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XPS study of Cu-clusters and atoms in Cu/SiO$_2$ composite films

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Introduction

Investigation of optical and electrical properties of composite metal-insulator materials has been the topic of a considerable number of recent papers. For metallic particles in the size range of about 10 Å the phenomenon of macroscopic charge quantization is observed [1], which could make materials of this kind useful for creating single-electron devices. In order to produce these properties, it is necessary to know the chemical state of the cluster-forming atoms, the average cluster size and the average distance between them. One of the most effective ways to study the chemical state of elements is x-ray photoelectron spectroscopy, or XPS. Chemical states of atoms are determined by analyzing the chemical shifts of the photoelectron lines associated with changes in the binding energies E_b of core electrons arising from changes in the interaction with neighbouring atoms. In this work we have attempted to obtain composite metal-insulator films of Cu/SiO$_2$ containing Cu-clusters and atoms in the unoxidized state. When an oxide is used as the insulator it is important to control the degree of oxidation of the metal introduced. We have aimed to develop the diagnostics for the chemical state identification of metal atoms and for obtaining parameters of ensemble of metal-clusters which are important for the single-electron tunneling processes.

Methods

The composite thin films of Cu/SiO$_2$ were obtained by simultaneous sputtering of copper and quartz targets on a SEM-450 (Alcatel) setup after first pumping the chamber down to 10^{-5} Pa [2]. The deposition took place in an atmosphere of pure argon at a pressure of 0.3 Pa. The substrates temperature never exceeded 100°C. The films were deposited on a substrate made of Si that was first oxidised in dry oxygen, producing an oxide layer 500 Å thick. The sublayer of SiO$_2$ acted as a barrier to diffusion of copper into the substrate during the annealing of the composite films (see below). In this paper we discuss composite films with a thickness of 2000 Å in which the copper content was around 5 vol%, according to microanalysis data. A part of our films were annealed in an atmosphere of hydrogen at 850°C for 30 min. In the course of the annealing, clusters form, which are clearly visible in the transmission electron microscope (TEM). It is clear from TEM photograph that copper clusters with a characteristic size 50 Å form nonuniformly in the bulk of the film. There are no clusters with sizes larger than 10 Å in a subsurface layer of thickness about 150 Å (the resolution of the microscope was around 10 Å). The reason for this depletion of large clusters near the surface is unclear. This region has been a subject of our particular interest because it could be a promising material for single-electron devices if there are clusters there with sizes around or smaller then 10 Å. The concentration and chemical states of copper near the surfaces of the as-grown and annealed samples were measured by XPS using AlK$_\alpha$

x-rays (1486.6 eV). A Leybold-AG LHS-11 electron spectrometer was used. The films were cleaned with low energy ($E_i = 500$ eV) Ar^+ ions to reduced the possible influence of ion bombardment on the chemical state of the films under study to 1–2 atomic layers.

Results

The relative content of main elements was determined from the intensity of the corresponding photoelectron lines using element sensitivity coefficients determined earlier. In this measurements, the ratio of the numbers of silicon and oxygen atoms turns out to be close to stoichiometric for SiO_2 in both the as-grown and the annealed films. The measured copper concentration in the subsurface region was $C_{Cu} = 5 \pm 1\%$ for the as-grown sample and $C_{Cu} = 4 \pm 1$ % for the annealed sample, in agreement with the average concentration obtained by x-ray microanalysis.

Analysis of chemical shifts of these photoelectron lines was complicated by static charging of the samples in the photoemission process. The amount of chemical shift due to charging was determined by comparing the position of the Si_{2p} line with literature data for SiO_2 ($E_b = 103.4$ eV [3]). The average value of the shift due to charging of the as-grown sample was $\Delta E = 10.0$ eV, while $\Delta E = 3.0$ eV in the annealed sample. This increase in the line shift as a result of annealing is connected with a decrease in the conductivity of the material and is an additional evidence of segregation of copper of the as-grown sample into clusters. The spectra of $Cu_{2p_{3/2}}$ photoelectrons and CuLVV Auger electrons shown in Fig. 1 and Fig. 2 were corrected for the value of static charge. Figure 1a shows $Cu_{2p_{3/2}}$ spectra obtained before ionic cleaning of the sample surface. The intense low-energy satellites are present only in the oxide and hydroxide spectra of divalent copper (CuO, $Cu(OH)_2$). The satellite and the corresponding hydroxide shoulder of the fundamental line disappear almost completely when a layer of thickness 10–15 Å is etched from the surface (Fig. 1b). Hence, the photoelectron spectra leads us to conclude that copper at the surface was oxidized by atmosphere oxygen and it is not oxidized to its divalent state in the bulk region of either samples. A second conclusion that follows directly from Fig. 1 is that annealing changes the chemical state of copper
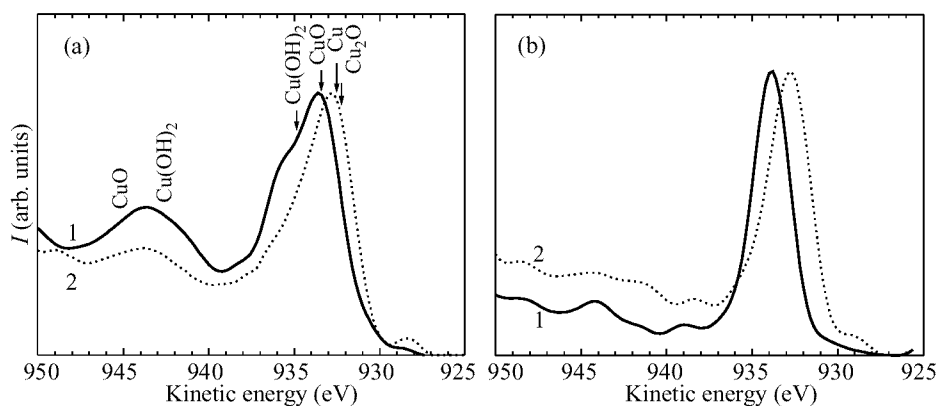

Fig 1. $Cu_{2p_{3/2}}$ XPS spectra of as-grown (1) and annealed (2) samples measured on the original (a) and cleaned (b) surfaces.

