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PREPARATION AND CHARACTERIZATION OF ZnO AND TiO_2 SOL-GEL THIN FILMS DEPOSITED BY DIP COATING

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ZnO and TiO_2 thin films were prepared by sol-gel technique. Dip coating was applied for film deposition and withdrawal velocity was varied in order to control the film thickness. The deposited films were annealed to remove additives and obtain oxide layers. Large silicon and glass substrates were coated with homogeneous, reflective semiconductor layers of different refractive index values. UV-Vis spectroscopy and scanning angle reflectometry measurements were performed to determine refractive index and thickness values. The using of different stabilizers for ZnO precursor sol preparation resulted in different layer thicknesses and very different response to the varying of the withdrawal speed. According to photoluminescence measurements ZnO films are of good crystallinity. Thicknesses of deposited films were found to be in the range of 6-200 nm. TiO_2 coatings show strong interference colours due to their high refractive index.

Keywords: ZnO, TiO_2, sol-gel coating, scanning angle reflectometry, UV-Vis spectroscopyIntroduction

Nanostructured wide gap semiconductors emerged in the last decade and many researchers [1, 2, 3, 4] began to pay attention to unique properties of these materials. Oxide semiconductor thin films, aerogels and nanocrystals can be used in photonic devices, drug delivery, sensors, solar cells, wastewater treatment etc. Among these promising materials ZnO and TiO_2 are the most versatile ones, since their non-toxicity, stability and ease to prepare. ZnO has been recently used in UV LEDs as light emitting material [5, 6] and in solar cells as transparent conductive oxide [7, 8], while TiO_2 plays the basic role as electron acceptor in the Grätzel cell [9, 10], and also used as antimicrobal and self-cleaning coating [11] because of its photocatalytical property [12, 13, 14]. Thin films of ZnO and TiO_2 can be deposited by many methods, e.g. chemical bath deposition [15, 16], spray pyrolysis [17, 18], rf magnetron sputtering [19, 20]. Among them sol-gel technique [21, 22] and dip coating provide low-cost deposition method which can be applied in large scale production and allows the possibility to tailor the film properties.

Refractive index and thickness of thin films used in optical devices have to be adequately controlled. Determining these parameters is of great importance in many optical applications [23, 24] and particularly in the semiconductor industry [25, 26]. Ellipsometry provides means to perform fast and non-destructive measurements [27, 28] on thin films however for very thin coatings (e. g. film with thickness below 100 nm, nanoparticulated layers and monomolecular coatings) scanning angle reflectometry (SAR) [29, 30, 31] can be an other appropriate choice. This method possesses the capability to determine those important parameters very precisely since it operates with polarized monochromatic light and measurements are usually performed in angle range around the Brewster angle of the substrate/air interface providing good sensitivity due to the lack of reflected light from the substrate. SAR also can be used for measurement of layers on transparent substrates.

Our investigation focused on the preparation of oxide semiconductor coatings and adjusting their thicknesses and refractive indices. Deposition method and starting precursor sol have obvious influence on sol-gel film properties. Several additives such as monoethanolamine [32], triethanolamine [33] and acetic acid [34] are used for ZnO precursor sol preparation to stabilise the sol and control the hydrolysis. In this work two different ZnO precursor sols were prepared and thin films were deposited from each sol by dip coating using different withdrawal velocities.

The influence of chemical composition of precursor sols on the optical properties and thickness of mono- and multilayered coatings were investigated by optical methods. Since TiO_2 possesses many properties similar to ZnO our investigation was extended to TiO_2 thin films. TiO_2 precursor sol was prepared and TiO_2 films were deposited and characterized on the same way as ZnO films.

Experimental details

Preparation of precursor sols

Different ZnO precursor sols were prepared using polyvinylpyrrolidone (PVP) [35] or diethanolamine (DEA) [36] as stabiliser. In the former case 1.098 g zinc acetate dihydrate (A.C.S. Reagent, 98+%, Sigma-Aldrich) was added to 50.0 ml ethanol (a. r. >99.7%, Reanal). Under vigorous stirring 0.450 ml distilled water (conductivity: 18.2 mS/cm, purified with Millipore Simplicity 185 filtration system) was added drop by drop to the solution in order to promote the hydrolysis. After 15 minutes 2.000 g PVP K90 (M.W. 360000, Fluka) was added to the solution in small portions. The sol became clear after 20 minutes. The sol was aged for 24 hours under continuous stirring at room temperature then it was labelled as PVP-ZnO and was stored in the dark.

