CuO films deposited by superimposed high power impulse and DC magnetron sputtering

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Abstract. Copper oxide films have been successfully deposited onto glass, fused quartz and Si(100) substrates by superimposed high power impulse (HIPIMS) and DC reactive magnetron sputtering. The deposition rate, adhesion, structure, wettability and optical properties of the obtained films were compared with those of CuO films deposited by conventional DC sputtering. X-ray diffraction analysis revealed that nanocrystallite size, single phase cupric oxide thin films with monoclinic structure were formed in all deposition modes. However, superimposing the direct current during off-time of HiPIMS pulsing allowed formation of denser film with smooth surface and good optical properties.

1. Introduction
Copper oxide films with semiconducting properties widely used as active layers in solar cells, sensors, batteries and other devices [1–3]. For the practical application, films of two compositions are interesting: cuprite (Cu2O) and cupric oxide (CuO) [4]. Both Cu2O and CuO are p-type semiconductors with band gap ranges within 1.8–2.5 eV and 1.2–1.9 eV, respectively [5, 6]. Most researchers have shown that the band gap of copper oxides also strongly depends on the growth methods and deposition parameters. For the deposition of copper oxide films, a wide range of methods are used, such as, chemical vapour deposition [7], sol-gel [8], electro-deposition [9], and thermal oxidation [10]. But the most widely used method is reactive magnetron sputtering [11, 12], which enable films deposition on large area substrates.

Reactive magnetron sputtering allows relatively easy to form mixtures of different Cu-O compounds. Different types of magnetron sputtering are used, such as direct current (DC) sputtering [13], mid-frequency (10–250 kHz) and high frequency (HF) sputtering [14, 15], high power impulse magnetron sputtering (HIPIMS) [16]. Recently, researchers have given the greatest interest to HIPIMS due to the possibility of obtaining a high plasma concentration (up to 10^{12} \text{ cm}^{-3}) and the degree of ionization of sputtered atoms [17, 18]. However, the disadvantage of this method is a decrease in the film deposition rate as compared with the DC sputtering mode. The reason for this is the attraction of ionized sputtered material back to the target. The disadvantage of sputtering in the DC mode, in turn, is the quality of the formed films, which have insufficient density due to the low plasma concentration (10^9–10^{10} \text{ cm}^{-3}).
In this work, copper oxide thin films were prepared by superimposed high power impulse (HiPIMS) and DC reactive magnetron sputtering and properties of the films were compared with properties of the films deposited in DC sputtering mode.

2. Methodology and materials
Copper oxide thin films were obtained by reactive magnetron sputtering of a Cu target (99.9% purity) with a diameter of 100 mm and a thickness of 6 mm at a DC and hybrid DC + HIPIMS modes. In both cases, the average discharge power was 500 W. In the DC mode, the power supply APEL-M-5PDC (Applied Electronics Ltd.), providing an average output power up to 5 kW, a voltage in the range from 300 to 650 V and an output current up to 8 A was used. DC + HIPIMS mode was realised using the APEL-M-5PDC power supply, APEL-M-5HIPIMS impulse power supply and a matching device, which periodically stopped the supply of constant voltage to the target and generated high-current voltage pulses. A glass with a size of 30×20×1 mm³, fused quartz with a size of 25×15×1 mm³, as well as single crystal silicon (100) with a size of 10×10×0.3 mm³ were used as substrates. The substrates were cleaned in an ultrasonic bath filled with acetone, isopropyl alcohol and distilled water for 10 minutes. After this, the substrates were dried and fixed on a substrate holder, located at a distance of 120 mm from the magnetron. The vacuum chamber was pumped to a residual pressure of $5 \times 10^{-3}$ Pa.

Before film deposition, the substrate surface was cleaned by an ion source with a closed electron drift. The discharge voltage was 1 kV at a current of 40 mA. In this case, argon with a pressure of 0.1 Pa was used as the working gas. After that, the CuO film was deposited at a pressure of 0.3 Pa. For all sputtering modes, the Ar and O₂ flow rates were constant and equal to 27 and 22.5 sccm, respectively. The thickness of the obtained CuO films varied from 100 nm to 1000 nm and regulated by deposition time.

