ZnO Nanostructures for Potential Applications in Organic Solar Cells

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Metal oxides are the key ingredients for the development of many advanced functional materials and smart devices. Nanostructuring is one of the best ways to exploit their properties. Zinc oxide (ZnO), is a material that have been studied for various nano-applications. Metal oxides can be prepared in various sizes and geometries, but one of the greatest challenges remains the precise control of the particle size, shape, crystalline structure and processing properties. The present contribution presents preliminary results of chemical synthesis and characterization of nanostructured low work-function ZnO for potential applications in organic solar cells as electron extraction interlayer.

Keywords: zinc oxide, chemical growth, structuring, properties

Zinc oxide (ZnO) is one of the most studied materials in the later years due to its unique properties which make it suitable for an extremely large range of applications as presented by Arya at al. in 2012 [1], Klingshirn in 2007 [2, 3] and in 2008 [4], Ozgur et al. in 2005 [6] and in 2009 [6]. Nearly all known physical and chemical growth techniques are involved in the growth of crystalline and polycrystalline films and structures as proved by Fan and Lu in 2005 [7]. Even so, there are still a lot of unknown or not yet fully understood parameters controlling the structuring of ZnO. It is known that while the use of physical growth techniques leads to well controlled, reproducible structured films with good quality onto a variety of substrates, chemical techniques are simple and inexpensive suitable rather for the growth of powders and highly nano-structured films with interesting "flower-like" and rod features. A quite extensive review on semiconductor materials by chemical growth methods was published by Warad et al. in 2005 [8].

Despite to huge efforts over the last few years the use of chemical techniques for controllable good quality ZnO thin films is still challenging for a number of interesting applications [9-21]. In line with this, the present contribution contains some preliminary studies on growth kinetics of ZnO from a non-aqueous precursor solution. It is known that the dissolution of zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$ accompanies solvation of zinc and acetate ions by methanol at low water concentrations and leads through hydrolysis and polymerization reactions to the generation of poly-nuclear zinc hydroxide clusters [22]. These clusters can be transferred from solution onto substrate and thermally decomposed to ZnO. Based on these growth procedures, the Dynamic Light Scattering (DLS) technique was involved in order to study the polymerization during the above chemical process. Evolution of structure growth from 355 nm to 2.4 μm was monitored and successful transfer of structures from the solution to the substrate, in different stages of growth was performed. Scanning Electron Microscopy characterization for films obtained in different reaction stages was performed. Growth kinetics studies proved that controlling chemical growth parameters, good quality thin films with desirable ZnO structure size onto rigid and flexible substrates can be obtained.

Experimental part

ZnO nanoparticles were prepared according to a literature method developed by Pacholski with some modification [23].

Zinc acetate ($Zn(Ac)_2$, 0.82 g, 4.46 mmol) and 250 μL of water was added into a flask containing 42 mL of methanol. The solution was heated to 60°C under magnetic stirring. 0.3g natrium hydroxide (NaOH) was dissolved into 23 mL of methanol as the stock solution that is dropped into the flask within 10-15 min. The solution was further kept at a constant temperature of 60°C for 2 h and 15 min and cooled down at room temperature without stirring for about half hour for decantation. 20 mL from the upper part of the solution were removed and a sample at this stage of growth was kept for DLS experiments.

Then it is reheated for another 5 h before stopping the heating and stirring. The upper fraction of the solution is removed after 30 min. Methanol (50 mL) is added to the solution and stirred for 5 min. The upper fraction of the solution is discarded again after 30 min.

This process is repeated twice. For the second washing, the upper fraction of the solution is taken away after overnight staying. Using the modified method presented here, it takes a few hours to obtain <4 μm rods.

Solutions were analyzed by dynamic light scattering (DLS) in time, accompanied by particle transfer onto cleaned glass substrates. The deposited films were characterized by optical microscopy, Scanning Electron Microscopy (SEM) and UV-VIS spectroscopy. SEM characterization was performed using a JEOL JSM 6362LV

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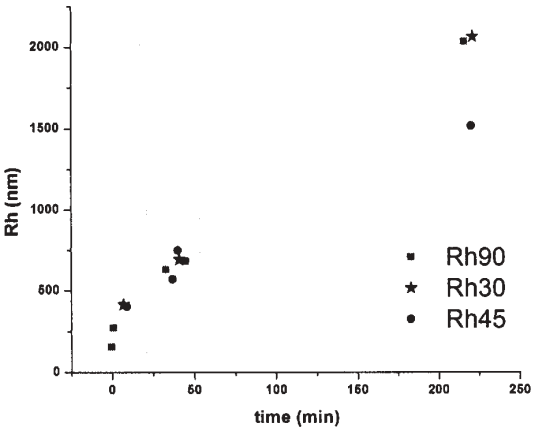