Precursor sol containing diethanolamine was prepared by dissolving 5.488 g zinc acetate dihydrate in 50 ml ethanol. After 30 minutes of vigorous stirring 2.4 ml DEA (for synthesis, ≥98%, Merck) was added dropwise to the solution. In a few minutes after adding DEA the solution became clear. It was aged for 24 hours under continuous stirring at room temperature before film deposition. The sol was labelled as DEA-ZnO and was kept in the dark.

In order to obtain TiO_2 precursor sol [37], 11.74 ml tetrabuthyl orthotitanate (purum, ≥97.0%, Fluka) was dissolved in 55.40 ml ethanol under continuous stirring at room temperature. It was followed by addition of 65% HNO_3 (RPE, Carlo Elba) to adjust the pH of the sol to ~1.5. Then 0.453 ml distilled water was added to the solution then it was stirred with 400 rpm. at 60 °C for 2 hours before film coating.

Precursor sols were stored in closed containers to prevent evaporation. ZnO sols can be used for film coating even after 2 months, but TiO_2 sol showed slow gelation resulting in solidification in two weeks.

Deposition of thin films

Thin films from different precursor sols were deposited by dip coating (dip coater, MFA, Hungary). This equipment provides withdrawal velocities between 0.1–18.0 cm/min. Glass microscope slides (Menzel-Gläser, 76×26 mm, refractive index: 1.517) were used as substrates for purposes of SAR and spectroscopy measurements. Thin films for photoluminescence investigations were coated onto Si (100) substrates. Prior to dip coating all substrates were cleaned consecutively with detergent, cc. HNO_3, distilled water and ethanol. After cleaning they were dried in dust free environment.

After preliminary tests a range of withdrawal velocities were applied, films from PVP-ZnO sol were deposited with rates of 1, 4, 8 and 12 cm/min, while films from DEA-ZnO and TiO_2 sols were prepared using 12, 15 and 18 cm/min withdrawal velocities. All films were deposited from freshly prepared precursor sols. After coating PVP-ZnO films were dried at room temperature for 5 min then annealed at 500 °C for 1 h. TiO_2 films also were dried at room temperature for 5 min then treated at 450 °C for 30 min. DEA-ZnO films were placed into hot (250 °C) furnace immediately after coating and annealed at 500 °C for 1 h. All films were heated up with 5 °C/min heating rate.

Investigation methods

Refractive indices and thicknesses of thin films were determined by UV-Vis spectroscopy and scanning angle reflecometry (homemade SAR device, He-Ne laser, wavelength: 632.8 nm, power: 17 mW, Melles-Griot). Measured reflectance curves were smoothed before evaluating to eliminate the effect of interference. Refractive index and thickness values were obtained by fitting simulated reflectance functions [38]. UV-Vis spectroscopy measurements were performed by Agilent 8453 spectrophotometer. Crystalline quality was investigated with photoluminescence measurements performed by Perkin Elmer LS50B fluorimeter.

Results and discussion

The resulted thin films were found to be transparent, visually homogeneous and reflective as can be seen in *Fig 1*.

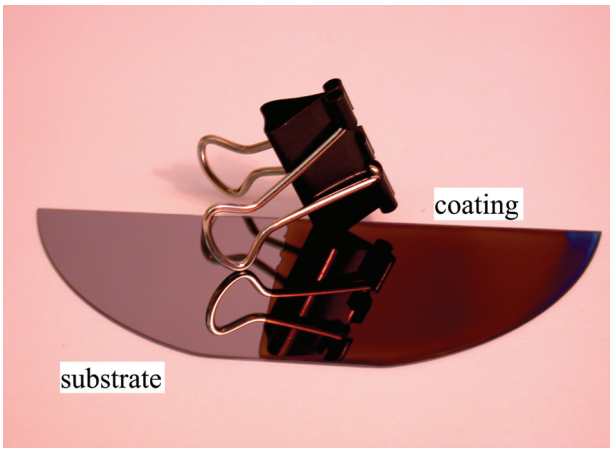

Figure 1: Smooth and reflective surface of TiO_2 film on a piece of 3” Si wafer

UV-Vis transmittance spectra of PVP-ZnO films prepared with different withdrawal speeds are shown in *Fig. 2*. Decrease of transmittance around 380 nm (transmittance edge) is related to the band gap of ZnO. Transmittance around this wavelength decreases with increasing velocities indicating increase of thickness of the thin film. Theoretically, in case of ideal fluids the thickness of fluid film stacked onto the substrate increases with ascendent velocity [39]. Therefore the

