Publ. Astron. Obs. Belgrade No. 102 (2022), 129 - 132 *Contributed Paper*

COMBINING PLASMA-ASSISTED SYNTHESIS OF METAL OXIDE NANOPARTICLES WITH THIN FILMS DEPOSITION

NATALIE TARASENKA, VLADISLAV KORNEV, ALENA NEVAR, MIKHAIL NEDEL'KO, ANTON RADOMTSEV and NIKOLAI TARASENKO

B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, 220072, Belarus
E-mail natalie.tarasenka@dragon.bas-net.by

Abstract. Two approaches were developed for the simultaneous synthesis and deposition of metal oxide nanostructured thin films based on atmospheric pressure electrical discharge in contact with liquid and laser ablation in the applied electric field. Both techniques allowed formation of uniform thin films of zinc oxide promising for photovoltaic and photodetector applications. Laser-assisted approach demonstrated the possibility of non-spherical flower-like nanomaterials deposition that may find application in fabrication of supercapacitors electrodes.

1. INTRODUCTION

Nanosized materials offer a row of improved characteristics that can result in expanding the application range and overcoming the limitations and drawbacks of many current devices. Among the fields that are intensively developing due to the application of novel nanostructured materials is energy generation and storage. Recent advances in this field are associated with the development of new composite nanostructured materials, such as nanomaterials based on carbon, nanostructured inorganic materials, coordination polymers, perovskites, nanostructures of transition metal oxides, etc (Wang et al. 2020). Typically, nanoparticles (NPs) properties are determined by their size, composition and structure. In addition, a number of applications often require NPs deposition into thin films and ordered structures that imply that apart from the development of novel NPs synthesis methods, the new efficient techniques for NPs deposition are required. In this work we report on new approaches based on laser- and plasma-assisted synthesis of NPs in liquids with their simultaneous electrodeposition from a colloidal solution onto the substrate for thin films formation. These approaches allow gaining the main benefits of the plasma-assisted NPs synthesis in liquids: a versatility, simplicity, possibility of control over the particles formation processes along with the deposition of homogeneous nanostructured layers. Plasma-assisted synthesis based on pulsed laser ablation in liquid (LAL) and on gaseous discharge in contact with liquid are known as the 'green synthesis' techniques as they provide non-inhalable colloidal NPs with no residues or chemical by-products, while often no further purification is required.

The developed approaches have been verified for the production of ZnO and CuO thin films on the conductive substrates such as a transparent conductive oxide or any other metal plate. In recent years, much attention has been paid to the production and study of semiconductor oxide thin films, which is associated with the wide possibilities of their practical application, in particular, for the creation of various types of detectors, photo- and optoelectronic devices (Velusamy et al. 2017). Among them, CuO and ZnO form an important pair for making heterojunctions for photodetectors and solar cells (Prabhu et al. 2017, Yang et al. 2014).

2. EXPERIMENTAL

For the synthesis of NPs and their deposition two methods were used, the schemes of the experimental setups used in the experiments are shown in Fig. 1. First, the method of electrodeposition from a colloidal solution formed in the process of an electrical discharge over the surface of the solution was used (Fig. 1a). In this setup, metal oxide NPs are produced by the method of electrical discharge with a liquid electrode. The discharge was powered by a stabilized source with a maximum voltage of 3.6 kV and a current of 5 mA. As a cathode, a thin hollow metal capillary was used with argon flowing through it, the argon flow rate was about 20 mL/min. The cathode was made of stainless steel with outer and inner diameters 800 μm and 500 μm, respectively, and was located at a distance of 3 mm from the liquid surface. As an anode, zinc or copper plates were used, immersed in a cuvette with a liquid. The advantage of this approach is that it operates under normal atmospheric conditions and does not require a sealed chamber. As the power source voltage increased, a breakdown of the discharge gap between the liquid surface and the end of the opposite electrode occurred, and a glow discharge of atmospheric pressure was ignited. The magnitude and stability of the discharge current characteristics depended on the source voltage and the argon pumping rate. To deposit the resulting NPs on the substrate and form thin-film structures, an additional substrate was placed in the cuvette, which was a glass plate with a sputtered ITO (indium tin oxide) layer. This substrate was connected to the power source through an additional ballast resistance (6.8 MΩ). The composition, morphology, and optical properties of the resulting nanoparticles and films have been studied by means of UV-Vis, Raman and FTIR spectroscopy, scanning and transmission electron microscopy.

The second approach uses laser ablation for the NPs synthesis. The scheme of the setup is presented in Fig. 1b. In the proposed scheme, the target is included in the electrical circuit as an anode, while as a counter electrode the conducting substrate can be used (metal foil, ITO, carbon fiber). In such a configuration NPs morphology and composition can be varied by changing not only laser parameters (wavelength, pulse duration, laser fluence), liquid and target composition, but also upon the variation of the applied electric field. The production of particles in the presence of an external field leads to the deposition of the forming nanostructures on the cathode, which can serve as a tool for assembling the resulting particles into ordered structures.

