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SYNTHESIS AND COMPARATIVE STUDY OF NANOSCALE THIN-FILM STRUCTURES BY VACUUM PULSED LASER DEPOSITION AND LASER ABLATION IN LIQUIDS

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The low-cost, non-toxic nature and abundance of the copper oxide makes it a suitable option for the various applications. The production of copper oxides-based nanoscale structures is of both fundamental and practical interest for their use in fabrication of solar cells, sensors, photodetectors and other optoelectronic devices as well as for biomedical applications [1, 4]. An important task is to find efficient methods for the controlled synthesis of nanostructures. One of the promising methods for obtaining NPs and thin films nanostructures without the use of chemical reagents is pulsed laser ablation (PLA) of bulk targets in liquid or gas/vacuum. Some of the advantages of such techniques are that the energy source is well confined at the surface of the target, and by that it contributes to the efficiency, the flexibility and the control of the processes [2, 3].

In the present study, properties of copper oxides nanostructures prepared by vacuum pulsed laser deposition (VPLD) and laser ablation in liquid (LAL) are discussed. The morphology, structure and optical properties of the prepared samples were analysed by the XRD, EDX, SEM techniques, UV-Vis absorption and Raman spectroscopy (RS). Laser sputtering experiments in both methods were carried out by focusing the radiation of a Nd:YAG laser operating at 1064 nm on a surface of the prepared target. A pressed target was formed from the ceramic copper oxide powder (99.9%) followed by annealing in muffle furnace in a temperature range 900–1100 °C.

The parameters of Nd:YAG laser radiation for the VPLD experiment were: pulse duration 30 ns, pulse energy 0.35 J, intensity in the target irradiation zone 10^7–10^9 W/cm^2, pulse repetition rate 1 Hz. Laser-sputtering setting, consisting from laser and vacuum chamber was used. Maximum residual presser in vacuum chamber was $2\text{x}10^{-6}$ mm Hg.

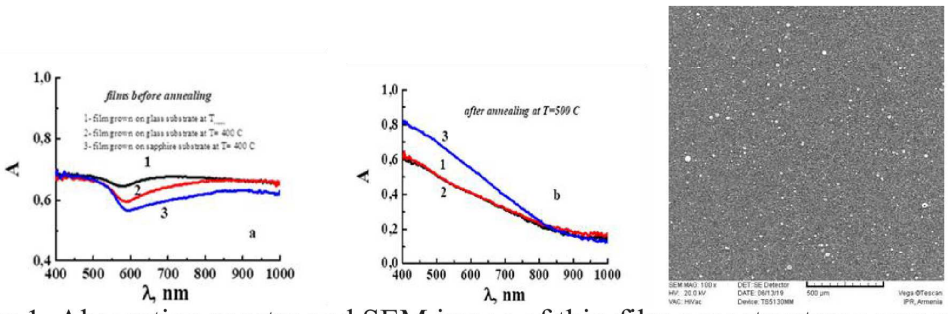

Figure 1. Absorption spectra and SEM image of thin-film nanostructures prepared by VPLD before (a) and after (b) annealing; 1,2 – on glass substrate, 3- on sapphire substrate.

Thin-film nanostructures on glass and sapphire substrates at room temperature and T_{grown} = 400 °C were obtained. As-deposited films of a thickness of 70 nm were annealed at different temperatures in the range of 500-700 °C. The nature of the absorption spectra relationship A(λ) regardless of the growth temperature at both T_{room} and at T=400 °C is the same for all films (Fig. 1).

The parameters of laser radiation for the LAL experiment were: 80 mJ/pulse energy, repetition rate 10 Hz, pulse duration 8 ns. The radiation of the Nd:YAG laser (LOTIS TII, LS2134D), operating in a double-pulse mode at 1064 nm was focused on a surface of metallic copper and CuO targets placed in the cell filled with a liquid (water or isopropyl alcohol). Quasi spherical nanoparticles (NPs) with similar morphology were obtained by laser ablation (LA) of the CuO target in both solutions.

As can be seen from the absorption spectra, the presence of copper plasmon resonance peak at 600 nm indicates that after laser ablation of CuO target in i-PrOH metallic copper NPs are formed opposite to the LA in water where the particles composition most probably corresponds to the CuO target composition (Fig. 2). This result was also confirmed by X-ray microanalysis.

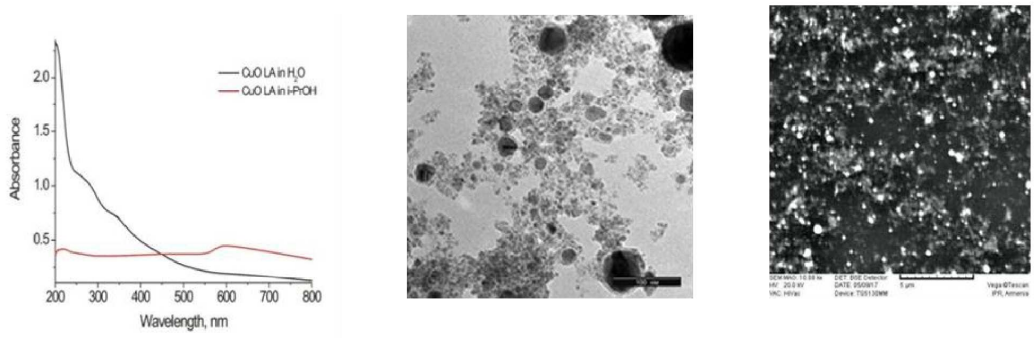

Figure 2. Absorption spectra, TEM and SEM images of the samples prepared by LAL.

Using two different methods copper oxide NPs and thin-film nanostructures were synthesized on glass and sapphire substrates at different growth conditions. SEM images confirmed the production of tightly packed structures with an average grain size 50 nm (LAL) and up to 150 nm (VPLD). According to EDX, the composition of the obtained films is close to the composition of copper oxide CuO, which is in a good agreement with XRD and Raman measurements. The results obtained showed that the control of stoichiometry, as well as stability, size and crystallinity of the formed samples has been achieved by a proper selection of the experimental parameters such as a composition of a liquid used (LAL) or annealing and growth temperature (VPLD), laser fluence, interpulse delay and ablation exposition.

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