Electrochemically formed ZnO and Au/ZnO opal films

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Abstract

ZnO inverse opal films were synthesized electrochemically using aqueous and non-aqueous zinc acetate electrolytes and ITO deposited polystyrene opal matrices. The following thermal oxidation in air was performed for further application in optoelectronics. The overall composition and deposition potentials varied to reach uniform porous films with opal structure. Most uniform photonic film of ZnO with zincite structure has been deposited from DMSO electrolyte. Photoluminescence spectra of the ZnO coverages showed more complex spectra for precipitates sedimented from aqueous baths than from DMSO. Less deficient films of opal ZnO films deposited from DMSO demonstrated lower scattering effect compared to coverages deposited from aqueous electrolytes. Magnetron sputtering was applied for Au/ZnO composite film formation. The optical spectra of the Au/ZnO composite coverages correlate to spectra of uniform Au opal films.

Keywords Zinc oxide · Electrocrystallization · Photoluminescence · Inverse opal · Gold · Plasmon spectra

1 Introduction

Many methods for ZnO coverage deposition have been discussed in the past years. Such methods as spray pyrolysis [1], thermal or magnetron sputtering [2], pulsed laser deposition [3], have demonstrated rather limited ability to deposit ZnO coverages with a complex architecture with improved optical characteristics for smart engineering solutions and optoelectronics [4, 5]. At the same time electrochemical methods [6, 7] and “chemie douce” methods [8] are still topical and have great potential in such specific applications. Electrochemical deposition is a reproducible and low-cost method for preparing continuous or porous coverages with an increased surface area via templating. Complex interfaces belong to a mainstream for optoelectronic development including photovoltaics [9], fuel cells [10] and switching devices. Transparent semiconductive photonic structures are also promising for electrocatalysis, photocatalysis, and sensors. Optical sensors based on

surface-enhanced Raman spectroscopy is a rather fresh technology studied rather sufficiently at the moment.

Surface-enhanced Raman spectroscopy is a promising analytical technique which is fast and easy handling for routine testing and analyses [11]. Inverse opals of gold serve as high efficient substrates for SERS analysis because of their unique Plasmon characteristics. Inverse opal substrates demonstrate both plasmonst of individual gold particles and also localized Mie and delocalized Bragg plasmons in its reflectance spectra [12]. Different combinations of transparent semiconducting oxides and noble metal nanoparticles were investigated recently [13]. High enhancement factor has been observed for Ag/ZnO-nanorods composite coverage [14] that make an insight for new investigation of such compositions.

Different types of electrolytes can be used for preparing metal zinc or ZnO films by electrodeposition. Aqueous electrolytes are based on zinc chloride [4, 7, 15], sulfate [16], nitrate [17, 18], or zinc acetate [19]. Non-aqueous electrolytes could be based on zinc chloride

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[20], nitrate [21] or perchlorate [20, 22] with dimethylsulfoxide (DMSO), dimethylformamide (DMF) or hexamethyleneamine (HMT) as solvents. Despite all zinc chloride and zinc nitrate are commonly used as zinc precursors in electrolytes. Most publications on the deposition of ZnO using zinc chloride or sulphate baths declare growth of aligned zinc nanorods. Zinc nitrate leads to a uniform film growth when heated up to 80 °C only, while individual ZnO particles are round-shaped or hexagon-like depending on deposition conditions.

During the past decade, the template methods based on silica or polystyrene (PS) colloidal crystal was developed to obtain periodic porous structures known as inverse opals [23]. This method usually assembles close-packed arrays of monodisperse microspheres, and then it fills the interstices between the close-packed arrays of beads forming a solid skeleton around the spheres. However, for products made using a liquid-phase pouring process, the inorganic solid component is originally amorphous and needs to be annealed that usually results in crack growth and collapse in the pore structure during the removal of templates. Most of electrolytes work in a range of 60–80 °C that is not suitable for polymer-based electrodes or polymer matrices. Electrodeposition inside a matrix on heating is difficult because of its delamination during the process. Here we have investigated a number of zinc electrolytes for ZnO deposition using a polystyrene template at room temperature (RT) conditions. Recently, Baumberg et al. reported electrodeposition of metal zinc using aqueous acetate or zinc chloride baths with PS opal as a template [24]. Hexamethylenetetramine (HMTA) [25] and citric acid [26] were proposed as additives for zinc acetate aqueous electrolytes later on. It has been found that HMTA leads to ZnO nanorod formation, while citric acid as a complexing agent improves the opal quality forming round-shaped crystallites. Nevertheless, electrochemical growth of ZnO is still not a routine method, and corresponding chemical processes are to be optimized.

