

Preparation of copper oxide films on alumina in a hot-target HiPIMS process

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Abstract. Copper oxide thin films are widely used in many fields, such as solar cells, optoelectronics, catalysis, biosensors, photoelectrochemical sensors, supercapacitors, lithium-ion batteries, infrared photodetectors, electrochemical sensors, and gas sensors. They can also be applied to improve adhesion of comparatively thick copper coatings for ceramic PCB metallization. Here, we report the results of Cu_xO_y deposition on alumina substrates in a hot-target HiPIMS discharge. The experiments were carried out in a magnetron deposition facility with thermally insulated copper target. Cu_xO_y films with thickness around 2–3 μm were prepared. Their structure was studied with scanning electron microscope, and the composition was measured by EDS and XRD methods. The results showed predominant growth of stoichiometric CuO films. The correlations between deposition parameters and coating characteristics are discussed.

Keywords: reactive magnetron sputtering, evaporation, HiPIMS, hot-target magnetron, copper oxide

1. Introduction

One of the basic processes in production of electronic devices is the metallization of dielectric substrates, and particularly, preparation of ceramic print circuit boards (PCBs). There are various methods suitable for applying a conductive copper layer to a dielectric substrate. These include active metal brazing (AMB), cold gas-dynamic spraying (CGS), direct bonded copper (DBC) lamination, and a number of thick-film and thin-film vacuum technologies. The usage of plasma deposition methods for ceramic metallization is limited, mainly due to the relatively low productivity. However, in some applications, for example, when it is necessary to metallize substrates of complex topology, plasma methods might outperform popular mass production technologies in terms of quality and efficiency.

To improve adhesion of comparatively thick (more than 20 μm) magnetron deposited copper coatings, a dedicated intermediate layer of Cu_xO_y can be introduced between the substrate and the film. That prolongs the service life of a ceramic PCB. However, copper oxide is also widely used in other fields, such as solar cells, optoelectronics, catalysis, biosensors, photoelectrochemical sensors, supercapacitors, lithium-ion batteries, infrared photodetectors, electrochemical sensors, and gas sensors [1–3].

Here, we report the results of comparatively fast CuO deposition on alumina substrates in a hot-target HiPIMS discharge.

2. Experimental setup

The experiments were carried out in a magnetron deposition facility with thermally insulated copper target. To form the discharge, an APEL-M-5HPP-1200 power supply was used. Initially, the magnetron was separated from the substrate by a shutter. In the beginning of the process, the target was heated and melted by a HiPIMS discharge in Ar, at 0.5 Pa pressure and average power 1000 W. Then desirable O₂ flow was set, while Ar flow was decreased down to zero. The shutter was opened, and the oxide deposition was performed.

In the experiments the average discharge power was fixed at 1000 W, operating oxygen pressure in the deposition stage was 5.5×10^{-3} Torr (no argon). The HiPIMS repetition frequency range was 250–1000 Hz. Pulse duration was varied in the range 100–400 μs.

