

# Phase transitions in copper oxide thin films under proton irradiation

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**Abstract.** The variation in the atomic composition of thin CuO films under irradiation by proton beams with different doses was experimentally studied by X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), and high resolution transmission electron microscopy (HRTEM). The chemical composition and corresponding changes of crystal phases were found after proton irradiation at various doses according to the XPS, EELS, and HRTEM data. It was demonstrated that the selective removal of oxygen atoms was accompanied by a phase transition to Cu<sub>2</sub>O during the gradual recovery of the virgin CuO.

## 1. Introduction

Physical basis underlying the process of selective removal of atoms (SRA) under the low energy proton irradiation of thin films was demonstrated experimentally in [1]. This SRA radiation technology allowed producing various functional nanoelements based on the thin-film materials with the possibility to control the composition and properties in different layers of multilayer structures, as well as recover materials from their chemical compounds without surface sputtering. The selective removal of atoms was carried out at low ions energies in the range of (0.1-4) keV with proton irradiation, which distinguished this process from the effects of selective sputtering of atoms and ion-induced mixing of atoms at the interface between the two phases [2].

In this work, CuO reduction was carried out under proton irradiation. The purpose of this work was to study the evolution of the structural-phase state of the films during low energy proton irradiation. CuO thin films were good model objects to demonstrate the SRA process, because the copper oxides easily underwent the hydrogen irradiation [1]. The SRA process of CuO thin films under proton-reduced irradiation was studied in this work using several techniques: X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), and high resolution transmission electron microscopy (HRTEM).

## 2. Materials and experimental methods

Initial samples containing copper and oxygen (CuO) were prepared by cathode sputtering of copper target on a single crystal silicon substrate coated with a 0,15 μm layer of amorphous silicon oxide SiO<sub>2</sub> followed by the oxidation in air at 500°C for 1 h. The thickness of the initial films was about 10 nm.



CuO thin films were irradiated by ion beams extracted from high-frequency discharge plasma. Proton beam irradiation was performed with particle energies about 1 keV in a dose range  $(0.03-1.4) \cdot 10^{18} (\text{H}^+/\text{cm}^2)$ .

Phase and chemical composition of initial sample CuO were studied using “Titan 80-300ST” transmission electron microscope, operated at 200 kV, equipped with a GIF-2001 energy loss spectrometer. The EEL spectra were obtained with an energy dispersion of 0.5 eV/ch; convergence angle  $\alpha$  was 10 mrad, and collection angle  $\beta$  was 14.85 mrad. Cross sections of the samples CuO/SiO<sub>2</sub>/Si were prepared by FIB “Helios Nanolab 650”.

Quantitative EELS analysis was carried out with equation (1):

$$\frac{N_A}{N_B} = \frac{I_A(\beta, \Delta)}{I_B(\beta, \Delta)} \cdot \frac{\sigma_B(\beta, \Delta)}{\sigma_A(\beta, \Delta)}, \quad (1)$$

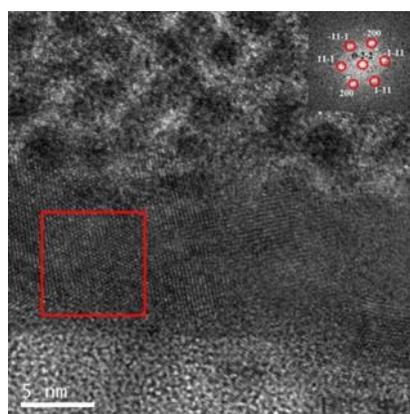
where  $I_A$  and  $I_B$  are integrated intensities of the EELS peaks after background subtracting, and  $\sigma_A$  and  $\sigma_B$  are ionization cross-sections [3].

The phase composition in the initial and irradiated samples was obtained from the corresponding HRTEM image using Fourier transform diffraction pattern technique similar to the one used in [4].