Fig. 1. Plot of Rh time-evolution measured by DLS

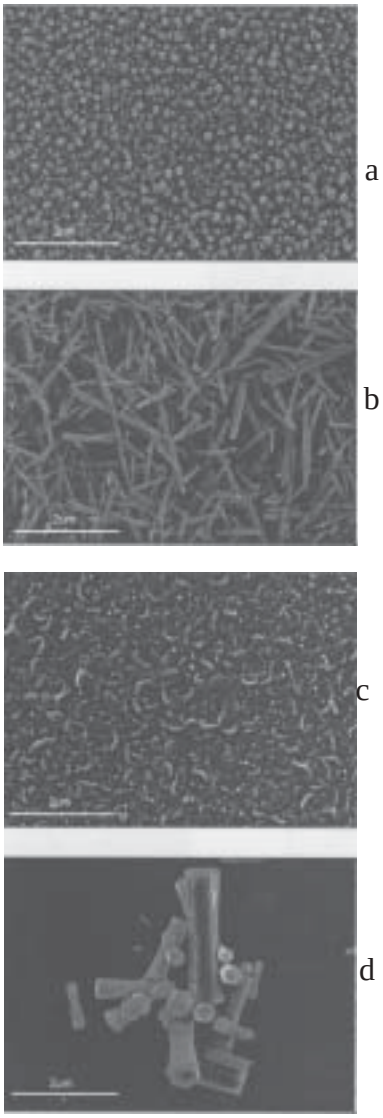

Fig. 2. SEM images of four ZnO films resulted from different growth stages in the precursor solution **a** and **b** –early stage, **c** and **d** final stage of growth. The scale is similar for all images. Uncoated samples

electron microscope in high vacuum mode. UV-VIS spectroscopy was performed using a Shimadzu UV2401PC spectrophotometer. The apparent hydrodynamic radius of the ZnO particles is measured by dynamic light scattering (DLS) technique. Measurements were made at room temperature using a laser having wavelength of 635 nm and 90° scattering angle. The diffusion coefficients were calculated using the auto correlation function and the particle size was calculated using the Stokes-Einstein's equation.

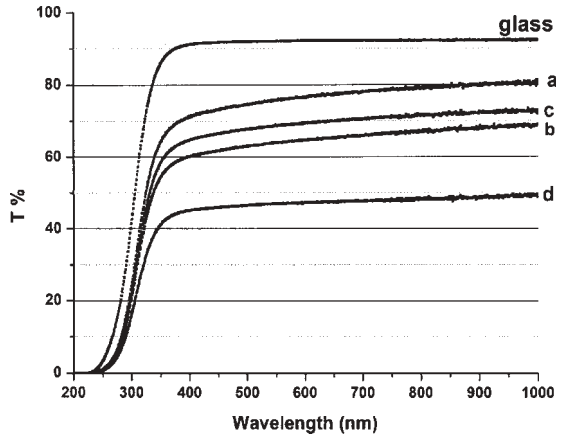

Fig. 3. Optical transmittance spectra for films presented also in the SEM characterization

Results and discussions

The time-evolution of the scattering intensity and the apparent hydrodynamic radius Rh of the ZnO particles were monitored by DLS measurements at 30, 45 and 90° angles simultaneously. The plot of Rh time-evolution is shown in figure 1. The intensity has been normalized to the initial value. The initial values of the hydrodynamic radius correspond to the hydration radius of a single particle of ZnO growth early stages.

At the initial stage, ZnO particles are about 100 nm. In the initial stage, they are agglomerating fast. The final stage shows the presence of large non-spherical crystals with size above 2μm. Additional investigations at 120° angle correlated with static light scattering measurements showed that in the final stage are present two predominant size particles: one of ~600 nm and another of 2.4μm. These estimations were fairly confirmed by examination of the ZnO films deposited onto cleaned glass substrates from each analyzed solution at the sample collection growth stages.

The ZnO films were checked by optical microscopy for film quality and homogeneity onto the substrate. Films that were inhomogeneous were discarded. The good quality films were further analyzed by SEM.

SEM images of four such ZnO films are presented in figure 2.

The main scope of the present experimental work is to obtain nanostructured low work-function ZnO films with controlled morphological, dimensional, optical and electrical properties for integration in organic solar cells as electron extraction interlayer. The optical transmission of ZnO films grown as described above was analyzed by UV-VIS spectroscopy. Optical transmittance spectra for films presented also in the SEM characterization are shown in figure 3.

As one can see, the films shows medium optical transmittances between 85% for the thinnest (~200 nm) and 55% the thickest (~2.5μm) films. Optical bandgap estimation from the absorbiton spectra of various ZnO films deposited during this experimental work showed values of 3.1-3.2 eV smaller than ZnO bulk material (3.37eV) proving suitability for the targeted application. Electrical measurements were performed using the two points contact method and van der Pauw method (Hall Effect). Thinner ZnO films show electrical resistivity from 10 to 150 ohm/sq and quite symmetric I-V curves during the

four pints contact measurement while thicker films showed non-symmetrical I-V characteristics due to their homogeneity and could not be properly measured although they seem to have better local conductivity across their surface. It is visible also from the SEM images of the four ZnO uncoated samples.

Conclusions

This work prove that desired properties for nanostructured low work-function ZnO films with controlled morphological, dimensional, optical and electrical properties for integration in organic solar cells as electron extraction interlayer can be achieved also using transfer onto substrates from a simple, cheap chemical growth method. Particle growth control in the solution allow ZnO layer onto substrate engineering.

Acknowledgements.Part of the work was partially supported by the strategic grants POSDRU/159/1.5/S/133652 and POSDRU/159/1.5/S/137750, co-financed by the European Social Fund within the Sectorial Operational Program Human Resources Development 2007 – 2013 and by the grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2012-3-0202.

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Manuscript received: 28.06. 2015