The article compares films obtained in the three deposition modes with the parameters that are shown in table 1. The first is the DC mode with a discharge power of 500 W. The second and third are hybrid modes in which the discharge power of both DC and HIPIMS was 250 W, the pulse duration in a high power impulse mode was 100 μs (see scheme on figure 1c). In the second mode, the repetition rate of high-current pulses was 500 Hz, and in the third mode – 100 Hz. A decrease in the repetition frequency of high-current pulses in the hybrid mode led to an increase in the amplitude of the discharge voltage and current.

| Sputtering mode | Maximum discharge voltage and current | $U_{\text{HIPIMS}}$ (V) | $I_{\text{HIPIMS}}$ (A) | $U_{\text{DC}}$ (V) | $I_{\text{DC}}$ (A) |
|-----------------|--------------------------------------|-------------------------|-------------------------|-------------------|---------------|
| DC 500 W        |                                      |                         |                         |                   |               |
| DC 250 W + HIPIMS 250 W, 500 Hz | 372 | 40 | 324 | 0.77 |
| DC 250 W + HIPIMS 250 W, 100 Hz  | 445 | 100 | 333 | 0.76 |

The crystal structure of the films was identified by glancing incident X-ray diffraction (GIXRD, Shimadzu XRD 6000) and the Cu-Kα radiation was used as the X-ray source. The incident angle was fixed at 2°. The analysis of the phase composition was carried out using the PDF 4+ database, as well as the full-profile analysis program POWDER CELL 2.4. The surface morphology of the films was investigated by a QUANTA 200 scanning electron microscope. The water contact angles (WCA) of the thin films were determined on the EASY DROP installation. To measure the adhesive strength of the film, the Micro-Scratch Tester MST-S-AX-0000 was used. To study the optical parameters, such as the refractive index and extinction coefficient, the spectral ellipsometric complex “Ellipse 1891 SAG” was used. It recorded spectra in the wavelength range of 350–1000 nm with a resolution of 2 nm. Thickness of the deposited films was measured by MII-4 interference microscope (LOMO corp.).
3. Results and Discussion

3.1. Process characteristics

Typical feature of reactive magnetron sputtering is formation of compound on the target surface (target poisoning). Therefore, depending on the oxygen flow rate, three operation modes of the magnetron are distinguished: metallic, oxide and transition [19]. Deposition from a fully poisoned target (oxide mode) allows for growth of stoichiometric oxide films, but with the lowest rate. Therefore, many researchers try to work in a transition mode, where it is possible to form stoichiometric films with a higher deposition rate. In order to determine the boundaries of these modes, the dependences of the discharge voltage on the oxygen flow rate were measured (figures 1a and 1b).

![Figure 1](image_url)

In both DC and DC + HIPIMS mode the dependencies of the discharge voltage on the oxygen flow rate have a similar appearance. With increasing oxygen flow rate up to ~ 15 sccm, the discharge voltage increases. This is metal mode of sputtering. When the oxygen flow is increased, the discharge voltage decreases sharply indicating the transition from the metal to the oxide sputtering mode. When oxygen flow rate is more than ~ 28 sccm, the discharge voltage varies slightly. In this mode, the magnetron target is "poisoned". As a working point, we chose an oxygen flow rate of 22.5 sccm, and then the deposition of CuO films was carried out at this point of the transition mode.

Table 2 shows the variation of CuO films deposition rate as a function of sputtering mode. The maximum films deposition rate (102 nm·min⁻¹) was obtained in the DC mode. The deposition rate decreases 3–4 times in DC + HIPIMS mode.

| Sputtering mode | \( d \) (nm) | \( v_d \) (nm·min⁻¹) | \( E_g \) (eV) | \( \theta \) (°) |
|----------------|--------------|----------------------|--------------|-------------|
| DC 500 W       | 153          | 102                  | 2.27         | 101         |
| DC 250 W + HIPIMS 250 W, 500 Hz | 165          | 33                   | 2.11         | 91          |
| DC 250 W + HIPIMS 250 W, 100 Hz | 136          | 25                   | 2.10         | 97          |

\( d \) – film thickness, \( v_d \) – deposition rate, \( \theta \) – water contact angle, \( E_g \) – optical band gap.