The electrochemical deposition of ZnO is available in different solvents to avoid hydration of zinc. Ethanol [27] and dimethyl sulfoxide (DMSO) [20, 22, 28] are promising solvents for electrolytes. The reaction mechanism involved in the electrochemical formation of a ZnO film in DMSO electrolytes is not based on hydroxide ions, and another recently reported mechanism may correspond to the presence of molecular oxygen as an oxidant [29]. Both phase composition and microstructure of coatings are to be different for coatings obtained in aqueous and non-aqueous electrolytic baths. These factors are to affect physical properties of the films, such as recombination lifetime, exciton pair generation, transmittance and conductivity of the coverages.

Grain boundaries are main structural defects in polycrystalline coatings, and they have a significant influence on electrical properties of the films. In general, grain boundaries have a dual effect on the electronic properties of material. The potential barrier related to grain boundaries controls the charge carrier mobility μ_e increasing its effective resistivity if particle dispersion grows up [30]. At the same time, a grain boundary, being a serious violation of the crystal lattice perfection, plays a role of an effective internal getter, which facilitates the purification of the bulk of the material from residual impurities and intrinsic point defects.

In present manuscript new methods for synthesis of ZnO opal have been proposed. The samples with optimal microstructure have been covered by gold nanocoating to analyze photonic properties of composite films.

2 Experimental

ZnO films were fabricated by electrodeposition of zinc and zinc oxide onto 0.6 mm thick ITO covered glass substrates ($< 10 \Omega/\text{sq cm}$). The process was carried out in a three-electrode cell at room temperature in acetate aqueous or DMSO baths. The reference electrode was an aqueous Ag/AgCl/KCl_(s) electrode connected to the cell via a Luggin capillary. A platinum wire of 0.5 mm diameter was applied as a counter electrode. The samples with a different theoretical thickness of $h = 50\text{--}200 \text{ nm}$ were prepared. The amount of the precipitated metal and, consequently, film thickness h , was estimated using Faraday law from the deposition charge under the assumption of 100% current efficiency. To obtain zinc oxide with wurtzite structure the samples were annealed additionally at 500 °C for 3 h in air according to previous results [31].

Zinc acetate dihydrate (purum, Reachim), sodium ethylenediaminetetraacetate (Na₂EDTA, Sigma-Aldrich), and DMSO (purum) or distilled water ($\sim 18 \text{ M}\Omega$) were compounds of electrolytes. All baths contained similar concentration of zinc acetate, potassium nitrate and ethanol, two baths contained 0.05 M Na₂EDTA (see Table 1). The working and counter electrodes have been placed parallel to each other and separated by a distance of 2 cm.

In the presence of zinc acetate the following reaction takes place:

The overall reaction for the formation of zinc oxide ZnO is

Polystyrene beads for template formation were prepared via a homogenous polymerization process. The colloid beads are of $400 \pm 20 \text{ nm}$ according to DLS data.

Table 1 Zinc deposition electrolytes and used electroplating modes

Electrolyte (sample name)	Composition
Electrolyte 1 (ZnO-1)	H ₂ O: 0.2 M Zn(CH ₃ COO) ₂ ; 0.5 M KNO ₃ ; 3.5 M C ₂ H ₅ OH
Electrolyte 2 (ZnO-2)	H ₂ O: 0.2 M Zn(CH ₃ COO) ₂ ; 0.5 M KNO ₃ ; 0.1 M Na ₂ EDTA; 3.5 M C ₂ H ₅ OH
Electrolyte 3 (ZnO-3)	DMSO: 0.2 M Zn(CH ₃ COO) ₂ ; 0.5 M KNO ₃ ; 0.05 M H ₂ O ₂
Electrolyte 4 (ZnO-4)	DMSO: 0.2 M Zn(CH ₃ COO) ₂ ; 0.5 M KNO ₃ ; 0.05 M H ₂ O ₂ ; 0.05 M Na ₂ EDTA

For the template formation ITO/glass substrates have been applied as working electrodes. The colloidal crystal growth was carried out according to procedure reported recently in Ref. [32]. After the electroplating process the matrix was removed chemically by toluene (chem. purum, "IREA-2000").