growing tendency of film thicknesses is expected for films prepared with increasing velocities. UV-Vis spectra seem to confirm our expectation. For further confirmation SAR measurements were performed. They are shown in *Fig. 3*. Results can be found in *Table 1*. Thickness values grow with increasing velocities and refractive index values are lower in comparison to one of the substrate except for film prepared with 1 cm/min. Low refractive indices can be attributed to interstices formed due to the burnout of the polymer (PVP) during annealing. Low refractive indices resulted in faint antireflection effect. Transmittance maxima corresponding to this effect can be recognized in spectra of films prepared with rates of 8 and 12 cm/min, however the interference is not severe enough for the correct quantitative analysis.

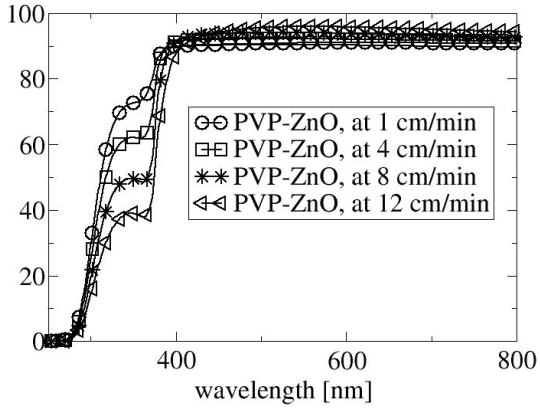

Figure 2: Transmittance spectra of PVP-ZnO films prepared with different withdrawal velocities

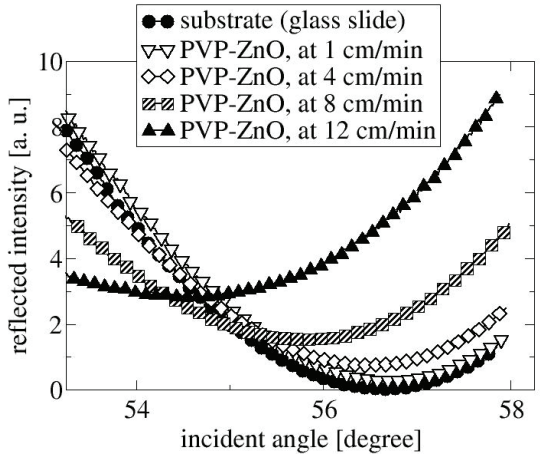

Figure 3: Result of SAR measurements on PVP-ZnO films prepared with different withdrawal velocities

Table 1: Results of SAR measurements on PVP-ZnO films

Withdrawal velocity	**Refractive index**	**Thickness**
1 cm/min	1.684	6.2 nm
4 cm/min	1.338	16.7 nm
8 cm/min	1.420	45.4 nm
12 cm/min	1.404	72.9 nm

Effect of varying withdrawal speed on film thickness was also studied for films prepared from DEA-ZnO and TiO_2 precursor sols. In both cases it was found that those precursor sols are not appropriate for the preparation of films at velocities below ~10 cm/min. Films prepared with lower velocities were inhomogeneous, which might be caused by contraction of thin fluid film before gelation. Therefore films were deposited at higher velocities. Withdrawal speed did not influence significantly the light transmittance of DEA-ZnO films. Transmittance at 380 nm, as can be seen in *Fig. 4*, only decreases few percents with growing velocity, indicating only slight increase of film thickness. Probably because of material properties of that precursor sol the differences between applied speeds are too small to observe notable change in film thickness. For preparation of multilayered films 15 cm/min speed was applied.