![Table 2](image_url)
3.2. GIXRD of deposited films

Figure 2 shows the GIXRD patterns of 1-µm-thick CuO films deposited on Si substrates. XRD patterns show that all the deposited films are polycrystalline with monoclinic structure. GIXRD pattern shows a strong peaks at $2\theta = 35.53^\circ$ (002) and $38.4^\circ$ (111). Only one phase of copper oxide (CuO) is formed, while Cu$_2$O phase was not detected. The peaks position matches very well with the PDF Card No. 01-070-6829. There is a left-shift of the experimental diffraction lines relative to the control sample, indicated by the dotted lines in figure 2. This shift corresponds to the expansion of films in the out-of-plane lattice spacing which suggests that films have an in-plane compression. Table 3 shows the ratios of the integral intensities of (002) and (111) diffracting lattice planes. $I_{(002)}/I_{(111)}$ of DC-sputtered CuO films was less than that of films deposited in hybrid mode. This implies that the volume fraction of the (002)-oriented crystallites is larger than the volume fraction of the (111)-oriented crystallites. $I_{(002)}/I_{(111)}$ changed because surface energy is lesser for (002) plane than (111) plane. Analysis of diffractograms showed that the film deposited in the DC mode has a larger average crystallite size calculated by Scherrer formula and smaller internal stresses in compare with films deposited in hybrid modes (table 3).

![GIXRD patterns of CuO films deposited in (1) DC 500 W, (2) DC 250 W + HIPIMS 250 W, 500 Hz, (3) DC 250 W + HIPIMS 250 W, 100 Hz sputtering modes.](image)

3.3. Surface morphology analysis

Scanning electron microscopy (SEM) analysis was performed in order to investigate the surface topography of 1-µm-thick CuO films deposited on Si substrates films in more details. The films surface morphology was in strong relationship with deposition mode. Film deposited in DC mode has the roughest surface as shown in figure 3a. Films deposited in hybrid mode show smoother, denser and less defective surface.
Table 3. X-ray diffraction data of CuO films deposited in different modes of magnetron sputtering.

| Sputtering mode                  | Lattice parameters (Å) | Average crystallite size (nm) | $\Delta d/d \times 10^{-3}$ | $I_{(002)}/I_{(111)}$ |
|----------------------------------|------------------------|-------------------------------|-----------------------------|------------------------|
| DC 500 W                         | $a = 4.7049$           | 16                            | 3.2                         | 0.97                   |
|                                  | $b = 3.4300$           |                               |                             |                        |
|                                  | $c = 5.1012$           |                               |                             |                        |
|                                  | $\beta = 98.9722$      |                               |                             |                        |
| DC 250 W + HIPIMS 250 W, 500 Hz | $a = 4.6905$           | 10                            | 4.8                         | 1.22                   |
|                                  | $b = 3.4418$           |                               |                             |                        |
|                                  | $c = 5.1079$           |                               |                             |                        |
|                                  | $\beta = 99.2766$      |                               |                             |                        |
| DC 250 W + HIPIMS 250 W, 100 Hz | $a = 4.6697$           | 10                            | 4.5                         | 1.16                   |
|                                  | $b = 3.4253$           |                               |                             |                        |
|                                  | $c = 5.1368$           |                               |                             |                        |
|                                  | $\beta = 99.3485$      |                               |                             |                        |

Figure 3. Surface SEM images of CuO films deposited in (a) DC 500 W, (b) DC 250 W + HIPIMS 250 W, 500 Hz, (c) DC 250 W + HIPIMS 250 W, 100 Hz sputtering modes.
In hybrid DC + HiPIMS mode plasma is more ionized. As a consequence, more ions bombard the surface of the growing films which enhances the mobility of adatoms. Therefore the surface morphology of the films deposited in hybrid mode is relatively denser than that of DC mode.

3.4. Optical properties

Figure 4a shows the UV-V is transmission spectra of the CuO thin films deposited onto fused quartz substrates. The thickness of the obtained films is shown in table 2. Figure 4a shows that all spectra had a broad absorption edge, same as was also observed in [20].

Also reflectance spectra of CuO thin films in the same wavelength range were measured. Reflectance of less than 30% was observed for all deposited films. Low reflectance values very important for antireflection coatings used in solar cell fabrication.