The sample morphologies of ZnO films were examined using a Leo Supra 50 VP scanning electron microscope or a Carl Zeiss NVision 40 scanning electron microscope (SEM). Both the instruments are equipped with EDX Oxford Instruments attachments for the local chemical analysis.

GIXRD analysis was carried out using Rigaku SmartLab diffractometer equipped by 9 kW rotating Cu anode and Goebel mirror for parallel beam. Grazing incident geometry (omega = 0.5°) was applied with parallel slit analyzer of 0.5° on diffracted beam.

The atomic force microscopy (AFM) data were obtained using INTEGRA AURA (NT-MDT) with diamond tips on was silicon cantilevers. Image processing and analysis was performed using free FemtoScan Online software by ATC Co. The images were obtained in semi-contact mode with scanning rate of 10 nm/s.

Emission spectra were collected with a multichannel spectrometer S2000 (Ocean Optics) with a nitrogen LGI-21 ($\lambda_{\text{ex}} = 337$ nm) as an excitation source at 293 K and 77 K. All spectra were corrected for the wavelength response of the system.

UV-vis reflectance spectra collected using a UV-vis spectrometer Lambda 950 (PerkinElmer). Measurements have been performed in a spectral range of 350–800 nm with a step scan of 1 nm with scanning rate of 2 nm/s using quartz glass as a reference at 298 K. UV-vis reflectance spectra were obtained using a UV-vis spectrometer Lambda 950 (PerkinElmer) with an attached universal reflectance accessory (URA). Measurements were performed in the spectral range 250–850 nm with a step scan of 1 nm. Angles of incidence of 8° and 64°.

3 Results and discussion

The interval of deposition potentials was chosen according to the cyclic voltammetry (CV) data (Fig. 1). The main cathodic process for aqueous electrolytes (due to the

electrolyte 1 CV curve) starts already at about –0.80 V versus Ag/AgCl/KCl(sat.) but the film growth is very slow.

The voltammetric characteristics of the ITO substrate in aqueous zinc acetate electrolytes 1 and 2 are shown in Fig. 1a. Sweeping negatively from an initial potential of –0.10 V, a reductive peak is observed. An increase in cathodic current is observed at a negative potential of –0.65 V. This peak can be related to the reduction of nitrate ions of NaNO₃ and the formation of hydroxide ions [33] according to Eq. (3):

Any kinds of metal reduction processes at –0.65 V were not observed. A further increase in observed currents at a negative potential of –0.90 V can be associated mainly with water decomposition process which releases molecular hydrogen and hydroxide ions [34]. Some amount of hydroxyl OH[–] ions can be supplied through the hydrolysis of acetate anion [35] additionally but in near-electrode region its concentration higher, obviously. Hydroxide anions are responsible for zinc oxide deposition onto the ITO substrates according to the following principal Eq. (4):

Fig. 1 Cyclic voltammograms of ITO electrode in zinc acetate electrolytes: **a, b** aqueous electrolytes (electrolyte 1 and electrolyte 2). **c, d** DMSO-based electrolytes (electrolyte 3 and electrolyte 4). Scan rate—50 mV/s. Ag/AgCl/KCl(s) reference electrode

For electrolytes 1 and 2 the deposit potential was varied within the range of -0.95 to -1.10 V to find the optimal deposition potential for the smallest grain size. Experimentally we found that growth of large crystallites often lead to a deformation of polystyrene matrix.