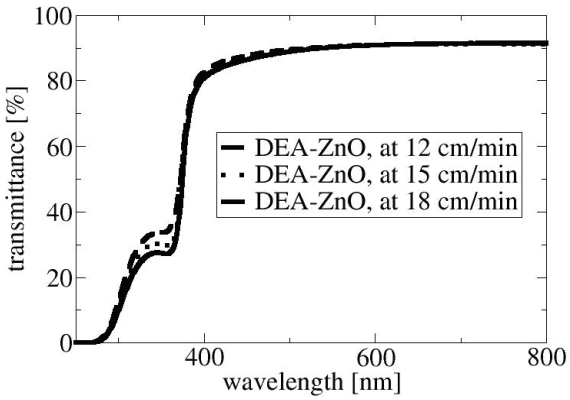

Figure 4: Transmittance spectra of DEA-ZnO films prepared with different withdrawal velocities

DEA-ZnO films containing 1, 2 and 3 layers were prepared. Heat treatment was repeated and UV-Vis as well as SAR measurements were performed after deposition of each layer. Measured spectra and reflectance curves are shown in *Figs. 4* and *5*, respectively. Transmittance spectra of films containing two and three layers show interference extrema, hence refractive indices and film thicknesses can be calculated by analyzing the positions of extrema [40]. Results can be found in *Table 2*. Since transmittance of the three-layered film at the maxima is higher than transmittance of the substrate (~92%), this film is thought to be optically inhomogeneous [41] and its refractive index should decrease towards the outer layer. This phenomenon can be caused by consecutive annealing steps: the inner layer was treated at high temperature three times, while the outer one just once. Therefore the inner parts of the film can be denser and possess higher refractive index. To confirm these results, SAR measurements were performed. As can be seen in Table 2 values obtained by applying different measurement methods are in reasonable agreement for the two layered film, but there is notable difference between refractive index values calculated from UV-Vis and SAR measurements in case of the three-layered film. This deviation is probably caused by the aforementioned refractive index inhomogeneity of that film. These refractive index values

are only reported as rough estimation. This phenomenon must be subjected to further investigations and analysis.

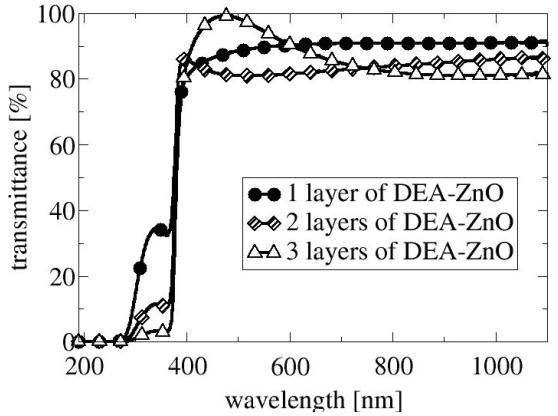

Figure 5: Transmittance spectra of DEA-ZnO films containing 1, 2 and 3 layers

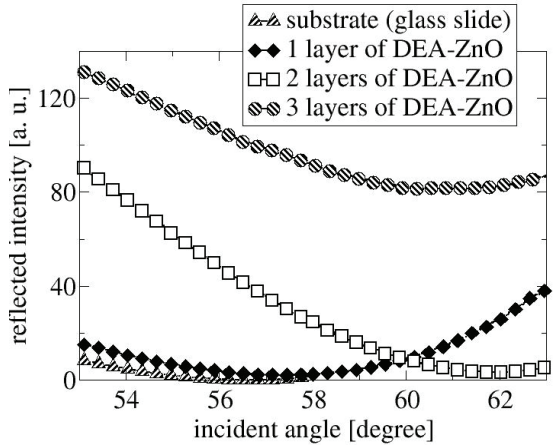

Figure 6: Results of SAR measurements on DEA-ZnO films containing 1, 2 and 3 layers

In case of TiO_2 thin films transmittance spectra show interference extrema due to high refractive index of the films. (Refractive index of anatase (rutile) is 2.52 (2.72) [42], while bulk ZnO possesses refractive index of 2.08. [43]) Therefore refractive indices and film thicknesses were calculated by analyzing positions of interference extrema. Transmittance spectra of TiO_2 films deposited at different withdrawal velocities are shown in *Fig. 7*. As can be seen in *Table 3* film thicknesses rise with ascendent velocity. Refractive index values show slight decrease.

Much like in the case of ZnO, TiO_2 films containing 1, 2 and 3 layers were prepared and examined. Transmittance spectra and measured reflectance curves are reported in *Figs. 8* and *9*, respectively. As can be seen in Table 3, film thickness can be risen up to ~200 nm by repeating layer deposition three times. On the three-layered film there was no SAR measurement performed, since it was too thick to obtain precise results. Values obtained by different methods are in reasonable agreement. No sign of optical inhomogeneity could be observed.