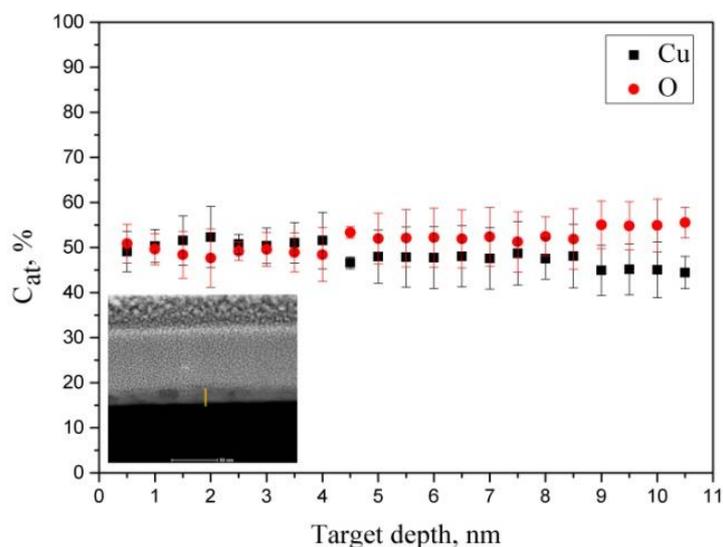
The identification of different chemical states of copper Cu<sup>2+</sup>, Cu<sup>+</sup>, and Cu<sup>0</sup> in thin films at different ion irradiation doses was performed using XPS taking into account the difference in peaks shape and corresponding chemical shift of energy spectra position. XPS analysis was performed on “Quantera Scanning XPS Microprobe System”, using monochromatic Al K- $\alpha$  X-rays. The spectra were obtained with 112 eV pass energy and 0.2 eV energy step size. To eliminate energy shift due to possible surface charge, the spectra were referenced to adventitious C<sub>1s</sub> peak at 284.8 eV.

### 3. Results and discussion

The standard copper oxidation method [5] in air for 1 hour at 500°C allowed obtaining the 10-nm-thick copper oxide layer as determined by HRTEM. Transmission electron microscopy data showed that initial films had polycrystalline structure with different grain orientations. Analysis of diffraction patterns showed that individual grains of initial material corresponded to a monoclinic CuO phase system (C2/c) with the unit cell parameters:  $a=0.4662$  nm,  $b=0.3417$  nm,  $c=0.5118$  nm,  $\alpha=\gamma=90^\circ$ ,  $\beta=99,48^\circ$  (Fig. 1). Elements depth-profile distribution in initial CuO film obtained by EELS technique in STEM mode is shown in Figure 2. Depth distributions of copper and oxygen relative concentrations in Figure 2 were calculated from EELS data using Eq. (1). Figure 2 proved the uniform distribution of the elements through the depth of the film, both average oxygen and copper content in the film was about 50% at.



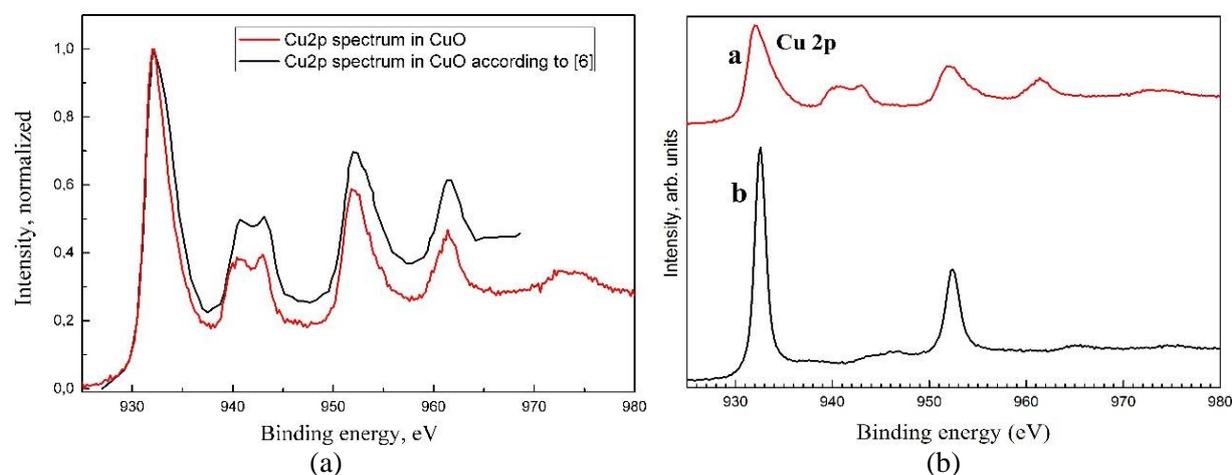
**Figure 1.** Bright-field HRTEM images of CuO film cross section synthesized on a SiO<sub>2</sub> substrate, in initial state, diffraction (inset).



