Structural, optical and photocatalytic properties of ZnO thin films and nanostructures deposited by different chemical routes

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Extended abstract

Over the past years, the synthesis of ZnO has been the subject of intense research due to its potential applications in ultraviolet emitting diodes, gas sensors and transparent conducting thin films for solar cells. In this work, ZnO and ZnO:Al (1,3,5%) nanostructures and thin films were synthesized by chemical route techniques.

Sol-gel / spin coating films were prepared as follows. Zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and aluminum nitrate nonahydrate ($Al(NO_3){\cdot}9H2O$) were dissolved in a solution of 2-methoxyethanol and monoethanolamine (MEA) at 60°C. The molar ratio of MEA to zinc acetate was 1.0 and the concentration of zinc acetate was 0.75 mol/l. The concentration of Al as a dopant was of 1.0, 3.0 and 5.0 at.% with respect to Zn. The resultant solution was stirred at 60°C for 1 h to yield a clear and homogeneous solution and allowed to cool down to room temperature. ZnO and Al-doped ZnO films were prepared on glass (Corning Inc. 7059) substrate by repeated coating. Spin coating was performed at room temperature, with a rate of 3000 rpm for 20 sec. After deposition, the samples were preheated in air at 300°C for 10 min to evaporate the solvent and to eliminate the organic component in the film. After repeating the coating procedure up to six times, the films were finally postheated at 400, 500 and 600 °C for 1 h in air using an electronic furnace.

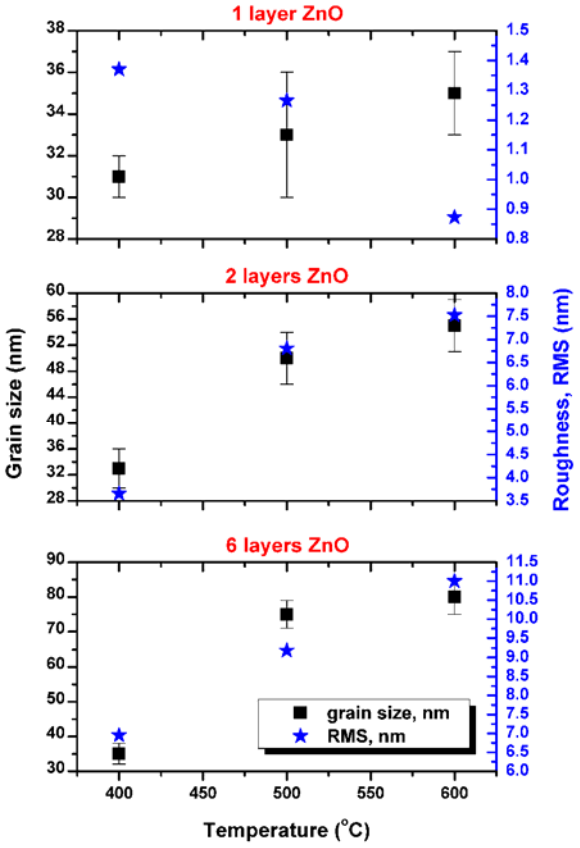

Fig. 1. Grain size (black) and RMS variations (blue) of 1-6 layered ZnO films vs. the growth temperature.

For USP deposition, the aqueous solution of zinc acetate dehydrate (0.5 mol/L) was chosen as the precursor. The aerosol of precursor solution was generated by a commercial ultrasonic nebulizer (Frequency is 2.7 MHz) and transported to the substrate heated at 450 °C by high-purity nitrogen gas.

The fabrication of versatile ZnO nanostructures with controlled morphology and high surface-to-volume ratio was achieved by aqueous chemical growth (ACG), a novel, simple, environmental-friendly and inexpensive method at mild temperatures using an equimolar (0.01M) aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)2{\cdot}6H_2O$) and hexamethyltetramine ($C_6H_{12}N_4$) as a precursor. Corning glass and ZnO thin films on Corning glass grown by sol-gel, were placed in Pyrex glass bottles with polypropylene autoclavable screw caps containing the precursors described above, and heated at 95 °C for 5 h. After each induction time, the substrates were thoroughly washed with MilliQ water to eliminate residual salts or amino complexes, and dried in air at the same temperature.

In all cases, before deposition, the substrates were cleaned using a piranha solution (3:1 mixture of sulfuric acid and 30% hydrogen peroxide), washed with MilliQ water and dried under a N_2 gas flow.