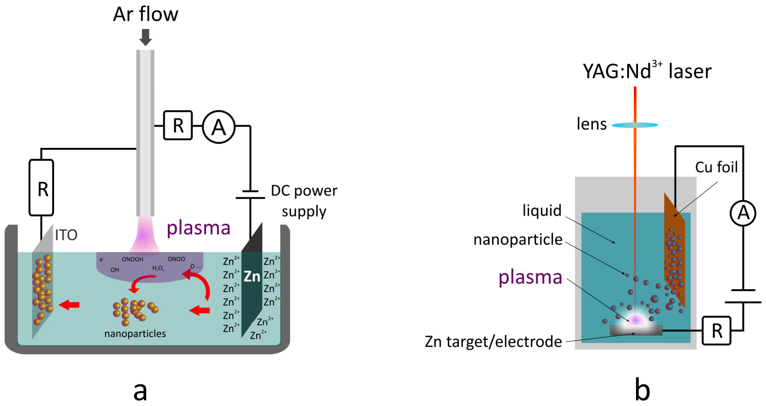

Figure 1: The experimental setups for simultaneous synthesis and deposition of NPs based on electrical discharge in contact with liquid (a) and laser ablation in liquid (b).

3. RESULTS AND DISCUSSION

Both techniques demonstrated a possibility of metal oxides thin-film layers formation on conductive substrates immersed in a solution during the plasma-assisted synthesis. In a discharge with a liquid electrode, plasma is formed between an electrode in the gas phase and a solution surface with a metal electrode immersed in the solution. The presence of electrons and ions in the gas discharge leads to the flow of current through the solution and to the initiation of electrochemical reactions, including dissolution of metal at the anode and reduction of metal cations from the solution at the cathode. Charged particles from the solution further migrate towards the conductive ITO plate at the cathode forming the thin film. As can be seen from its typical SEM image (Fig. 2a), the deposited films are composed of evenly distributed densely packed clusters of particles. Upon closer examination of the samples, it can be found that the shape of the particles is close to spherical, the average particle size is 50-80 nm, while the particles have a rather narrow size distribution. The particles had a hexagonal wurtzite-type ZnO structure that can be concluded from the Raman spectra analysis, shown in Fig. 2b. The major peaks found at 99 cm^{-1} and 437 cm^{-1} correspond well to the E_2^{low} and E_2^{high} vibrational modes in hexagonal ZnO crystal. The high intensity of these modes compared to the defect-induced LO band typically observed at around 580 cm^{-1} indicates of a high crystal quality of the formed nanocrystals (Mediouni et al. 2022). The deposited ZnO film was further used for preparation of multilayered thin film structures. As an example, a heterostructure has been formed by deposition of CuO over the ZnO layer. The resulting thin film heterostructure shows a photosensitive nature demonstrating a nonlinear diode-like behavior as shown in Fig. 2c. From the i-V characteristics, it is found that the forward threshold or turn-on voltage (V_{on}) of the fabricated n-ZnO/p-CuO heterojunction is 2.0 V. Thus, the fabricated from ZnO/CuO heterojunctions can be used for production of low-cost photodiodes, photodetectors, solar cells and gas sensors.

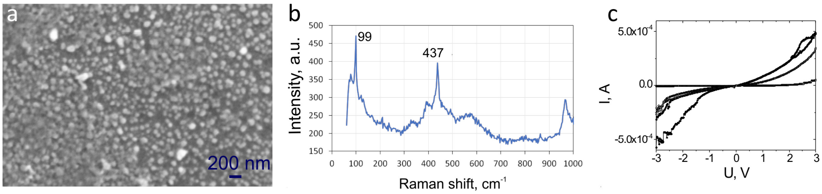

Figure 2: Thin films formed by electrodeposition from a colloidal solution prepared by atmospheric pressure plasma in contact with the solution: a - SEM image of the ZnO film, b - Raman spectra of ZnO, c – current-voltage characteristics of the bilayer ZnO/CuO heterostructure in the dark and under illumination ($100\ mW/cm^2$).

The second approach based on laser ablation of a target in a liquid in the applied electric field also showed the applicability towards thin films formation. The results showed that application of the external electric field may serve as a tool to control the morphology of the prepared NPs. For example, nanostructures having a complex lamellar structure that are combined into layered flower-like structures with a size of several μm can be formed. Such structures, consisting of several interconnected layers, may have great prospects for use as a material for supercapacitor electrodes, since they can significantly increase the surface area while maintaining a small volume.

The analysis of the plasma evolution allowed drawing the conclusion on much shorter plasma lifetime if the external electric field is applied to a Zn target. Formation of non-spherical nanostructures can be attributed to the difference of NPs formation mechanism in electrical-field assisted laser ablation. By variation of the liquid composition it is possible to extend the possibilities of the developed approach that has been demonstrated by the formation of composite metal-carbon nanoparticles promising for supercapacitor applications. In general, the method introduces new possibilities for the control of morphology and composition of nanostructures obtained by laser ablation in a liquid.

The work was partially financed by the National Academy of Sciences of Belarus under project Convergence 2.2.05 and by the Belarusian Foundation for Fundamental Researches under Grants No. F 21KOR-006 and F21RM-104.

References

Mediouni, N., Guillard, C., Dappozze, F., Khrouz, L., Parola, S., et al. : 2022, *J. Hazard. Mater. Adv.*, **6**, 100081.
Prabhu, R.R. et al. : 2017, *Mater. Sci. Eng. B*, **220**, 82.
Velusamy, T., Liguori, A. et.al. : 2017, *Plasma Process. Polym.*, **14**, 1.
Wang, H., Liang, X., Wang, J., Jiao, S., Xue, D. : 2020, *Nanoscale*, **12**, 14.
Yang, C., Xiao, F.,Wang, J., Su, X. : 2014, *J. Colloid Interf. Sci.* **435**, 34.