At the same potentials starting from -0.968 V versus Ag/AgCl/KCl(s.) at zero pH and decreasing with pH growth the simple reduction process of Zn^{2+} cations to $\text{Zn}_{(s)}$ could take a place. Nevertheless, no black or dark colour sediments were observed by naked eye or microscopically. All deposits processed using electrolytes 1 and 2 had white colour and no mirror effect from the back side of the WE. Most likely, thin metal films of reduced zinc oxidized by dissolved or air oxygen too rapidly for analysis.

A small cathodic wave at -0.92 V is observed on the cyclic voltamogram for electrolyte 2 (with an additional amount of Na_2EDTA) that probably corresponds to the reduction of some Zn(II) complexes present in the solution in small amounts. This technically decreases the value of overvoltage in the deposition process.

The corresponding CV data obtained for electrolyte 3 is shown in Fig. 1b. The cathodic current at about -1.20 V observed towards negative potentials is attributed to the Zn(II) reduction to metallic zinc. Hydroxyl species OH^- produced in this process react with Zn(II) ions forming ZnO through a heterogeneous precipitation reaction [22]. According to these results, ZnO electrodeposition can be carried out at cathodic potentials of -1.20 V or higher. The cathodic branch on cyclic voltamogram for electrolyte 3 (Fig. 1c) demonstrates characteristic zinc reduction wave at higher potentials. The film deposition was carried out in potentiostatic mode at potentials of -1.20 V, -1.60 V, -1.80 V or -2.00 V. In this case, the overvoltage resulted in growth of zinc dendritic deposits as seen from

micrographs and XRD data. The CV curve for the electrolyte 4 (with Na_2EDTA) Fig. 1d is different and demonstrates a reduction process at lower potentials at -1.25 V– 1.45 V and the following deposition of metal zinc at higher voltages. Probably, the wave at -1.25 V corresponds to zinc complexes with EDTA as observed for the aqueous electrolyte 2.

To avoid metal zinc formation, sodium nitrate (0.1 M) for electrolytes 1 and 2 and hydrogen peroxide for DMSO electrolyte (electrolytes 3 and 4) were added to the baths as additional oxidants. The ratios of metal zinc to zinc oxide were changed insignificantly despite the presence H_2O_2 for films deposited in electrolytes 3 and 4 at different potentials. To complete the zinc oxide deposition process, the oxidation of metal zinc film to ZnO oxide was carried out by thermal oxidation in air.

GIXRD data of the resulting 200 nm thick films after calcinations at 500°C for 1 h are shown in Fig. 2. Reflections at 31.66° , 34.38° , 36.26° , and 61.68° correspond to zinc oxide (wurtzite-type structure) according to PDF2 file 75–1526. The diffractograms contain relatively strong characteristic reflections of indium oxide substrate (PDF2 file 74–1990) including intensive reflections at 21.46° , 30.53° , 35.41° , 37.63° , 45.58° , 50.95° , and 60.51° . Thin and intensive reflections in the diffractograms of electrolytic deposits are related to metal zinc with hexagonal lattice (PDF2 file #4–831). The observed reflections of metal zinc are (002), (100), (101), (102), (103), (110). The reflections of metal zinc disappear for the samples exposed to thermal oxidation in air at 500°C for 3 h. Some silica reflections were observed for the samples after the calcination processes.

After 1 h of annealing in air the films deposited from aqueous acetate baths contain some zinc hydroxycarbonate (PDF2 file # 19–1458). XRD reflections of ZnO with a

Fig. 2 **a** GIXRD data for ZnO films deposited from DMSO and aqueous zinc electrolytes after the annealing at 500°C for 1 h in air. **b** Raman spectra of ZnO films

large FWHM demonstrate low crystallinity of the zincite. After 3 h of annealing all films are white-colour in two sides that makes nanosized ZnO to be a presumable additional compound. The characteristic cell parameters estimated from diffractograms are the following:

$$a = 3.250(1) \text{ \AA}, \quad c = 5.214(2) \text{ \AA}, \quad V_{\text{cell}} = 47.7 \text{ \AA}^3.$$

Raman spectra of coverages demonstrate characteristic Raman modes of zinc oxide [36]. The strongest modes are E_{2L} at 100 cm^{-1} , $2E_{2L}$ at 119 cm^{-1} and E_{2H} at 440 cm^{-1} (Fig. 2b). Less intensive are the following vibrations $3E_{2H}-E_{2L}$ at 330 cm^{-1} , $A_1(\text{LO})/E(\text{LO})$ at 585 cm^{-1} . The weakest band observed is $A_1(\text{TO}) + E_1(\text{TO}) + E_{2L}$ at 990 cm^{-1} . No additional bands observed in the spectra that correlates with XRD data.