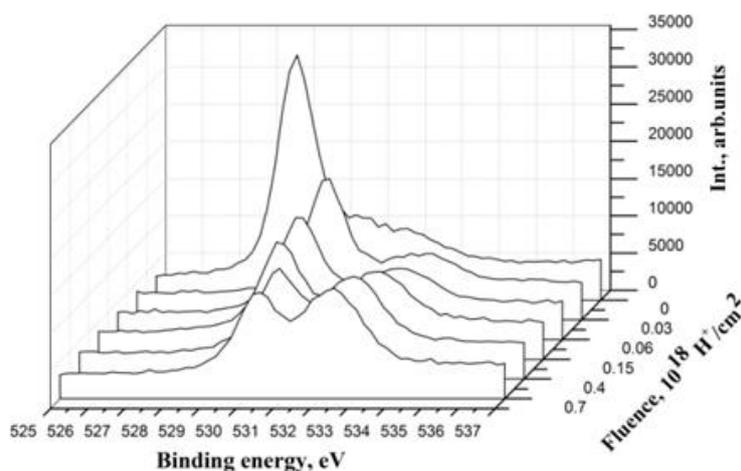
**Figure 2.** Elements distribution profile on the film depth for one grain (STEM image insert) calculated from EELS analyzing data.

The copper oxide CuO was formed from initial Cu film after thermal oxidation in air. Regardless of the valence state, Cu phase was characterized by Cu2p<sub>3/2-1/2</sub> doublet. The CuO XPS spectrum is characterized by high-intensity shake-up satellites at 9 eV higher binding energy than the main 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks, which are in addition considerably broader than in the case of bulk CuO and Cu metal [6, 7]. Figure 3a demonstrates a good correspondence for normalized Cu2p<sub>3/2-1/2</sub> XPS spectra obtained for CuO film in this paper and the one obtained for fully oxidized CuO surface according to [6]. Figure 3b shows XPS spectra of initial CuO film (curve a) compared to the one irradiated up to a dose of  $0.7 \cdot 10^{18} \text{ H}^+/\text{cm}^2$  (curve b).

After proton irradiation of initial CuO film up to  $1.4 \cdot 10^{18} \text{ H}^+/\text{cm}^2$ , the phase transition with formation of Cu<sub>2</sub>O occurred. Figure 3 (curve a) shows XPS spectra of irradiated CuO film up to a dose of  $1.4 \cdot 10^{18} \text{ H}^+/\text{cm}^2$ . Cu2p peak in the initial sample fitted the Cu<sup>2+</sup> state [7] with shake up satellites at high binding energies, absent in the spectra of irradiated samples (Fig. 3). Cu2p<sub>3/2</sub> peak position for irradiated samples (932.7 eV) as compared to the one for initial state (934.2 eV) also indicated the change of Cu valence state from 2 toward 1 or even 0. Thus, we observed a typical change in the spectrum during SRA process.



