SCALABLE AUTOMATICAL SILAR METHOD FOR OBTAINING NANOSTRUCTURED ZINC OXIDE LAYERS

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Thin-film technologies allow the deposition of nanostructured semiconductor materials with new electrical and optical properties to create sensors, solar cells, batteries, thermoelectric, piezoelectric, and triboelectric generators, information storage devices, large-area electronics, and optoelectronics. This explains the development of various methods of synthesis. In comparison with other methods, Successive Ionic Layer Adsorption and Reaction (SILAR) is a simple, inexpensive, and less time-consuming method for depositing binary, triple, and even quadruple semiconductor thin films. It is also applicable for the deposition of thin films over large areas. In the SILAR method, the substrate is immersed separately in two aqueous precursor solutions, and washed in between with water to get rid of loosely bound particles. Thus, typically, one SILAR cycle consists of cation precursor adsorption, water washing, anion precursor adsorption followed by reaction, and repeated washing. Unfortunately, methods that work in the laboratory cannot always be applied on an industrial scale, where it is important that the process be cost-effective, high yielding and easy to implement.

Therefore, here we propose a scalable automatic SILAR method based on the use of universal motorized computer numerical control (CNC) platform. Such platforms are widely used in conventional commercial 3D printers. As an example, we chose the SILAR deposition of nanostructured films of zinc oxide (ZnO), which, due to its interesting properties, has been the subject of study by many researchers. Using g-code, all steps of the SILAR method were programmed, and reproducibility of the substrate immersion speed and time of each deposition step was ensured with an error of < 0.1%.

In this study, for the deposition of ZnO films well adhered to glass substrates by the SILAR method, an aqueous solution of zinc sulfate (1 M $ZnSO_4$) was used as a cationic precursor, to which ammonium hydroxide (NH_4OH) was added to pH 12.1. One growth cycle included three stages, such as: (i) immersion of a glass substrate in the cationic precursor solution for 10 s; (ii) its immersion in hot (90°C) distilled water (anionic precursor) stirred with a magnetic stirrer for 10 s; (iii) rinsing it in cold unstirred distilled water for 5 seconds in order to remove weakly bound particles from the substrate. For 50 cycles of SILAR growth, ZnO films with an average thickness of ~4 μm were obtained, which was determined gravimetrically, assuming a bulk density of ZnO of 5.61 g/cm^3. The use of automation made it possible to obtain good reproducibility of ZnO films. All samples showed nanostructured morphology and high light scattering. Their Urbach energy is ~1.5 eV. The optical band gap of the obtained films is about 3.0 eV, which is typical for direct allowed transitions in well-crystallized nanostructured ZnO layers without quantum confinement.