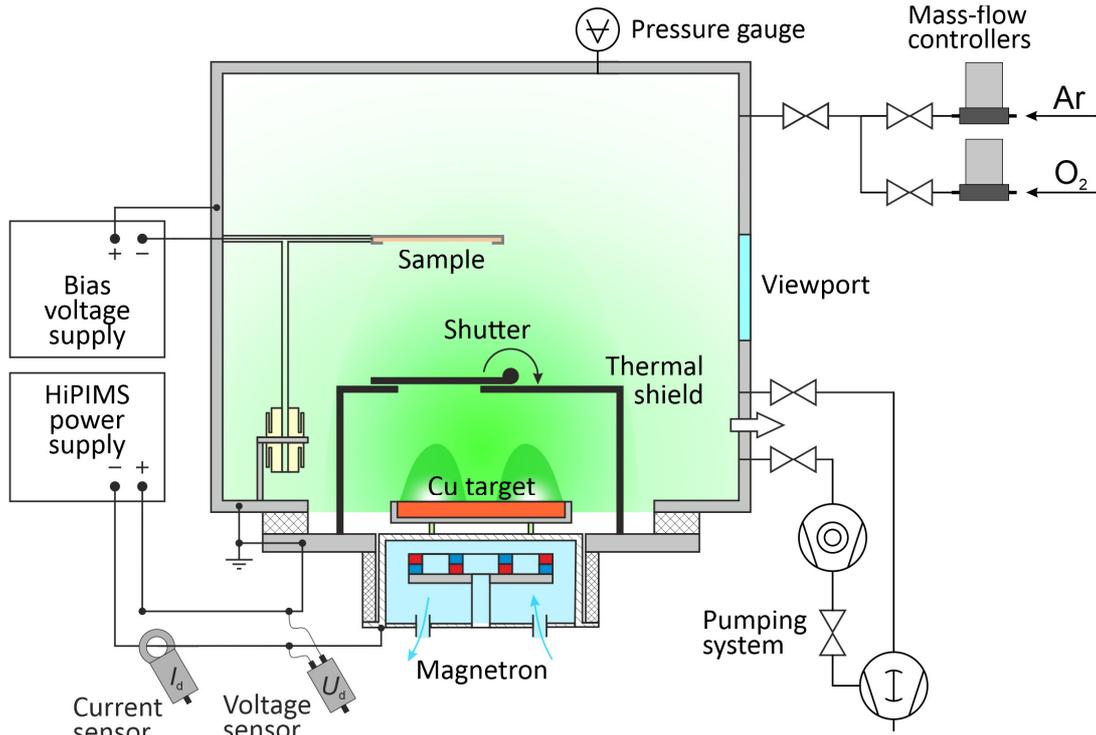


Fig.1. Experimental setup.

Cu_xO_y films with thicknesses 1–6 μm were prepared. Their structure was studied with scanning electron microscope (SEM) Tescan Vega 3, and the composition was measured by EDS (Oxford Instruments X-Act) and XRD methods. The film thickness and surface roughness was measured with a surface profiler Veeco Dektak 150.

3. Results and discussion

3.1. Deposition rate

The film thickness dependences on pulse duration and on repetition frequency are shown in Fig.2. Thickness values are listed in Table 1.

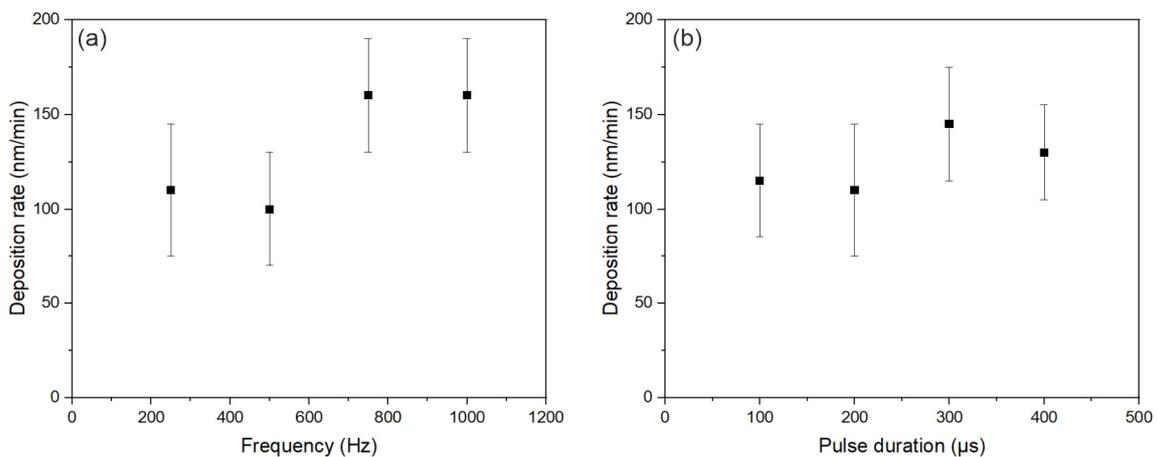


Fig.2. Film thickness dependences (a) on repetition frequency and (b) on pulse duration.

The current in the HiPIMS pulse increased with decreasing both frequency and duration, and in these experiments it was 5–45 A, which is much higher than in DC mode. By looking at the

thickness curves of the obtained oxide films (Fig.2), we can conclude that with an increase in the discharge current density in a pulse, the average deposition rate somewhat decreases, which is in accord with the conventional HiPIMS behavior. However, the absolute deposition rate values of around 100–200 nm/min are very promising for applications. The surface roughness of initial samples is preserved in the coatings ($R_a \sim 0.3 \mu\text{m}$).

