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Published in:

Journal of Physics: Conference Series (Online)

DOI (link to publication from Publisher):

[10.1088/1742-6596/2015/1/012148](https://doi.org/10.1088/1742-6596/2015/1/012148)

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Publication date:

2021

Document Version

Publisher's PDF, also known as Version of record

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Solovey, V. R., Yakubovsky, D. I., Ermolayev, G. A., Lebedinskij, Y. Y., Markeev, A. M., Voronov, A. A., Zamboni, F., Popok, V., Arsenin, A. V., Volkov, V. S., & Novikov, S. M. (2021). UV/Ozone Treatment and Open-Air Copper Plasmonics. *Journal of Physics: Conference Series (Online)*, 2015, [012148]. <https://doi.org/10.1088/1742-6596/2015/1/012148>

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To cite this article: V. R. Solovey *et al* 2021 *J. Phys.: Conf. Ser.* **2015** 012148

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UV/Ozone Treatment and Open-Air Copper Plasmonics

Solovey V. R.^{1, a)}, Yakubovsky D. I.¹, Ermolayev G. A.¹, Lebedinskij Y. Y.²,
Markeev A. M.², Voronov A. A.¹, Zamboni F.³, Popok V. N.³, Arsenin A. V.¹,
Volkov V. S.¹ and Novikov S. M.¹

¹Center for Photonics and 2D Materials, Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Russia

²Center of Shared Facilities in Nanotechnology, Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Russia

³Department of Materials and Production, Aalborg University Skjernvej 4A, 9220 Aalborg, Denmark

^{a)}Corresponding author: solovey.vr@phystech.edu

Abstract. Thin copper films with thickness ~28 nm deposited on SiO₂ substrate with the vacuum electron beam evaporation method and treated by UV-ozone are studied. It was found that a UV-ozone treatment of the copper film causes rapid formation of the thin ~3-4 nm oxide film. XPS analysis showed that CuO oxide predominates in this film. The formed oxide film effectively protects the copper against the following oxidation. The presented method of UV-ozone treatment is a simpler and cheaper approach compared to many other ways to form protective coatings of copper to preserve its functional properties. This method can be useful in nanoelectronic, nanooptical, and biosensors applications.

Introduction. Metals with plasmonic properties in the visible and near-infrared (NIR) ranges such as gold, silver, and copper can be used for optical, electronic, sensing and other applications, which are currently of high interest [1, 2]. The important issue is the stability of plasmonic properties, which often limits the use of some metals due to their chemical reactivity and the possibility of spurious effects. The most common material used for plasmonic is gold, which demonstrates excellent optical properties as well as resistance to oxidation. The limitations of gold in plasmonics include its high price and incompatibility with microelectronic technological processes. Silver shows superior performance due to low optical losses and also widely used [3-7] but generally considered to be less attractive due to lower chemical and, thus, plasmonic stability [8]. Copper is another metal, which has excellent optical properties. Compared with gold, it is inexpensive and has lower optical losses in the visible and NIR range. The advantages of copper in plasmonic applications were exploited for instance in the ultralow-loss copper plasmonic waveguides and biosensing applications [9-13]. Copper is prone to relatively fast surface oxidation upon exposure to an ambient atmosphere [14]. Under normal conditions, the dominant product is Cu₂O with a minor or no contribution of CuO. Thus, to use Cu films for plasmonic applications, one needs to protect the surface of structures against oxidation-induced degradation. It can be done by applying a protective shell/coating of SiO₂, Al₂O₃ or even graphene [10, 15]. In this work, we test a simple method of UV-ozone treatment, which leads to the rapid formation of a thin oxide layer on a copper film. This oxide layer effectively protects the copper against the following oxidation-related degradation of the plasmonic properties, which was recently proven for Cu nanoparticles [16]. We performed a complex analysis of the formed oxide layers. We anticipate that the presented results will be of interest as a simple and effective method for preserving the plasmonic properties of thin copper films to be used in non-linear optics or sensing applications.