Micrographs of the ZnO films obtained in electrolyte 1 at different deposition potentials are presented in Fig. 3. The surface morphology of polycrystalline ZnO films obtained at various potentials is always different including different porosity and particle size. The sample deposited at $E_d = -1.1 \text{ V}$ demonstrates significant irregularity of thickness, uniform macropores, and sponge-like structure. Uniformity is more characteristic, and roughness is smaller for samples prepared at -1.09 V and -1.05 V . The samples are sufficiently X-ray amorphous and have a complex branched structure. The preferred deposition potential for ZnO is -1.00 V , which promotes the most controllable synthesis. Grains have a complex shape of crystallites of anisomeric polyhedral shape with an average length along the diagonal of $350 \pm 50 \text{ nm}$ and thickness of $60 \pm 20 \text{ nm}$. Thus, the shape of individual ZnO nanostructures depends

on the potential depositions. To reduce the grain size some complexing additives were added to an aqueous electrolyte.

Figure 4 shows the microstructure of ZnO films deposited from aqueous acetate electrolytes with and without a portion of additional $0.1 \text{ M Na}_2\text{EDTA}$ as a complexing agent (electrolytes 2 and 1). The optimum zinc oxide deposition potentials for these electrolytes are -1.00 V and -0.95 V , respectively. The grain size of films deposited from electrolyte 2 at -0.95 V is equal to $75 \pm 25 \text{ nm}$, that is more advantageous for further application of ZnO films as electron transport material of photoanodes with developed surface. The average values of grain size are presented in Table 2.

Figure 5a, b and c, d demonstrates the microstructures of ZnO films deposited from electrolyte 3 at potentials of -1.60 V and -1.80 V , respectively. At a greater overvoltage the sample grows faster forming dendrites, and the resulting structure is much more heterogeneous in thickness, and the sediment itself is more friable and amorphous. A good matching of the growth rate with a crystalline homogeneous solid structure with a grain size of about $150 \pm 50 \text{ nm}$ is achieved using a -1.60 V deposition potential. The deposition potential of -1.80 V produced more porous coatings with larger individual particle size (Fig. 6c, d). Such films are microporous and are formed with large flake-like individual particles.

The heat treatment conditions are important for the characteristic continuity of coatings, as well as optimal optical characteristics, and lifetime and mobility of charge carriers. All these characteristics depend on the grain size. The most continuous ZnO films are obtained using

Fig. 3 SEM micrographs of ZnO coverages deposited in standard aqueous bath (electrolyte 1) at 25°C at different applied potentials: **a** -1.10 V , **b** -1.09 V , **c** -1.05 V , and **d** -1.00 V versus Ag/AgCl

Fig. 4 SEM of ZnO films deposited from aqueous acetate electrolyte with Na₂EDTA (electrolyte 2) at different deposition potentials E_d of: **a** – 0.95 V, **b** – 1.05 V, **c** – 1.09 V versus Ag/AgCl. The deposition performed at 25 °C. The micrographs correspond to the films after heat treatment at 500 °C for 3 h

Table 2 Characteristics of zinc oxide coverages (300 nm thick) deposited from three electrolytes after annealing at 500 °C for 3 h

Electrolyte and deposition potential	Grain size (nm)	R_a (nm)	R_q (nm)	Optical transmittance at 550 nm (%)	Charge carrier lifetime (μ s)
Electrolyte 1 – 1.0 V	350 ± 50 60 ± 20	201	264	–	2.1 ± 0.1
Electrolyte 2 – 0.95 V	75 ± 25	18	21	58	4.9 ± 0.1
Electrolyte 3 – 1.6 V	150 ± 50	60	77	52	5.5 ± 0.1

an acetate nonaqueous electrolyte (electrolyte 3), with a grain size of 150 ± 50 nm obtained after calcinations at 500 °C. The films deposited from aqueous electrolytes 1 and 2 were also annealed at 500 °C for 3 h to compare the input of annealing processes in recrystallization processes.