3.2. Coating structure

The coating surface images taken with SEM are presented in Fig.3.

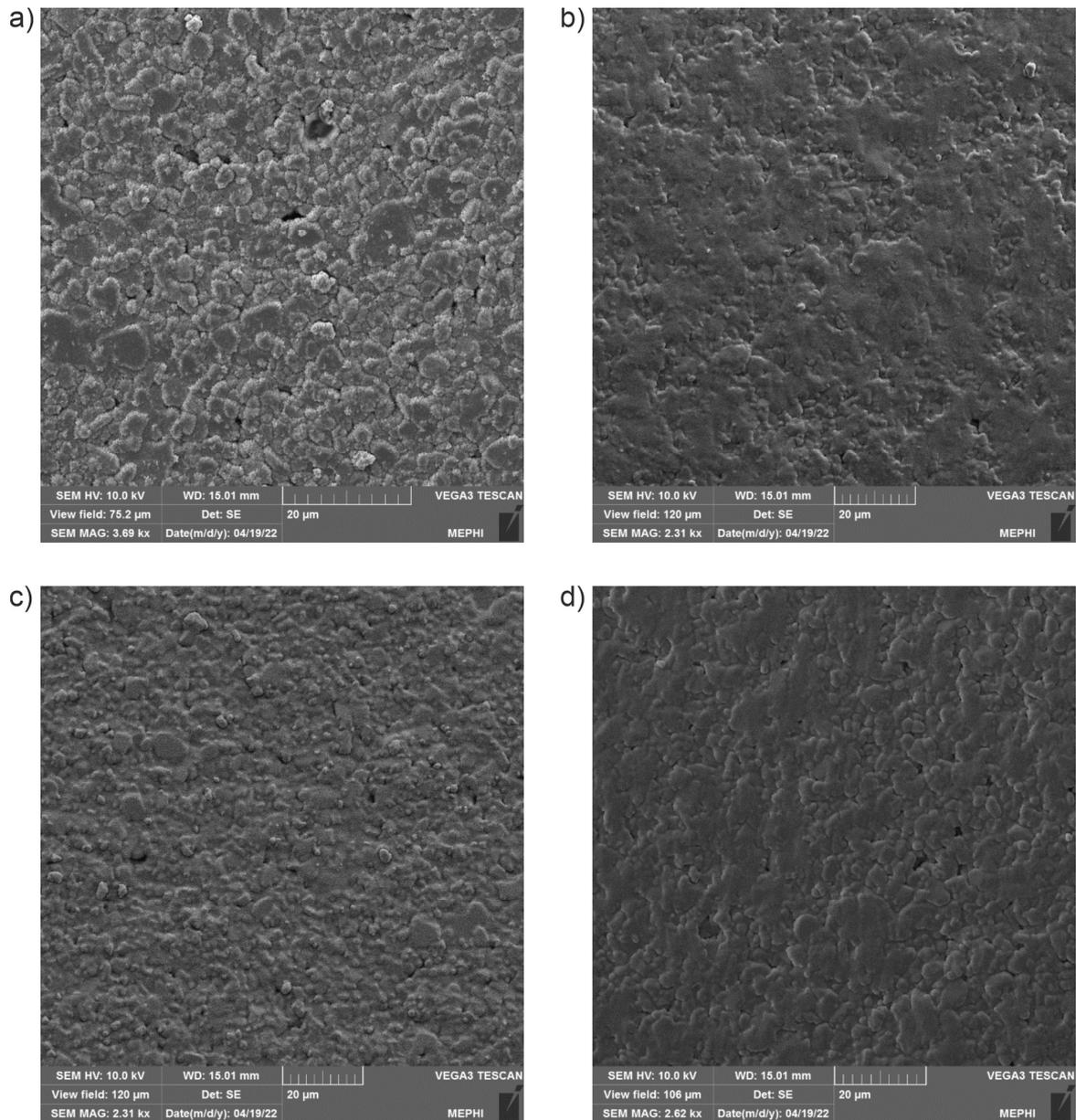


Fig.3. SEM images of coating surface: (a) $\tau = 200 \mu\text{s}$, $f = 1250 \text{ Hz}$; (b) $\tau = 200 \mu\text{s}$, $f = 250 \text{ Hz}$; (c) $\tau = 400 \mu\text{s}$, $f = 250 \text{ Hz}$; (d) $\tau = 100 \mu\text{s}$, $f = 250 \text{ Hz}$.