Sample Fabrication. Copper films with thicknesses of 28 nm were deposited using electron beam evaporation in a NEE-4000 E-Beam Evaporation system. Clean silicon wafers capped with a top layer of 2 nm thick SiO₂ were placed in the vacuum chamber of the e-beam evaporator at a pressure of 3×10^{-7} Torr, at room temperature. As a material for deposition, granules of copper with a purity of 99.99% were used. The deposition rate was approximately 2 Å/s. 8 identical samples were fabricated simultaneously in one cycle. The quoted "thickness" of the copper films is the



average value measured by the quartz oscillator. The fabricated films were subsequently imaged by scanning electron microscope (SEM) JEOL JSM-7001F (Figure 1b).

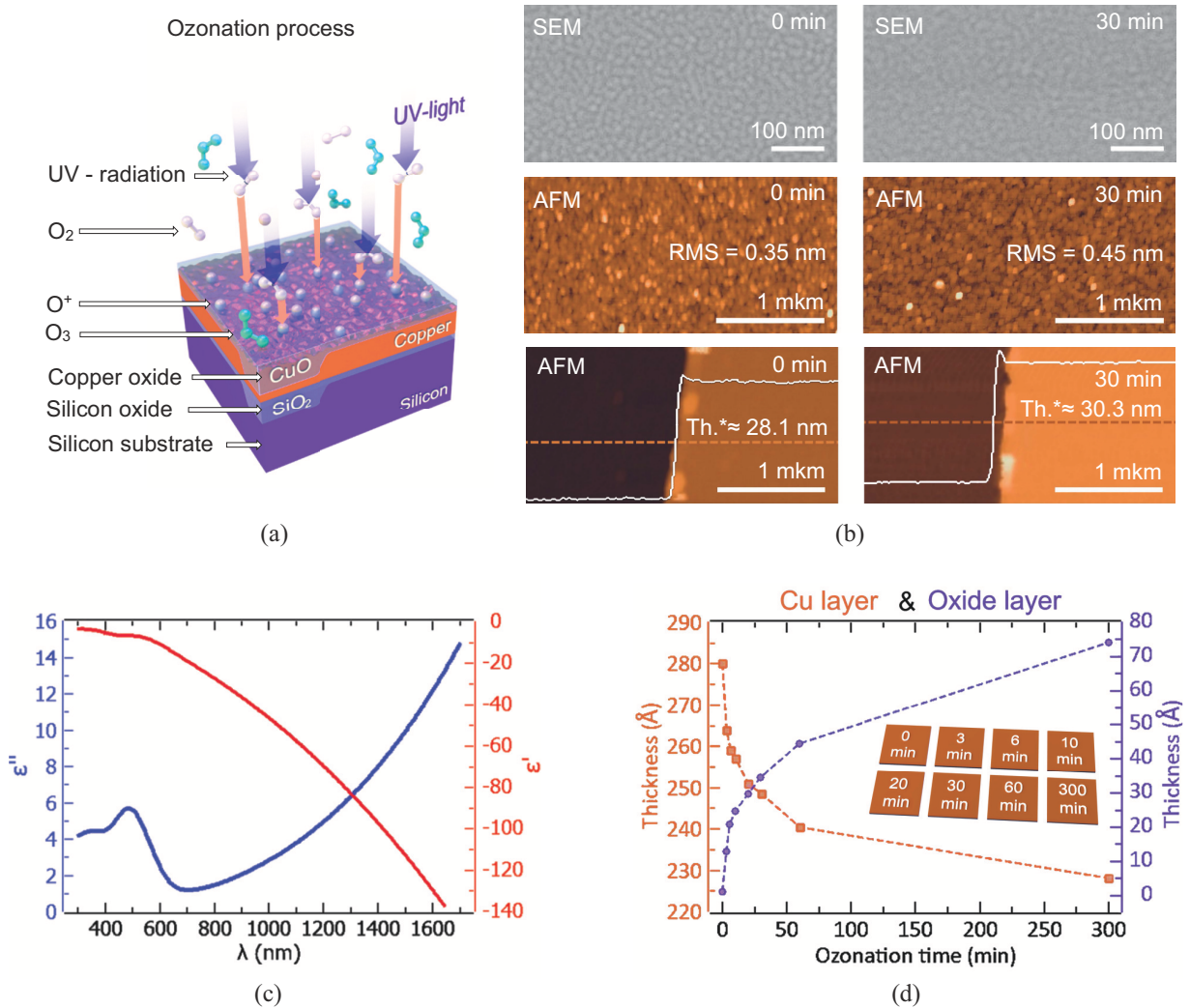


FIGURE 1. (a) The synthesis scheme of the CuO layer on the surface of a thin copper film using UV-ozonation, (b) SEM and AFM images of the surface of the deposited copper film (after 0 and 30 min ozonation); (c) Dependence of the real and imaginary parts of the dielectric function on wavelength for the pure copper film on a SiO₂/Si substrate, (d) Dependence of the thickness of a copper film on the time of UV-ozonation and schematic representation of samples in the inset.

Right away after deposition, 7 out of 8 substrates were treated by the UV Ozone Cleaner (Ossila Limited). During UV-cleaning, the ultraviolet radiation breaks the oxygen-oxygen double bond resulting in the formation of two free radicals of oxygen O. These free radicals can react with molecular oxygen producing ozone molecules O₃. The mixture of O and O₃ can lead to a rapid oxide film formation on the copper surface (Figure 1a). In order to estimate the oxide film growth versus time, substrates were UV treated with different duration of time as 3, 6, 10, 20, 30, 60, and 300 min, see Figure 1d (each sample has only one own processing time). One Cu film was not treated by UV and was used as a reference sample for the measurement of Cu film optical properties.