In Fig. 6 characteristic micrographs of ZnO deposited in all four kinds of electrolytes are presented. The micrographs demonstrate that more uniform flat coverages have been deposited from the aqueous zinc acetate electrolyte with Na₂EDTA (electrolyte 2) while the worst coverages have been obtained in electrolyte 4.

The typical AFM images are given in Fig. 7. The highest roughness was observed for the sample deposited from electrolyte 1. The average roughness value (R_a) for this sample is 201 nm. For samples deposited from electrolytes 2, 3 and 4, the average roughness values are 18 nm, 60 nm and 38 nm, respectively. A significant advantage of the aqueous electrolyte with a complexing agent (electrolyte 2) originates from low overvoltage of the deposition processing. Most likely, medium roughness value and its lateral size of ZnO grains obtained in electrolyte 3 in a restrained overvoltage mode results from lower rate of particle growth in the DMSO electrolyte. In case of the films deposited from electrolyte 4 the average roughness is lower and the films are much more uniform while the average particle size is larger.

According to Maache et al. [37] spin coating processing of ZnO and AZO films using zinc acetate and aluminium nitrate as precursors leads to round-shaped particles of 25–40 nm in diameter. Comparing to this technique the proposed electrodeposition methods result in larger particle size with increased roughness values. On the other hand, thick porous films of ZnO are of important practical use for optical devices and catalysis.

The electrodeposition of inverse opal films has been carried out using both aqueous and DMSO electrolytes at a cathodic potential of – 0.95 V and – 1.60 V, respectively. The typical opal architecture is demonstrated by micrographs in Fig. 8. The the film deposited from an aqueous electrolyte with Na₂EDTA is presented by porous structure with a macropore diameter of 240 ± 40 nm. Individual grains in the film are of 60 ± 20 nm in diameter and are

Fig. 5 SEM of ZnO films deposited from DMSO electrolyte (electrolyte 3) at different applied potential: **a, b** – 1.6 V and **c, d** – 1.8 V, respectively. The micrographs correspond to the films after heat treatment at 500 °C for 3 h

Fig. 6 SEM micrographs of ZnO films deposited from aqueous and non-aqueous electrolytes: **a** electrolyte 1, – 1.20 V; **b** electrolyte 2, – 0.95 V; **c** electrolyte 3, – 1.60 V; **d** electrolyte 4, – 1.60 V. The micrographs correspond to the films after heat treatment at 500 °C for 3 h

round- or ellipse-shaped. This result is comparable with ZnO opal reported in Ref [26], where citric acid was used as a complexing agent, and 30–50 nm round-shaped crystallites were observed. The obtained ZnO opal film could also be recommended for photodetectors and photovoltaic devices.

The film deposited from DMSO-based electrolyte 3 is different (Fig. 8b). It keeps the architecture of the template and shows macroporous architecture of inverse opal. In case of ZnO electrodeposition using DMSO-based electrolyte with Na₂EDTA (electrolyte 4), the

microstructure is similar. On the other hand, electrolyte 3 is recommended for inverse ZnO opal formation because of smaller average grain size.

According to AFM data (Fig. 9) the average roughness R_a of the ZnO inverse opal film is of about 32 nm and the average maximum height of 150 nm that correlates with SEM data. The AFM images demonstrate uniform ZnO nanoparticle distribution in the film with an average particle size of about 50 nm. The maximum height of profile R_z is about 175 nm and average distance between two closest maxima of the profile S_m is 410 nm that matches

Fig. 7 AFM micrographs and roughness profile: for the most uniform ZnO coverages deposited from aqueous electrolytes **a** electrolyte 1, **b** electrolyte 2, **c, d** DMSO-based (electrolyte 3 and 4) bath after annealing at 500 °C for 3 h. **e** for ZnO opal

Fig. 8 SEM micrographs of the porous ZnO opal films deposited in electrolytes **a** 2 and **b** 3 using polystyrene opals as templates

well the periodic structure of the matrices and inverse structures.

