxide nanoparticles with different types of matrices were determined.

1. Introduction
Composite materials based on metal oxide nano- microcrystals in/on organic and nonorganic matrices, have attracted increasing attention thanks to the possibility of tailoring their chemico-physical properties as a function of particle size, shape, composition and structure. As well known, the size, morphology and structure of nano- microcrystals as well as composition and morphological details of matrix have great effects on electrical and adsorption properties of the resulting nanocomposites. Besides the influence of the kind of matrix to directing the nano-unit nucleation and subsequent organization of metal oxide nanoparticles/ microcrystals is observed.

In the present research we investigated morphology and local atomic and electronic structure of copper oxide based nanocomposites by means of SEM and XAS. The aim of this study is to examine the relationship between local atomic and fractal structure of the copper-based metalorganic nanocomposite as well as to determine the mechanisms of these structures formation by means of XANES.

2. Experiment
Copper oxide films were prepared by sol–gel method on Si/SiO₂ substrates. In the citrate sol-gel process the alcohol solution of CuCl₂, ethylene glycol and citric acid were selected as starting materials. The details of the synthesis are published in [1]. The prepared films were dried at 150°C for 1 hour and then annealed at temperatures 250, 350 and 500°C with a fixed time of 2 hour in an ambient air. The total thickness of films equal 4.2 μm including silicon substrate with thickness order 3 μm, SiO sublayer with thickness equal 1 μm and Cu layer in order 0.2 μm.

Surface morphological study of the deposited film samples was carried out using a scanning electron microscopy (LEO 1560, ZEISS). The SEM operating voltage was employed at 5 kV.
The Cu K-edge XANES spectra of the CuOₓ thin films as well as referenced samples were measured in fluorescence mode at the bending-magnet beamline KMC-2 (BESSY II, Berlin) using double-crystal Si₁₋ₓGeₓ (111) monochromator [2]. To increase energy resolution, the beam was focused into an area smaller than 400 μm × 600 μm. A copper metal foil (first inflection point at 8979 eV) was used for energy calibration. Pre-edge features were collected using 0.3 eV steps whereas the main edge jump was collected with 0.7 eV till 240 eV above the absorption edge. Samples were set up at grazing incidence (~3° to the X-ray beam) in order to enhance the detection efficiency.

Collected spectra were corrected, energy calibrated, pre-edge subtracted and post-edge normalized using Athena package [3].

3. Results and discussion
The X-ray absorption near-edge structure spectroscopy (XANES) is successfully applied to provide information about oxidation states and symmetries as well as chemical nature of bonding investigating elements in thin films [4, 5]. Figure 1 shows the experimental XANES spectra of CuOₓ thin films annealed at 150, 250, 350 and 500 °C (we marked these samples as I, II, III and IV respectively) and few other copper-based materials (i.e. CuO, Cu₂O, Cu(OH)Cl etc.).

![A](image1.png) ![B](image2.png)

**Figure 1.** a XANES Cu K-edge spectra of the CuOₓ thin films in comparison with referenced compounds; b pre-edge region XANES Cu K-edge spectra of the CuOₓ thin films in comparison with referenced compounds.

It is clearly seen that there are two groups of spectra. Spectra for sample I and II are essentially identical and spectra III and IV are very similar. All spectra under study include main peaks A, B and C with average value of energy ~8987 eV, ~8998 eV and ~9015 eV respectively. One can see that between these groups the main differences in the spectra shape and the energy positions of the features are observed. It indicates that between 250° and 350°C there are some significant changes in local environment of copper. At the same time, this suggests no change in the copper valence and local structure of both samples annealed at 150° and 250° as well as samples annealed at 350° and 500° (fig.1a). We consider in more detail the differences in the spectra of these groups. The edge positions for both groups of samples and the Cu references have been determined from the first derivative function. The shift toward higher energy relative Cu foil (8979 eV) on ~5 eV is observed in the case of samples III and IV, that corresponds to energy position of CuO spectrum (8 983.6 eV) [6]. From
comparison of these spectra and measured reference compounds clear formation of CuO oxide after annealed at 350°C and 500°C, that could be explained by formation of CuO crystallites. The spectra I,II are characterized by the pre-edge peak A’ (~8977 eV) and broad peak B compared with the spectra of the CuO, shift of energy position of the absorption edge to high energy on ~3 eV (8986.8 eV). The organic component of the film begins to decompose at temperatures above 250°C. The main reason of this process is high concentration of CuCl₂ in starting solution compared with citric acid concentration. Therefore, we assume the XANES signal from a thin film I,II can be considered resulting in from a linear combination of signals from Cu atoms with neighborhood similar to that found in Cu(OH)Cl, CuO and some intermediate metalloorganic compounds that results to spectra broadening. The polymer resin (reaction of polycondensation) is formed at 100-110 °С. At any rate, three carboxyl groups of lemon acid take part in the formation of either chelates or the bond with ethylene glycol. As a result, a “nucleus” is formed. The following polymerization runs around the “nucleus”. The organic substances decompose only at temperatures above 250 °C and the CuO phase forms that is in good agreement with the SEM results and XANES results. Comparing the spectra of film annealed at 250° and reference compounds, one can observe that peaks A’, A, B, B’ and C can be used as a fingerprint for the formation of the Cu(OH)Cl phase during annealed. As was shown in [7] a weak pre edge peak around 8976–8978 eV like that of Cu²⁺ reference, indicating that the oxidation state of as-synthesized material is divalent because the reason of this peak is 1s – 3d transition and there is no 3d hole neither in Cu nor in Cu₂O (fig. 1b). At the same time, the K-edge peak A is associated with the main 1s – 4p transition for each of compared compounds [8].