Sample Characterization. The optical properties of copper films (reference and exposed to UV-cleaning) were studied with the V-VASE Ellipsometer (Woollam Co.). The spectral range was 300-1700 nm, and the angles of incidence of the light beam were 65°, 70°, and 75°. The thickness of the films was accurately measured by atomic force microscopy (AFM) at a step of the film on the substrate and it was found to be 28.0 ± 0.5 nm (Figure 1b). These measurements of the thickness are necessary to carry out a correct fitting of the ellipsometry data. The spectra of real

and imaginary components of the dielectric function of the copper film (reference sample) were found from data measured by a variable-angle spectroscopic ellipsometer (Figure 1c). The multilayered model consisted of Si substrate, Cu film and CuO layer (data based on XPS analysis) was applied [17]. It was found that the copper thickness decreases with the increase of ozonation time, which can be an indication of oxide layer formation at the expense of metallic copper (see Figure 1d). It should be noted that the above-mentioned model of thickness estimation has drawbacks, because it accounts only for CuO but does not consider the possible formation of other copper oxides or hydroxides. Also, AFM data shows that the thickness of Cu film increases after UV-ozone treatment in comparison with the reference Cu film, non-treated by UV-ozone. (Fig 1b).

Additionally, we measured the reflectance spectra (Figure 2a) and performed XPS analysis (Figure 2b). Figure 2a shows the dependence of the reflectance spectra of all samples on the ozonation time. The chemical state and composition of the samples were analyzed using the Theta Probe tool (Thermo Scientific) under high-vacuum conditions with a monochromatic Al K α X-ray source (1486.6 eV). The XPS analysis was carried 4 hours after the film fabrication and the samples were kept in an ambient atmosphere. The XPS spectra of the reference sample presented in Figure 2b show the characteristic bands at 932.6 and 952.4 eV. Unfortunately, Cu and Cu₂O have nearly the same binding energy, [18, 19], and the bands can be an indication of both Cu and Cu₂O. From the narrow bandwidth of Cu2p_{3/2} one can suggest that the signal comes from the metal but we must allow the Cu₂O formation during the time the samples were kept in the air.