Table 1. Binding energy E_b ($Cu2p_{3/2}$) and value of Auger parameter α for samples under study and number of compounds.

	E_b, eV	α, eV
Cu	939.7±0.2 [3]	1851.3±0.2 [3]
Cu_2O	932.6±0.3 [3]	1849.5±0.2 [3]
	932.0±0.2 [4]	
CuO	933.5±0.3 [3]	1851.5±0.3 [3]
	933.6±0.2 [4]	
$Cu(OH)_2$	935.0±0.2 [4]	—
$Cu{\rightarrow}SiO_2$	933.5 [5]	—
as-grown film	933.7±0.1	1847.2±0.2
annealed film	932.8±0.1	1851.2±0.2

markedly, since the binding energy of the core 2p electron changes. Among the possible remaining states we can list univalent copper oxide Cu_2O, elemental copper in the SiO_2 matrix, and metallic copper segregated into clusters.

Since reliable identification of the oxide Cu_2O and metallic copper based on core binding energy is hindered by the closeness of these energies, we extracted additional information from the Auger parameter $\alpha = E_b + E_A$, where E_A is the kinetic energy of the corresponding Auger electron [3]. The physical meaning of the Auger parameter implies that its change when one chemical state converted to another is very close to the change in relaxation energy for the same chemical change. The states of copper for the films under study was identified from data of Table 1, in which we list values of the α and E_b for various copper compounds averaged over the data compiled in Ref. [3] and also values of E_b we obtained previously using one spectrometer under the same condition [4]. Comparison of the measured value of E_b($Cu2p_{3/2}$) and of α for samples under study with literature one's for number of compounds allows us to conclude unambiguously that (i) a larger portion of copper is in the metallic state in the annealed sample, which can be true only if copper clusters form; (ii) practically all of copper is in the form of unoxidized atoms dispersed in the matrix of as-grown sample. The identification procedure is described in more details in our previous work [2].

Let us estimate the possible range of sizes of clusters. Based on the data from [6] for clusters of an element with similar electronic structure, silver, the values of E_b and α approach the metallic values in particles that include decades or more atoms, i.e., with diameters of the order of 10 Å or more. It is the average size of our clusters because the TEM data reveals no clusters with sizes larger than 10 Å in the subsurface region.

To describe the cluster ensemble we have to know the percentage of copper atoms in clusters. For this we consider the CuLMM Auger spectra (Fig. 2) for the as-grown (curve 1) and annealed (curve 2) sample, and also the Auger spectrum of bulk metallic copper (curve 3) after subtracting the background formed by multiple scattering of the Auger electrons [2]. The complex shape of the spectrum of the annealed material allows to assume that it is a combination of spectra of metallic and elemental copper strongly shifted with respect to one another. A numerical simulation of the Auger spectrum of the annealed sample by the combination of spectra of metallic copper (curve 3 in Fig. 2) and elemental copper in a SiO_2 matrix (curve 1 in Fig. 2) showed that 70% of copper atoms are segregated into clusters. It is seen from the Fig. 2 (curve 1′) that 5% of all
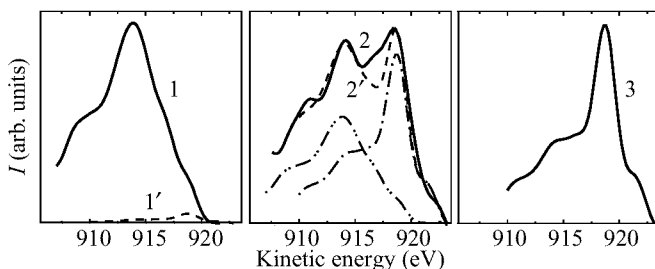
Fig 2. Spectra of CuLVV Auger electrons from the as-grown (1) and annealed (2) samples, and from metallic copper (3): $1'$ — contribution of metallic copper, $2'$ — model spectrum.

Table 2. The parameters of clusters in Cu/SiO_2 composite films.

	$\langle N \rangle$, Å	C_{cl}, cm^{-3}	$\langle l \rangle$, Å
as-grown film	45	$4.8 \cdot 10^{18}$	59
annealed film	45	$6.7 \cdot 10^{19}$	25

copper segregates into clusters even during the deposition and before annealing. Taking into account the percentage of copper atoms in clusters, the full copper concentration measured and the average cluster size $\langle N \rangle$, we can estimate the concentration of clusters and atoms and the average distance between neighbour clusters and atoms $\langle l \rangle$ (Tabl. 2).

Summary

Thus, the XPS-TEM study of Cu/SiO_2 composite metal-insulator films allowed us to develop the diagnostics of the chemical states of metal atoms and the parameters of the ensembles of metal-clusters and metal-atoms which are important for single-electron tunnelling processes.

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