Structure of the electrochemically deposited Cu nanoclusters on p-GaAs(100) surface in H₂SO₄ solution: x-ray absorption analysis

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Abstract. The local 3D structures of electrochemically deposited Cu nanoclusters on p-GaAs(100) with various coverages have been investigated by in-situ surface-sensitive x-ray absorption fine structure (XAFS) analysis. The experimental Cu K-edge XANES of Cu nanoclusters deposited on GaAs surface have been analyzed on the basis of full potential calculations of XANES in the combination with DFT geometry optimization. It has been shown that small partially oxidized Cu nanoclusters are formed when the surface coverage of the Cu overlayer is less than 0.25 monolayer. At higher coverage the Cu microclusters have a fcc structure and are almost not oxidized.

Introduction
For the last decade the study of the properties of the small size metal/semiconductor interfaces has attracted much attention [1-3]. It is due to the development and production of nanoscale Schottky contacts for microwave and terahertz applications as well as the attempts made to form planar and three-dimensional arrays of nanocontacts as the artificial nonlinear environment [4-7]. Semiconductor materials are the basis of modern big and super big integrated schemes which are mainly made using silicon. It should be noted that the creation of integrated schemes on the basis of GaAs leads to the reduction in size and the increase in speed of operation of semiconductor devices as well as decrease in power consumption.

The electrochemical growth of metal nanostructures is provoking an increasing interest, because, in contrast to the other well-known deposition techniques, the adjustment of the electrochemical potential via the electrode potential offers a unique method to control the speed of growth and the atomic structure of the interface. Although the structures of electrochemically deposited Cu on metal surface have already been investigated by several research groups [8-11], only a few studies on the electrochemical deposition of Cu on semiconductor films have been carried out [12-15].

The understanding of the solid/electrolyte interface structure is known to be hindered by the lack of the direct structural methods of investigation. For instance, a highly sensitive electrochemical method such as voltammetry [16] fails to provide reliable data on the structure under investigation. As to the
optical methods which are traditionally used in-situ for obtaining the information about electronic states, band structure, etc., they are not able to fully investigate the atomic structure of a solid/electrolyte interface. Practically there are only two structural methods that can be applied in-situ. They are the atomic force microscopy (AFM) and X-ray spectroscopy. AFM provides the structural information concerning the deposition layer only, the structure of an interface between the deposit/substrate cannot be obtained. Besides, the spatial resolution of AFM has an order of angstroms while to understand the nature of a chemical bond, the interatomic distances (bond length) must be determined with the accuracy of about several picometers. It has been shown recently, that x-ray absorption fine structure (XAFS) analysis allows obtaining the detailed information on local and electronic structure with high sensitivity even for the systems without the long-range order in the positions of atoms [17].

1. Experiment and method of calculation

The calculations of the Cu K-edge XANES spectra were performed using the full-potential FDMNES_2008 code, which runs within a real space cluster approach and uses the finite difference method (FDM) to solve the Schrödinger equation [18]. Its main advantage is the possibility to have a totally model free potential shape, thus getting rid of the muffin-tin approximation limitations, which were found to be a reason for significant mistakes in theoretical XANES for same cases [19]. This is a key point for the case of nanostructured materials because, the classical multiple scattering scheme [20, 21] which uses the muffin-tin approximation [22] is not able to give reasonable agreement with the experimental XANES spectra for atoms at the surface of clusters [23]. XANES simulations were performed using optimized geometries calculated by the all-electron density functional theory (DFT) approach implemented in the ADF2008 code [24]. Structures were obtained using the Generalized Gradient Approximation (GGA) with OPBE exchange-correlation potential [25]. The OPBE exchange-correlation correction is an equivalent to OPTX’s exchange [26] + PBE’s correlation [27].

X-ray absorption spectra were collected in the fluorescence mode with a grazing-incidence geometry (incidence angle was set at 0.4-1.6°) at the Photon Factory of High Energy Accelerator Research Organization in process of the electrochemical deposition of Cu [28]. The thickness (θ) of the Cu overlayers was estimated to be 0.05, 0.08, 0.17, 0.25, 1, and 6 ML for various deposition times.