The absorption coefficient \( \alpha \) was calculated based on the transmission and reflection spectra using the following relationship [21]:

\[
T \approx (1 - R^2) \cdot e^{-\alpha d},
\]

where \( d \) is the film thickness in cm.

Subsequently, the optical band gap of the films was estimated using Tauc’s equation [22]:

\[
(\alpha \cdot h\nu)^{1/n} = B^{1/n} \cdot (h\nu - E_g),
\]

where \( B \) is a constant, \( n \) is a constant depending on the quantum selection rules for particular materials.

Generally, \( n \) is 0.5 for materials with a direct band gap, and \( n \) is 2 for materials with an indirect band gap [23]. CuO mostly possesses a direct band gap [7].

![Figure 4. UV-Vis transmission spectra (a) and \((\alpha h\nu)^{1/n}\) versus \(h\nu\) of CuO thin films deposited onto fused quartz substrates.](image)

The optical band gap was further determined by plotting \((\alpha h\nu)^2\) versus \(h\nu\) and extrapolating the linear part. Figure 4b shows an extrapolation of the linear part of \((\alpha h\nu)^2\) versus \(h\nu\). Films obtained in the DC mode have an optical band gap of 2.27 eV, while films obtained in the hybrid deposition mode (DC + HiPIMS) have \(E_g = 2.1–2.11\) eV. The obtained results consistent with those reported by Pierson et al [24], who found that magnetron sputtered CuO films have a direct band gap of 2.11 eV.

The refractive index \( n \) is one of the fundamental properties of an optical materials and its value is important for films applications in integrated optic devices. The dependences of refractive index and extinction coefficient \( k \) on wavelength measured for CuO thin films by spectroscopic ellipsometry are shown in figure 5.
Figure 5. Measured spectral dependencies of refractive index and extinction coefficient of CuO films.

The values of the refractive index lie between 1.75 and 2.75 in the wavelength range between 350 and 1050 nm. The extinction coefficient decreases from 1.5 to 0.25 as function of wavelength. Measured values of refractive index and extinction coefficient match well with these characteristics of polycrystalline samples of monoclinic CuO grown by float-zone melting technique [25].

3.5. Wettability
Surface wetting is usually characterized by a contact angle, which is determined by the chemical nature of the surface and its roughness. The water contact angles of obtained CuO films are shown in table 2. The maximal value of WCA (101°) has the film deposited in DC mode. The films obtained in hybrid DC + HiPIMS mode have a slightly smaller WCA values (91 and 97°). Zhao et al [26] have shown that the wettability of Cu$_2$O/CuO composite thin films can be regulated in wide range by preparation conditions and changed from 59 to 151.

3.6. Adhesion
In order to determine the effect of the deposition regime on the adhesion of CuO films to glass substrates, the samples were subjected to a scratch test. To measure the adhesion of the films, controlled scratching of the sample was applied using a diamond indenter. The indenter passed over the surface of the film with increasing load $L$ from 0 to 15 N. At a certain critical load, the film began to break down. The critical load is determined using an acoustic emission sensor. Figure 6 shows the recorded acoustic emission signals, in which strong bursts of acoustic emission indicate the beginning of the film destruction.

It is seen that CuO films obtained in the hybrid DC + HiPIMS mode have better adhesion than films deposited in the DC mode. In hybrid DC + HiPIMS mode, instantaneous values of discharge current are significantly higher than in DC mode. At high discharge current, particles nucleating on the substrates have sufficient kinetic energy to undergo diffusion and reaction. The mobility of the nucleating particles is also increased, which leads to an increase in films adhesion.
4. Conclusion

Cupric oxide films were deposited onto glass, fused quartz and Si(100) substrates by reactive DC magnetron and hybrid DC + HiPIMS magnetron sputtering at room temperature. Results show only one phase copper oxide for films deposited in both modes. DC sputtering is characterized by higher deposition rate and films deposited in the DC mode have a larger average crystallite size and smaller internal stresses in compare with films deposited in hybrid modes. DC sputtered CuO films have an optical band gap of 2.27 eV and large value of water contact angle (101°). However, CuO films obtained in hybrid DC + HiPIMS sputtering mode demonstrate smoother, denser and less defective structure, better adhesion to glass substrate. They have an optical band gap of 2.10–2.11 eV and water contact angle in range of 91–97°.

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