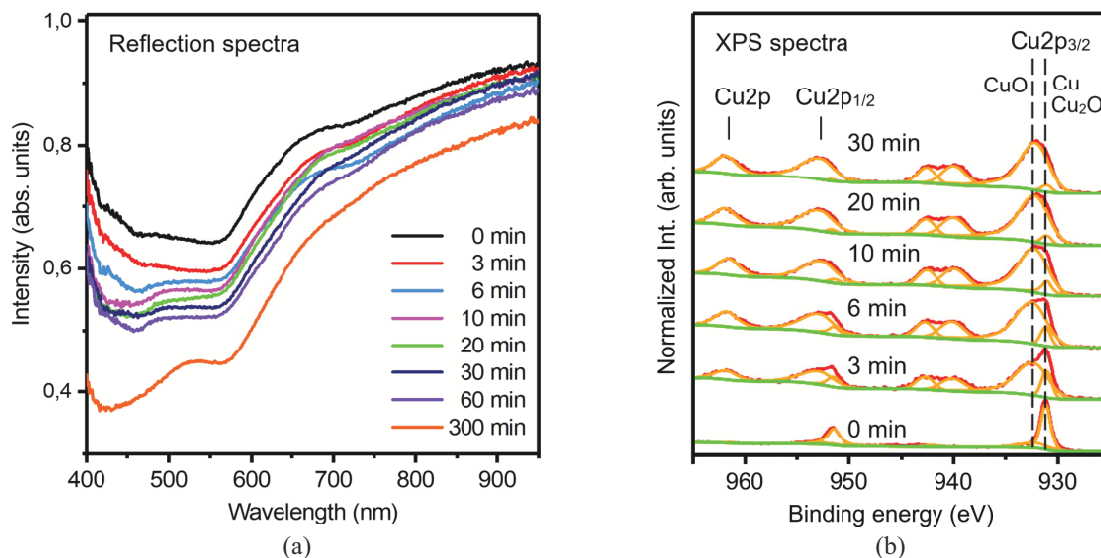


FIGURE 2. Reflection spectra (a) and XPS data analysis of the surface of a thin copper film in an air atmosphere and after UV-cleaning for 0, 3, 6, 10, 20 and 30 minutes (b).

The XPS spectra of the copper films ozonated for 0, 3, 6, 10, 20 and 30 min, are presented in Figure 2b. They show a significant increase of the Cu2p_{3/2} and Cu2p_{1/2} shoulders at 934.7 and 954.5 eV, respectively. The latter can be assigned to CuO, while the former one can correspond to copper dihydroxide, Cu(OH)₂ [19]. Two new strong satellites at 941 and 963 eV, which are typical for CuO spectra, are also observed [19]. The obtained results show a significant difference in the copper oxidation under the ambient conditions and UV-ozone treatment. While for the films oxidized in the ambient atmosphere the Cu₂O predominates with a minor or no contribution of CuO [20], for the UV-ozone treated copper film, the oxidation undergoes predominantly through the CuO formation. Based on the ellipsometry and XPS measurements (depth of XPS analysis is low, ≤ 3 nm) it is possible to estimate the thickness of formed oxide as 3-4 nm.

Summary. It was demonstrated that a UV-ozone treatment of the copper film causes rapid formation of the thin oxide layer. XPS analysis showed that CuO oxide predominates. This oxide layer can protect the metallic copper against the following oxidation. The presented method of UV-ozone treatment is a simpler and cheaper approach compared to many other ways utilizing protective coatings to preserve the metallic copper against chemical degradation. Thus, it can be recommended for the protection of copper surfaces to be used in plasmonic or sensing applications.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Ministry of Science and Higher Education of the Russian Federation (No. 0714-2020-0002) and the Russian Foundation for Basic Research (20-07-00475 and 20-07-00840). We thank the Shared Facilities Center of the Moscow Institute of Physics and Technology for the use of their equipment.

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