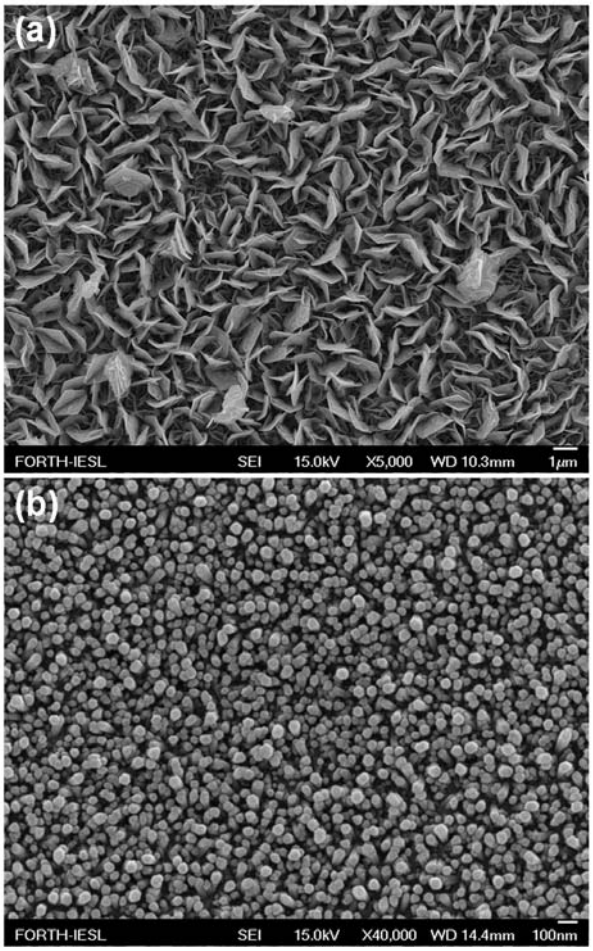

Fig. 2. (a) ZnO petal-like nanostructures grown on corning glass by USP at 450°C and (b) well-aligned nanorods grown by ACG at 95°C.

All samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV - visible spectroscopy.

It is revealed that the wurtzite ZnO structure is the only crystallographic phase detectable in all cases although the preferential orientation varies, depending on the growth conditions. The shape and the dimensions of the nanostructures were found to depend on the growth time, the concentration of the precursor solution and the dopant percentage. Transmittance measurements have shown that the ZnO thin films are transparent in the visible wavelength region.

The photocatalytic properties of the as grown samples were also measured by studying the rate of degradation of stearic acid upon exposure to UV radiation. A layer of stearic acid was applied to the sample (typically 12x12mm) using a 30μl aliquot of a 10mmol solution of stearic acid in chloroform, and then immediately spun for 30 sec at 2000rpm. The integrated area of the C-H stretching peaks (2800-3000cm^{-1}) was monitored using FT-IR and plotted as a function of timed exposure to 3mWcm^{-2} UV radiation (365nm, black light blue lamps). The photocatalytic activity was determined by the gradient of this line.

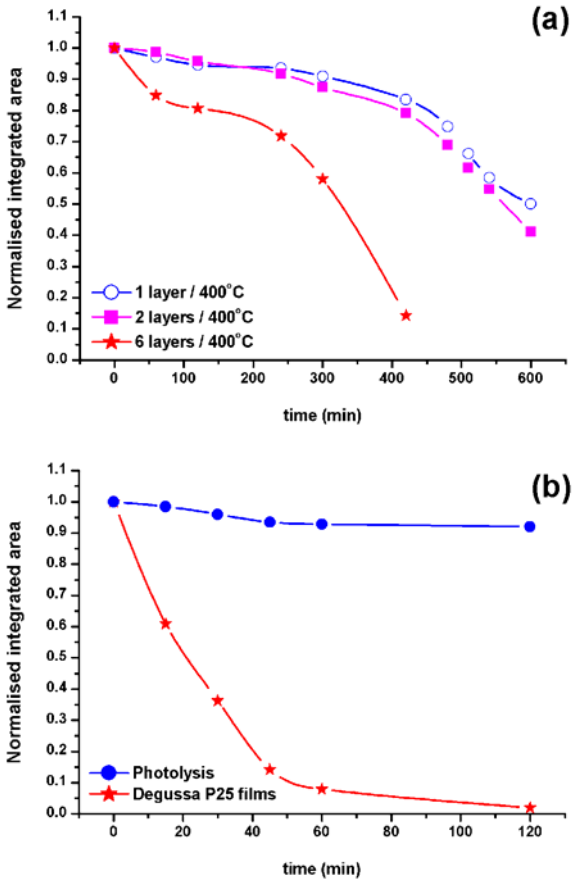

Fig. 3. Normalized integrated area vs. irradiation time for a series of 1-6 layered ZnO samples grown by sol-gel technique at 400 °C.
(b) Plot of stearic acid integrated area vs. irradiation time for Degussa P25 films and bare corning glass substrates. The irradiation source comprised five 4W blacklight lamps, i.e. 365 ± 20 nm light.

Keywords: ZnO, thin films, nanostructures, photocatalysis.