Table 2: Results of SAR and UV-Vis spectroscopy on multilayered DEA-ZnO films

Nr. of layers	**Thickness (SAR)**	**Thickness (UV-Vis)**
1	27.2 nm	-
2	88.0 nm	74.8 nm
3	129.3 nm	136.9 nm
Nr. of layers	**Refractive index (SAR)**	**Refractive index (UV-Vis)**
1	1.653	-
2	1.719	1.725
3	*2.278*	*1.724*

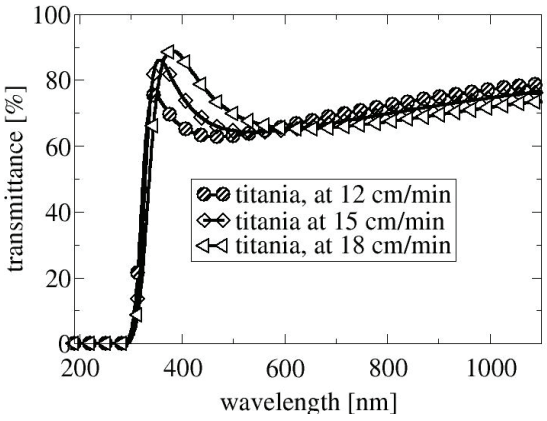

Figure 7: Transmittance spectra of TiO2 film prepared with different withdrawal velocities

Table 3: Results of SAR measurements and UV-Vis spectroscopy on TiO_2 films

Withdrawal velocity	**Refractive index**	**Thickness**
12 cm/min	2.073	57.0 nm
15 cm/min	2.044	65.9 nm
18 cm/min	2.023	79.6 nm
Nr. of layers	**Thickness (SAR)**	**Thickness (UV-Vis)**
1	60.6 nm	58.5 nm
2	133.9 nm	128.7 nm
3	-	201.6 nm
Nr. of layers	**Refractive index (SAR)**	**Refractive index (UV-Vis)**
1	1.994	2.073
2	1.978	1.998
3	-	2.079

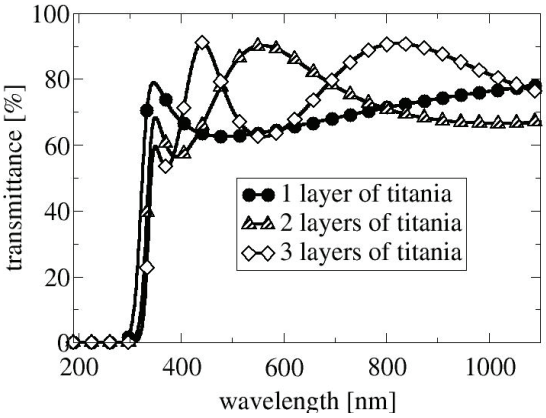

Figure 8: Transmittance spectra of TiO_2 films containing 1, 2 and 3 layers

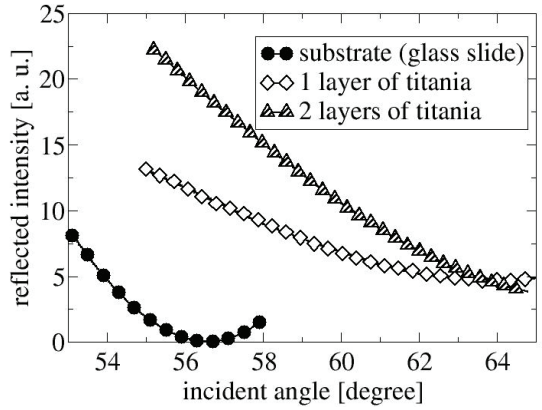

Figure 9: Results of SAR measurements on TiO2 films containing 1 and 2 layers

Films prepared from the same sol, under the same conditions were found to be highly uniform. UV-Vis measurements were performed for comparison. According to our estimation thin films can be prepared with max. 2% standard deviation of average thickness.