The photoluminescent characteristics of films were studied to compare the deficiencies of films deposited using different electrolytes (Fig. 10). The PL spectra collected at 293 K show some specifics demonstrating narrow and intensive near-band-edge (NBE) maxima in the UV ranges [7] at about 390 nm (3.19 eV) for precipitates from aqueous electrolyte 2. The strongest maximum is related not only to NBE processes but also transitions related to free exciton relaxation, longitudinal optical (LO)-phonon replicas, free-to-neutral acceptor transitions, etc. [38], so the value differs slightly from 3.22–3.24 eV typical for ZnO. The deep-level characteristic green emission band is found at 498 ± 10 nm (2.43–2.54 eV). The green band is originated from intrinsic V_{Zn} , V_O and Z_i defects [38, 39].

Less deficient films deposited from electrolyte 3 show the green band (less intensive) at about 500 nm (2.53 eV) and the strong band at 385 nm (3.22 eV) related to NBE and exciton impacts. The (LO)-phonon replicas described in Ref [38], are weak and difficult for analysis. The UV luminescence for these samples is less intensive than for deposited from electrolyte 2 while the green bands are less intensive. No additional blue bands are observed for

these ZnO coverages, probably, because of lower $[V_O^+]$ and $[Zn_i^+]$ defect concentrations and higher quality of resulting wurtzite polycrystallites.

At 77 K the strongest PL maximum is found at 370 nm (3.35 eV), and two bands (green and yellow) are presented at 490 nm (2.53 eV) and 550 nm (2.25 eV), respectively. According to the literature, the green photoluminescence is characteristic of wurtzite ZnO and is associated with its intrinsic defects, such as oxygen vacancy [15], interstitial zinc or zinc in oxygen position [3]. At low temperatures the 550 nm yellow band is stronger than the green band. The experiments were carried out to determine the lifetime of nonequilibrium charge carriers. In the case of samples obtained from a non-aqueous electrolyte, it is possible to trace a slight increase in the lifetime, which was 5.5 ± 0.1 μ s, while for samples obtained from an aqueous electrolyte, the lifetime is smaller and equal to 4.9 ± 0.1 μ s.

Optical characteristics of the ITO glass substrate play an important role for the ZnO film characteristics. A high-density (0001) oriented growth of ZnO nanorods on conductive substrates restrains the visible luminescence [7]. Here we observe the preferential ZnO crystal growth perpendicular to <001> direction with hexagon platelet-like morphology [6] that results in insignificant changes for relative intensity of the green PL emission band.

Thereafter the annealed ZnO films were studied using the optical spectroscopy technique to characterize their optical transparency and reflectance inputs. Figure 11 ITO substrates from aqueous electrolytes with Na_2EDTA and DMSO. The theoretical thickness of the deposited films was varied in a range of 100–1000 nm to reach full coverage of the ITO glass and also to reveal samples with the finest optical and structural characteristics. The transmission spectra (Fig. 12) show a significant improvement of optical transmittance characteristics for all the films after thermally activated oxidation of metal zinc by oxygen.

The most reliable results were observed for samples with theoretical thickness of 200 nm and 300 nm. The direct optical transmission of such films increases by 5–8% after the calcinations. The percentage of metal zinc in such films is rather low, and calcinations do not change significantly the optical spectrum profiles of these groups of samples. The optical transmission T of these films at 500 nm is in a range of 60–70%.

Thicker films of 1000 nm or more demonstrate the lowest transmission values of just about 40–50%. Such frustrating values result probably from strong reflectance input for the thickest samples. According to Ref [40] the strongest reflectance in 400–600 nm spectral range is typical for the <001> plane of ZnO grains, however, the anisotropy of reflectance is insignificant. In contrast, the finest films deposited from electrolyte 2 with a theoretical thickness of 100 nm demonstrated the highest T values

Fig. 9 **a** AFM data of the porous ZnO opal film with normalized thickness of 0.3 deposited in DMSO-based electrolyte 3. **b** Principal architecture of the sample with normalized thickness 0.3

which were equal to the data on the bare ITO glass. Most likely, such ZnO films are much more deficient than 100-nm thick ZnO films deposited from DMSO electrolyte. The films deposited from electrolyte 3 showed direct transmission of 65–70% at 550 nm wavelength.