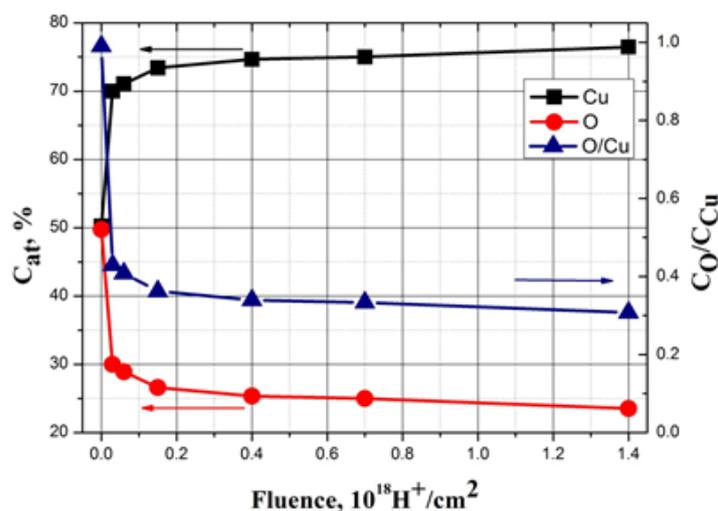
**Figure 3.** Cu2p<sub>3/2-1/2</sub> XPS spectra of (a) CuO film obtained in this paper and in [5], normalized for comparison; (b) initial CuO film (curve a) and irradiated up to the dose of  $0.7 \cdot 10^{18} \text{ H}^+/\text{cm}^2$  (curve b).



**Figure 4.** Evolution of O1s signal for Cu-O films: two features account for Cu-O and Si-O states.

It is well known that during the recovery process under ion beam irradiation of the different oxides films the thickness of the films decreases due to the removing of oxygen atoms according to SRA mechanisms [1]. Decreasing of the film thickness during the ion beam irradiation leads to the appearance of the silicon signal from the substrate in XPS spectra. Because of the well-defined chemical  $\text{Si}^{+4}$  state of silicon in thermal oxide in the substrate, there was easy to separate the part of oxygen signal corresponded to silicon oxidized state to get true oxygen concentration in Cu oxide film during irradiation.

For all the samples, O1s, Cu2p, and Si2p lines were analyzed. Si2p peak position was confined to (103.2-104 eV), indicating the oxide state of silicon. Figure 4 presented the evolution of O1s signal for Cu-O films during irradiation. Nature of the small arm on the part of high binding energy of oxygen O1s peak presented in the initial state is not clear. The shape of O1s peak for irradiated samples showed a complex structure implying at least two components (Si-bonded and Cu-bonded). Evolution of this peak could be characterized by decrease of oxygen component, associated with copper. This effect indicated the implementation of selective removal of oxygen atoms from initial compound of CuO. It was mentioned above that the weak Si2p peak was attributed to  $\text{SiO}_2$  substrate. The oxygen total amount was reduced by the value contained in the substrate to estimate the amount of Cu-bonded oxygen.



**Figure 5.** Dose dependencies of Cu and O atomic concentrations and Cu/O atomic ratio for CuO films under 1 keV proton irradiation.

Figure 5 shows O/Cu atomic ratio and corresponding Cu and O atomic concentrations in the film, obtained from XPS spectra analysis. At low irradiation doses, removal of oxygen atoms from the film was accompanied by a phase transition  $\text{CuO} \rightarrow \text{Cu}_2\text{O}$ . For higher irradiation doses up to  $1.4 \cdot 10^{18} \text{ H}^+/\text{cm}^2$ , the O/Cu ratio decreased, followed by the consequent removing of oxygen atoms from the film. Decreasing of the recovery speed with increasing of irradiation dose is a common feature of SRA process kinetics of different materials. It is clear from Figure 5 that complete recovering of CuO film to metal state would require higher doses of ion irradiation.

#### 4. Conclusion

To summarize results obtained in the present work, we can conclude that initial copper films oxidized in air have phase composition CuO. Further irradiation with 1 keV proton beams at different doses leads to phase transition  $\text{CuO} \rightarrow \text{Cu}_2\text{O}$ , which confirms that the process of selective removal of oxygen atoms takes place under 1 keV proton irradiation.

#### References

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