Sol-gel ZnO thin films generally consist of nano-sized wurtzite crystals. For comparison of crystalline quality of the DEA-ZnO and the PVP-ZnO films photoluminescence measurements were performed. Excitation wavelength was 310 nm; spectra were recorded using a 350 nm cut-off filter. Normalized PL spectra are displayed in *Fig. 10*. Both samples showed strong violet emission peak at 386 nm, indicating good crystallinity. This peak is related to band edge emission [44]. In the PL spectrum of DEA-ZnO a broad band centered at ~650 nm can be observed, which is related to carrier recombination due to defects, possibly interstitial oxygen ions [45]. The defect-related orange band is absent in the PL spectrum of PVP-ZnO, however a violet-blue peak is observable around ~430 nm, which can be ascribed to zinc-related defects [46].Therefore we can draw the conclusion, that different stabilisers for sol preparation result in diverse defect structures of ZnO thin films.

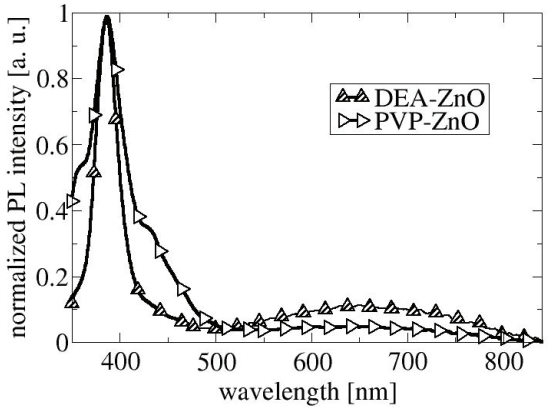

Figure 10: Photoluminescence spectra of DEA-ZnO and PVP-ZnO films

Conclusions

ZnO thin films were prepared from precursor sols containing diethanolamine or polyvinylpyrrolidone as stabiliser. Effect of varying withdrawal speed on refractive index and film thickness values were studied by means of UV-Vis spectroscopy and scanning angle reflectometry. Thicknesses of ZnO-PVP films were found to be in range of 6–74 nm, depending on the withdrawal speed. Refractive indices are low, indicating porous films and resulting in antireflection effect. Withdrawal speed seems to provide good control over thickness of PVP-ZnO layers in contrast with DEA-ZnO layers. In latter case the speed does not seem to possess severe influence on film thickness. TiO_2 thin films were also prepared at different withdrawal velocities and their thicknesses were found to be in the range of 43–80 nm depending on velocity. Multilayered DEA-ZnO and TiO_2 films were prepared; hence film thickness could be elevated up to ~130 nm in case of ZnO films and up to ~200 nm in case of TiO_2 films. Multilayered ZnO was found to be of in-depth optical inhomogeneity. Photo-luminescence measurements revealed good crystalline quality and diverse defect structures of films prepared from different precursor sols.

It is apparent that refractive index and film thickness can be properly tailored by using appropriate starting precursor sol, withdrawal velocity and/or by repeating film deposition. Therefore sol-gel technique and dip coating seem to provide powerful means to fabricate wide gap semiconductor structures with unique optical properties.

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REFERENCES

1 FERNANDES D. M., SILVA R., WINKLER HECHENLEITNER A. A., RADOVANOVIC E., CUSTÓDIO MELO M. A., GÓMEZ PINEDA E. A.: Synthesis and characterization of ZnO, CuO and a mixed Zn and Cu oxide, Materials Chemistry and Physics 115 (2009) 1, 110

2 IRIMPAN L., KRISHNAN B., NAMPOORI V. P. N., RADHAKRISHNAN P.: Nonlinear optical characteristics of nanocomposites of $ZnO–TiO_2–SiO_2$, Optical Materials 31 (2008) 2, 361

3 KURZ A., AEGERTER M. A.: Novel transparent conducting sol–gel oxide coatings, Thin Solid Films 516 (2008) 14, 4513

4 PÁL E., SEBŐK D., HORNOK V., DÉKÁNY I.: Structural, optical, and adsorption properties of ZnO_2/poly(acrylic acid) hybrid thin porous films prepared by ionic strength controlled layer-by-layer method, Journal of Colloid and Interface Science 332 (2009) 1, 173

5 KÖNENKAMP R., WORD R. C., GODINEZ M.: Ultraviolet electroluminescence from ZnO/polymer heterojunction light-emitting diodes, Nano Letters 5 (2005) 10, 2005

6 GUO H., ZHOU J., LIN Z.: ZnO nanorod light-emitting diodes fabricated by electrochemical approaches, Electrochemistry Communications 10 (2008) 1, 146

7 MARTÍNEZ M. A., HERRERO J., GUITÉRREZ: Deposition of transparent and conductive Al- M. T. doped ZnO thin films for photovoltaic solar cell, Solar Energy Materials and Solar Cells 45 (1997) 1, 75

