Study of the local atomic and electronic structure in Cu-doped WO_3 programmable metallization cell (PMC)

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Tungsten trioxide WO_3 is an important and well known material showing electro- and photochromic properties [1]. Recently, its applications have been extended into the field of programmable metallization cell (PMC) devices, a promising next-generation memory technology [2, 3, 4, 5], where WO_3 plays the role of solid electrolyte. The application of tungsten trioxide in the PMC memory devices has been demonstrated on an example of Cu-doped WO_3 films, which serve as an active media [3, 4, 5]. Such PMC device is composed of a thin film of solid WO_3 electrolyte sandwiched between a copper anode and an inert cathode. One believes that under the influence of an electric field, the electron current from the cathode reduces an equivalent number of Cu-ions injected from the anode, and a Cu metal-rich electrodeposit is formed in the WO_3 electrolyte [3]. The electrodeposit formation process can be reversed applying a bias with opposite polarity.

In this work we have performed X-ray absorption spectroscopy study of the local atomic and electronic structure around Cu and W ions in a-WO_3/Cu/a-WO_3/Si and a-WO_3/Cu/Si multilayered structures.

The samples were prepared on silicon substrates by dc magnetron sputtering of metallic tungsten in mixed Ar-O_2 atmosphere (a-WO_3 thin film layer) and by thermal evaporation of metallic copper (Cu thin film layer). The multilayered structures were used as-prepared and after annealing in air at $\sim$135°C. Pure amorphous a-WO_3 thin film, metallic copper foil, and polycrystalline CuO powder were also used for comparison. The Cu K-edge and W L_3-edge X-ray absorption spectra were recorded in fluorescence step-by-step scanning mode at the C (CEMO) beamline of the DORIS-III storage ring using the 7-cells silicon drift detector (SDD-M3). The EXAFS signals were extracted and analysed using conventional procedure as is implemented in the EDA package [6].

Comparative analysis of the W L_3-edge EXAFS spectra and their Fourier transforms (FTs) indicates that the local environment around tungsten atoms in both as-prepared and annealed multilayered structures is similar and resembles that of pure a-WO_3 thin film (Fig. 1). On the contrary, the local environment of copper atoms depends strongly on the type of the multilayered structure and annealing procedure. In the as-prepared samples, copper is mostly present in the metallic phase characterized by the strong peak at 2.1 Å in the FT of the Cu K-edge EXAFS signal: it corresponds to the distance Cu–Cu of about 2.56 Å. Also the outer peaks at 3-6 Å in the FT have a shape similar to that in metallic copper. The intensity of the FT peaks suggests stronger disorder and the presence of the size effect in the films. Closer inspection of the FT signals shows that some part of copper atoms is oxidized already in the as-prepared samples, as is evidenced from the peak at 1.43 Å, which is due to the bonds Cu–O.

The annealing of the multilayered structures at 135°C provokes further oxidation of copper. While metallic copper is still present in a-WO_3/Cu/Si after annealing, it disappears completely in a-WO_3/Cu/a-WO_3/Si. In both cases, the intensity of the peak at 1.43 Å due to the bonds Cu–O increases. A detailed analysis indicates that the copper coordination in the multilayers is equal to about two oxygen atoms located at the distance of about 1.88 Å. Such coordination of copper ions is close to that observed for Cu^+ in Cu_2O (N=2, R=1.85 Å) [7]. For comparison, copper coordination of four oxygen atoms at $\sim$1.94 Å was found in CuO, in agreement with crystallographic data [8]. The oxidation of copper ions in the multilayers upon annealing is also supported by the Cu K-edge shift of about 0.7 eV to higher binding energies, whereas no shift of the W L_3-edge was detected.

To conclude, we have shown that as-prepared a-WO_3/Cu/a-WO_3/Si and a-WO_3/Cu/Si multilayers contain nanosized metalllic copper, which is oxidized to Cu^+ upon annealing at $\sim$135°C. The

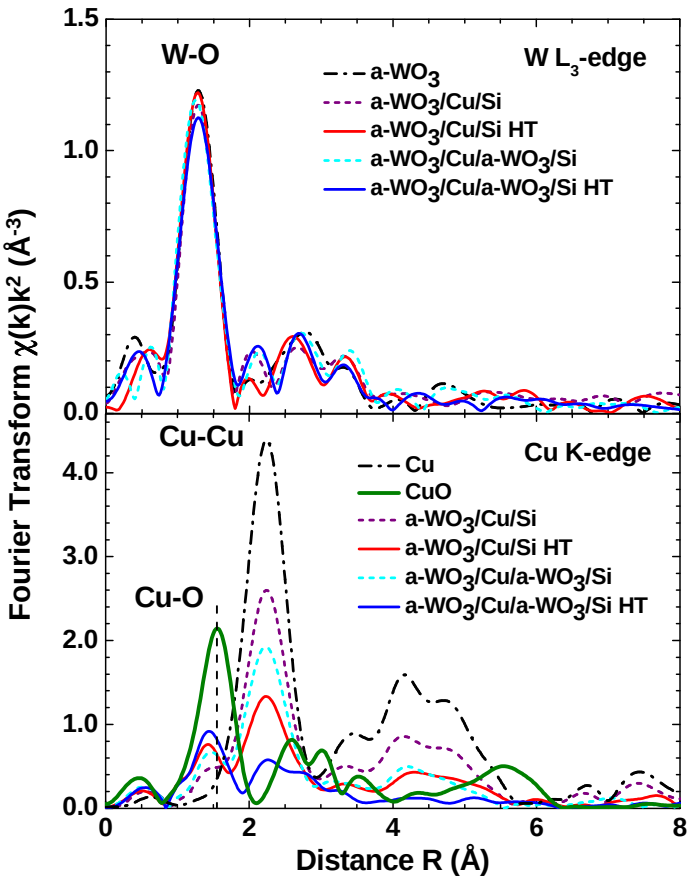

Figure 1: Fourier transforms of the W L_3-edge and Cu K-edge EXAFS $\chi(k)k^2$ spectra, recorded at 300 K, in a-WO_3/Cu/a-WO_3/Si and a-WO_3/Cu/Si multilayers before and after high temperature (HT) annealing at 138°C. The experimental data for metallic Cu, CuO, and amorphous a-WO_3/Si thin film are also shown for comparison.

monovalent copper ions with small ion size are able to diffuse across the multilayer and, thus, presumably participate in the formation of conducting pathways in the PMC cell.

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