From the SEM images, it can be concluded that as the current density in the pulse increases, the film surface becomes more uniform and smooth.

3.3. EDS and XRD measurements

EDS measurements for all samples showed nearly 1:1 fraction of Cu:O atoms indicating the film composition close to the stoichiometric CuO. The results are shown in Table 1.

X-ray analysis of the phase composition has been carried out for seven copper coatings on a corundum substrate (Al_2O_3). Recording of diffraction spectra to determine the phase composition of the samples and assess their structural state was carried out on a Bruker D8 Discover diffractometer using Cu $K\alpha$ radiation and a LynxEye position-sensitive detector. The analysis was carried out with a step of 0.01° along the 2θ Bragg angle and with accumulation time of 0.5 s for each detector strip, which in total gives about 85 s for each point along the angle. The BrukerAXS DIFFRAC.EVA v.4.2 software and the ICDD PDF-2 international database were used to identify the phases, TOPAS was used to determine the structural characteristics, and the X-ray reflection profile was corrected according to the data for the LaB_6 reference sample (NIST SRM 660b). According to the measured diffraction spectra, it was found that all coatings mainly consist of the following compounds: CuO (tenorite, monoclinic lattice) and $\text{Cu}_2\text{Al}_4\text{O}_7$ (cubic lattice). The spectra of coatings No. 1–4 contain lines of cuprite Cu_2O (cubic lattice) as well. Al_2O_3 substrate lines (rhombohedral lattice) are also visible in all spectra. The thickness of coatings No. 1–7 was measured. The coating thickness was evaluated as: $h = \sin\theta / (2\mu_{\text{coat}}) \times \ln(I_{\text{uncoat}}/I_{\text{coat}})$ where μ_{coat} is the linear absorption coefficient of the film ($\mu_{\text{CuO}} = 289 \text{ cm}^{-1}$), I_{uncoat} is the reflection intensity for a clean substrate, I_{coat} is the intensity for a coated substrate. All results are presented in Table 1.

Table 1. Deposition parameters and results of diagnostics for Cu_xO_y coatings

| Sample no. | f (Hz) | τ , μs | O:Cu (EDS) | 2θ , (deg.) | I | Thickness (XRD), (μm) | Thickness (profiler), (μm) |
|------------|----------|------------------------|------------|--------------------|------|------------------------------------|---|
| 1 | 250 | 100 | 1:1 | 57.48093 | 3130 | 2.87 | 2.3±0.6 |
| 2 | 250 | 200 | 1:1 | 57.48651 | 3130 | 2.87 | 2.2±0.7 |
| 3 | 250 | 300 | 1:1 | 57.51163 | 3206 | 2.67 | 2.9±0.6 |
| 4 | 250 | 400 | 1:1 | 57.51733 | 3230 | 2.61 | 2.6±0.5 |
| 5 | 500 | 200 | 1:1 | 57.55269 | 3556 | 1.81 | 2.0±0.6 |
| 6 | 750 | 200 | 1:1 | 57.50383 | 3124 | 2.89 | 3.2±0.6 |
| 7 | 1000 | 200 | 1:1 | 57.50168 | 3410 | 2.16 | 3.2±0.6 |

4. Conclusion

CuO deposition on alumina ceramic substrates was performed in experimental hot-target HiPIMS modes with melted copper target in pure oxygen atmosphere. It is shown that, depending on the pulse duration and repetition frequency, at constant power, the parameters of the deposited film change: the deposition rate is lower for modes with higher pulse current, however the structure morphology becomes better with increasing current. We demonstrated the implementation of a stable regime of copper oxide deposition in a pulsed magnetron in an oxygen atmosphere without argon with the required stoichiometry in a wide range of pulse parameters. The results showed predominant growth of stoichiometric tenorite CuO films with deposition rate of 100–200 nm/min.

Acknowledgements

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5. References

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