8 NÉMETH Á., MAJOR CS., FRIED M., LÁBADI Z., BÁRSONY I.: Spectroscopic ellipsometry study of transparent conductive ZnO layers for CIGS solar cell applications, Thin Solid Films 516 (2008) 20, 7016

9 KAY A., GRÄTZEL M.: Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder, Solar Energy Materials and Solar Cells 44 (1996) 1, 99

10 GRÄTZEL M.: Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells, Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 1-3, 3

11 EWANS P., SHEEL D. W.: Photoactive and antibacterial TiO_2 thin films stainless steel, Surface and Coatings Technology 201 (2007) 22-23, 9319

12 BOSC F., AYRAL A., GUIZARD C.: Mixed TiO_2-SiO_2 mesostructured thin films, Thin Solid Films 495 (2006) 1-2, 252

13 NASZÁLYI L., BOSC F., MANSOURI A. E., VAN DER LEE A., COT D., HÓRVÖLGYI Z., AYRAL A.: Sol-gel-derived mesoporous SiO_2/ZnO active coating and development of multifunctional ceramic membranes, Separation and Purification Technology 59 (2008) 3, 304

14 BOSC F., AYRAL A., GUIZARD C.: Mesoporous anatase coatings for coupling membrane sparation and photocatalyzed reactions, Journal of Membrane Science 265 (2005) 1-2, 13

15 WATANABE T., HAYASHI H., IMAI H.: Low-temperature praparation of dye-sensitized solar cell through crystal growth of anatase titania in aqueous solution, Solar Energy Materials and Solar Cells 90 (2006) 5, 640

16 WU Z. Y., CHAI J. H., NI G.: ZnO films fabricated form chemical bath deposition form zinc nitrate and ammonium citrate tribasic solution, Thin Solid Films 516 (2008) 21, 7318

17 ABOU-HELAL M. O., SEEBER W. T.: Preparation of TiO_2 thin films by spray pyrolysis to be used as a photochatalyst, Applied Surface Science 195 (2002) 1-4, 53

18 KRUNKS M., MELLIKOV E.: Zinc oxide thin films by the spray pyrolysis method, Thin Solid Films 270 (1995) 1-2, 33

19 PÁL E., SEEMANN T., ZÖLLMER V., BUSSE M., DÉKÁNY I.: Hybrid ZnO/polymer thin films prepared by RF magnetron sputtering, Colloid and Polymer Science 287 (2009) 4, 481

20 MAJOR C., NEMETH A., RADNOCZI G., CZIGANY ZS., FRIED M., LABADI Z., BARSONY I.: Optical and electrical characterization of aluminium doped ZnO layers, Applied Surface Science 255 (2009) 21, 8907

21 MURALI K. R.: Properties of sol-gel dip-coated zinc oxide thin films, Journal of Physics and Chemistry of Solids 68 (2007) 12, 2293

22 MOHAMMADI M. R., FRAY D. J., MOHAMMADI A.: Sol-gel nanostructured titanium dioxide: Controlling the crystal structure, crystallite size, phase transformation, packing and ordering, Microporous and Mesoporous Materials 112 (2008) 1-3, 392

23 SERÉNYI M., RÁCZ M., LOHNER T.: Refractive index of sputtered silicon oxynitride layers for antireflection coating, Vacuum 61 (2001) 2-4, 245

24 VOLK J., FRIED M., POLGÁR O., BÁRSONY I.: Optimisation of porous silicon based passive optical elements by means of spectroscopic ellipsometry, Physica Status Solidi A 197 (2003) 1, 208

25 FRIED M., LOHNER T., AARNINK W. A. M., HANEKAMP L. J., VAN SILFHOUT A.: Determination of complex dielectric functions of ion implanted and implanted-annealed amorphous silicon by spectroscopic ellipsometry, Journal of Applied Physics 71 (1992) 10, 5260

26 PETRIK P., POLGÁR O., FRIED M., LOHNER T., KHÁNH N. Q., GYULAI J.: Ellipsometric characterization of damage profiles using an advanced optical model, Journal of Applied Physics 93 (2003) 4, 1987

27 FRIED M., LOHNER T., POLGÁR O., PETRIK P., VÁZSONYI É., BÁRSONY I., PIEL J. P., STEHLE J. L.: Characterization of different porous silicon structures by spectroscopic ellipsometry, Thin Solid Films 276 (1996) 1-2, 223