2. Results and discussion

The structural parameters obtained by least-squares fit are summarized in Table 1.

| θ (ML) | Bond type | N   | R (Å)       | σ (Å) |
|--------|-----------|-----|-------------|-------|
| 0.05   | Cu-O      | 1.2±0.4 | 1.88±0.05 | 0.037f|
|        | Cu-Cu     | 1.9±0.3 | 2.16±0.04 | 0.086f|
| 0.08   | Cu-O      | 1.0±0.6 | 1.92±0.05 | 0.037f|
|        | Cu-Cu     | 1.6±0.6 | 2.16±0.04 | 0.086f|
| 0.17   | Cu-O      | 0.9±0.5 | 1.88±0.06 | 0.037f|
|        | Cu-Cu     | 1.6±0.4 | 2.14±0.06 | 0.086f|
| 0.25   | Cu-O      | 1.1±0.4 | 1.90±0.03 | 0.037f|
|        | Cu-Cu     | 0.9±0.5 | 2.16±0.04 | 0.086f|
| 1      | Cu-Cu     | 1.7±0.7 | 2.56±0.03 | 0.091f|
| 6      | Cu-Cu     | 8.5±0.8 | 2.530±0.007 | 0.091 |
|        | Cu-Cu     | 11.8±0   | 2.527±0.004 | 0.091 |

f Fixed value in the parameter fitting.
The EXAFS analysis results given in table 1 show that Cu-Cu distances for all thicknesses of the deposited layers are much shorter and coordination numbers are less than for bulk copper (for which distance Cu-Cu and a coordination number are equal to 2.56 Å and 12, accordingly).

As the probable structures formed at small deposition thickness of copper on GaAs surface, the following models have been considered: the copper atom on GaAs surface (Fig. 2a), CuO molecule on GaAs surface (Fig. 2b) and CuO$_2$ molecule on GaAs surface (Fig. 2c). For the analysis how the substrate influences the initial state of the cluster growth, a free small cluster of Cu$_2$O oxide (Fig. 2d) has been examined. The chosen models for the optimization process are the simplified representation of small copper clusters in the environment of oxygen atoms.

The comparison of the experimental Cu K-XANES spectra for $\theta=0.05$ ML with theoretical spectra of CuO and CuO$_2$ molecules on GaAs, Cu atom on GaAs and first coordination sphere of the copper oxide Cu$_2$O is shown in the Fig. 3. As one can see from figure 3 the shape of theoretical XANES obtained for the model “CuO at GaAs surface” is the closest to the shape of the experimental XANES for 0.05 ML coverage, thus one can conclude that at the initial stage of the Cu nanoclusters deposition the copper atoms are coordinated with the oxygen atoms (i.e. oxidized).

The comparison of the experimental XANES spectra for 6 ML deposition with theoretical Cu K-spectra for Cu, CuO and CuO$_2$ clusters consisting of 55 atoms is given in the Fig. 4. One can see that all main features of the experimental spectrum are well reproduced by metal Cu$_{55}$ cluster having fcc symmetry. Thus, it is possible to conclude, that the Cu microclusters with the fcc structure appeared at this high coverage.

**Figure 3.** The experimental Cu K-XANES spectrum for $\theta=0.05$ ML and theoretical spectra of CuO and CuO$_2$ molecules on GaAs, Cu atom on GaAs and first coordination sphere of the copper oxide Cu$_2$O.

**Figure 4.** The experimental XANES spectra for 6 ML deposition and theoretical Cu K-spectra for Cu and CuO$_2$ clusters consisting of 55 atoms.

Hereby, the Cu K–edge XANES spectra are found to be rather sensitive to the variations in the geometry of nanoclusters. Our investigation has shown that small Cu nanoclusters which were formed when the surface coverage $\theta$ of the Cu overlayer was less than 0.25 monolayer are characterized by a shorter Cu-Cu bond length than that of bulk copper. Cu atoms in small nanoclusters were coordinated with the O atoms. At the higher coverage the Cu microclusters are found to grow in the fcc structure and there is no evidence for the oxidation of copper atoms in these larger clusters.
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