To define the structures resulting from the synthesis of the composite materials at temperatures up to 250 degrees more precisely we carried out a computational modeling of X-ray absorption spectra by the finite difference method with FDM software [9] since in this code there is not muffin-tin approximation formalism of the Green’s potential that provides more accurate results for a number of compounds. The simulation results in comparison with experimental spectrum are shown in Figure 2. To compare we have chosen complex hydroxides Cu₃(OH)₂CO₃ and Cu(OH)Cl as well as chelate compound C₆H₁₀CuO₁₀ [10]. All of the structures were collected thanks to CCDC (Cambridge Crystallographic Data Center).

**Figure 2.** Theoretically calculated K-edge XANES spectra of the different compounds in the comparison with Sample II spectra: M1 – Cu K-edge XANES for Cu(OH)Cl, M2 – Cu K-edge
XANES for Cu$_2$(OH)$_2$CO$_3$, M12 – Linear combination of the M1 and M2 spectra, M3 - Cu K-edge
XANES for C$_6$H$_{10}$CuO$_{10}$.

This comparison confirms the assumption that nanocomposite thin film Sample II is formed by several inorganic phases. The main features of the linear combination of two XANES spectra of different complex hydroxides Cu$_2$(OH)$_2$CO$_3$ and Cu(OH)Cl are almost similar to those in spectrum for Sample II (energy position for the edge structure, peaks at 9010 and 9025 eV respectively).

XANES results and computational calculations are confirmed by scanning electron microscopy results (Fig. 3). Gradual decomposition of the organic component of the film leads to evolution of the final morphological structure as a function of annealing temperature. As a result, at temperatures above 550 ºC crystals of copper oxides are dominated and are converted into fractals with another level of organization.

Figure 3. SEM-images of the thin films annealed at: a) 250°C; b) 350°C; c) 500°C.

4. Conclusions
We have carried out a comprehensive both experimental and theoretical study of the organometallic nanocomposite thin films based on copper oxides. It was found that at the synthesis temperature below 250 degrees there is complex inorganic component in the structure of the film. With increasing annealing temperature up to 500 formation of CuO crystallites with fractal structure was observed. While temperature increases changes in the local atomic and electronic structure as well as in the morphology are happened. This phenomenon is explained by the decomposition of the initial organic phases at high temperatures. The copper (II) oxide crystallites are formed on the film surface that is confirmed by results of XANES and SEM investigation.

5. Acknowledgments
The research leading to these results received funding from the Ministry of education and science of the Russian Federation under grant agreement № 11.2432.2014/K. We thank HZB (Berlin, Germany) for the allocation of synchrotron radiation beamtime (Beam Line KMC-2 at BESSY II) and Institute for Nanometre Optics and Technology (HZB) for the provided opportunity SEM measurements.

References
[1] Myasoedova T.N et al 2014 Appl. Mech. and Mat. V 481 133
[2] A. Erko et al 2001 Nucl. Instr. and Meth. in Phys. Res. A 467–468
[3] B. Ravel and M. Newville 2005 J. Synchr. Radiat. 12 537–541
[4] A. Gaur and B.D. Shrivastava 2012 A Comp. St. of the M. of Spec. Us. XAFS V 121 647-652
[5] G.X. Shen et al 2005 Thin Solid Films 489 130
[6] R. Gago et al 2013 J. of Alloys and Comp. 561 87–94
[7] M. Vaseem et al 2008 Cat. Comm. 10 11–16
[8] J. Fulton et al 2000 J. Phys. Chem. A 104 (49) 11651–11663
[9] O. Bunau and Y. Joly 2009 J. Phys.: Condens. Matter 21 345501
[10] A. Lenstra and O.N.Kataeva 2001 Acta Crystallogr., Sect.B: Struct. Sci. 57 497