In Fig. 11 optical transmittance spectra of ZnO opal films deposited from electrolytes 2 and 3 are demonstrated. The average grain size for these coverages are 60 ± 20 nm and 140 ± 50 , respectively. The profiles of inverse ZnO opals differ from the profile of the transmittance spectrum of its ITO glass substrates. The spectra differ also from all spectra of uniform ZnO coverages shown in Fig. 10. Probably, this change is due to high continuity of the opal films and their low deficiencies, especially, low intrinsic defect concentration for deposits of electrolyte 3. Low transparency of in UV region is also a characteristic feature for inverse opal structures that originates from its secondary microstructure [41]. ZnO inverse opals absorb light much more efficiently in 300–400 nm diapason than the uniform films of the same thickness. On the other hand, the transmittance at 550 nm reaches 67% and 74% for inverse opals electrodeposited from electrolytes 2 and 3, respectively. Lower reflectance demonstrated for the inverse opal deposited from DMSO electrolyte (electrolyte 3) originates both from

higher quality of opal structure and lower point defect relaxation processes within the material.

Optical reflectance spectra of ZnO and Au/ZnO inverse opal films are demonstrated in Fig. 13. At the reflectance angle 64° films of ZnO and Au/ZnO inverted opals show the green band at about 500 nm (2.53 eV). According to reflectance spectra of the samples the reflectance coefficient R in 500–900 nm range grows up with gold sputtering. At the same time the characteristic minimum at 500 nm observed at a reflectance angle of 64° is found for the Au-coated opal films. Also the profiles of the UV–vis reflectance spectra of Au/ZnO opal films correlates well with corresponding reflectance spectra of Au inverse opal films obtained electrochemically [42]. Narrow minima at 563 and 690 nm presented in spectra are related to spectrophotometer laser changing.

4 Conclusions

Electrochemical crystallization is a powerful technique for preparing functional coatings on conductive surfaces. Electrochemically deposited ZnO porous coverages are promising for application as a part of “sandwich-type”

Fig. 10 Photoluminescence spectra of ZnO coverages deposited from zinc acetate electrolytes, namely, **a** aqueous electrolyte (electrolyte 2) and non-aqueous DMSO electrolyte (electrolyte 3) at 293 K, and **b** DMSO electrolyte (electrolyte 3) at 293 K and 77 K. The excitation laser – 337 nm

microelectronic structures because of their good adhesion and continuity. Polystyrene template provides uniform porosity of the samples with arranged macropores.

The presence of Na_2EDTA as a chelating agent for Zn^{2+} cations decreased the particle size. In case of DMSO electrolytes, Na_2EDTA increased the particle size with the growth of crystallization process.

ZnO opals synthesized using aqueous and nonaqueous electrolytes had most uniform structure in case of DMSO electrolytes. Such ZnO opal films had higher transmittance in yellow–red spectral region, likely, because of lower concentrations of point defects. Transmittance of the ZnO photonic crystalline films reaches 74% at 550 nm. Magnetron sputtering of 20 nm gold coverage onto ZnO opal film resulted in nanocomposite structure with similar optical characteristics as solid gold opal that makes them promising for SERS spectroscopy, photonic or optoelectronic applications.

Fig. 11 Optical transmittance spectra of ZnO coverages deposited from **a** aqueous electrolyte (electrolyte 2) and **b** DMSO electrolyte (electrolyte 3)—pristine and after annealing at 500 °C

Fig. 12 Optical transmittance spectra of ZnO inverse opal films deposited from (1) aqueous electrolyte (electrolyte 2) and (2) DMSO electrolyte (electrolyte 3 after annealing at 500 °C). (3) ITO transmittance spectrum is given as a black line

Fig. 13 Optical reflectance spectra of **a** ZnO and **b** Au/ZnO inverse opal films at different reflectance angle

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests

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