28 FRIED M., WORMEESTER H., ZOETHOUT E., LOHNER T., POLGÁR O., BÁRSONY I.: In situ spectroscopic ellipsometric investigation of vacuum annealed and oxidized porous silicon layers, Thin Solid Films 313-314 (1998), 459

29 REGALADO L. E., MACHORRO R., LEYVA-LUCERO M., GARCÍA-LLAMAS R.: Angle scanning reflecometry: study of two characteristic isoreflectance angles, Journal of Phyics D: Applied Physics 25 (1992), 1365

30 MANN E. K., VAN DER ZEEUW E. A., KOPER G. J. M., SCHAAF P., BEDEAUX D.: Optical properties of surfaces covered with latex particles: comparison with theory, Journal of Physical Chemistry 99 (1995), 790

31 KOPER G. J. M.: Optical properties of colloidal films, Colloids and Surfaces A: Physicochemical and Engineering Aspects 165 (2000), 39

32 CHENA J. T., WANGA J., ZHANGA F., ZHANGA G. A., WUA Z. G., YAN P. X.: The effect of La doping concentration on the properties of zinc oxide films prepared by the sol–gel method, Journal of Crystal Growth 310 (2008) 10, 2627.

33 SASANI GHAMSARI M., VAFAEE M.: Sol-gel derived zinc oxide buffer layer for use in random laser media, Materials Letters 62 (2008), 1754.

34 ARMELAO L., FABRIZIO M., GIALANELLA S., ZORDAN F.: Sol-gel synthesis and characterisation of ZnO-based nanosystems, Thin Solid Films 394 (2001) 12-13, 90

35 RATANA T., AMORNPITOKSUK P., RATANA T., SUWANBOON S.: The wide band gap of highly oriented nanocrystalline Al doped ZnO thin films from sol-gel dip coating, Journal of Alloys and Compounds 470 (2009) 1-2, 408

36 DUTTA M., MRIDHA S., BASAK D.: Effect of sol concentration on the properties of ZnO thin films prepared by sol–gel technique, Applied Surface Science 254 (2008) 9, 2743

37 TRAPALIS C., TODOROVA N., ANASTESCU M., ANASTESCU C., STOICA M., GARTNER M., ZAHARESCU M., STOICA T.: Atomic force microscopy study of TiO_2 sol-gel films thermally treated under NH_3 atmosphere, Thin Solid Films 517 (2009) 23, 6243

38 DEÁK A., HILD E., KOVÁCS A. L., HÓRVÖLGYI Z.: Characterisation of solid supported nanostructured thin films by scanning angle reflectometry and UV-Vis spectrometry, Materials Science Forum 537-538 (2007), 329

39 GUGLIELMI M., ZENEZINI S.: The thickness of sol-gel silica coating obtained by dipping, Journal of Non-Crystalline Solids 121 (1990) 1-3, 303

40 HILD E.: Period. Polytech., Chem. Eng. 19 (1975) (4), 291

41 HILD E., DEÁK A., NASZÁLYI L., SEPSI Ö., ÁBRAHÁM N., HÓRVÖLGYI Z.: Use of the optical admittance function and its WKB approximation to simulate and evaluate transmittance spectra of graded index colloidal films, J. Opt. A: Pure Appl. Opt. 9 (2007), 920

42 WELLS A. F.: Structural Inorganic Chemistry, 5th ed.; Claredon Press: Oxford, 1984

43 WYPYCH G.: Handbook of Fillers, 2nd ed., Chem. Tech. Publishing, Canada, 1999

44 SAGAR P., SHISHODIA P. K., MEHRA R. M., OKADA H., WAKAHARA A., YOSHIDA A.: Photoluminescence and absorption in sol–gel-derived ZnO films, Journal of Luminescence 126 (2007) 2, 800

45 O'BRIEN S., KOH L. H. K., CREAN G. M.: ZnO thin films prepared by a single step sol–gel process, Thin Solid Films 516 (2008) 8, 1391

46 VALERINI D., CARICATO A. P., CRETI A., LOMASCOLO M., ROMANO F., TAURINO A., TUNNO T., MARTINO M.: Morphology and photoluminescence properties of zinc oxide films grown by pulsed laser deposition, Applied Surface Science 255 (2009) 24, 9680