Characterization of sol gel $\text{Zn}_{1-x}\text{CaxO}$ thin layers deposited on p-Si substrate by spin-coating method

Afif Fouzri, Nouf Ahmed Althumairi, Vincent Sallet, Alain Lusson

► To cite this version:

Afif Fouzri, Nouf Ahmed Althumairi, Vincent Sallet, Alain Lusson. Characterization of sol gel $\text{Zn}_{1-x}\text{CaxO}$ thin layers deposited on p-Si substrate by spin-coating method. Optical Materials, 2020, 110, pp.110519. 10.1016/j.optmat.2020.110519 . hal-03046131

HAL Id: hal-03046131

<https://hal.science/hal-03046131>

Submitted on 9 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Characterization of sol gel $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin layers deposited on p-Si substrate by spin-coating method.

Afif Fouzri^{1,2,*}, Nouf Ahmed Althumairi^{1,2,3}, Vincent Sallet⁴, Alain Lusson⁴

¹Department of physics, College of Science, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31441, Saudi Arabia.

²Basic & Applied Scientific Research Center, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31441, Saudi Arabia.

³Department of Biology, College of Education, Majmaah University, P.O. Box 66, Almajmaah 11952, Saudi Arabia.

⁴Université Paris-Saclay, CNRS, Université de Versailles St Quentin en Yvelines, Groupe d'étude de la matière condensée (GEMAC), 45 Avenue des Etats-Unis, 78035 Versailles, France.

Abstract:

Thin films $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ ($0 \leq x \leq 6\%$) on a p-Si substrate are elaborated by sol-gel process and spin coating. X-ray diffraction displays a hexagonal wurtzite structure with an increase of lattice parameters confirming the substitution of Zn^{2+} by Ca^{2+} . The estimation of crystallite sizes along the three main crystallographic planes is practically constant (22 nm) suggesting a spherical symmetry shape of the crystallites which is confirmed by SEM. UV-visible reflectance spectra attest a band gap tuning from 3.144 to 3.262 eV which is confirmed by the PL measurement at 2 K for $\text{Zn}_{0.94}\text{Ca}_{0.06}\text{O}$ sample by the appearance of a broad band around 3.508 eV. Although the luminescence of the samples is weak, we well distinguish the free exciton emission (FX_A) positioned at 3.376 eV and the bound exciton recombination (D^0X) around 3.362 eV.

Keywords: $\text{Zn}_{1-x}\text{Ca}_x\text{O}$, Sol gel, spin coating, X-ray and Optical properties

* Corresponding author, E-mail: Anfouzri@iau.edu.sa

1. Introduction

Transparent conductive oxides (TCOs) have relatively low resistivity ($10^{-4} \Omega\cdot\text{cm}$), which makes them interesting for optoelectronic and electroluminescence applications [1]. At the forefront of these materials the zinc oxide (ZnO) semiconductor. It is considered a "twin" material of gallium nitride (GaN) with some advantages. Indeed, its constituents are abundant in nature and the massive crystallization technology is simpler, which already makes it possible to commercially produce ZnO substrates. It has a large exciton binding energy (60 meV) at room temperature, a wide band gap (3.37 eV), excellent thermal and chemical stability and is inexpensive as it is environmentally friendly [2,3]. Furthermore, zinc oxide can be doped with various elements to improve their electrical, optical, magnetic, piezoelectric and electronic properties [4,5]. Zinc oxide occupies an important place in the industry, can be used in various fields such as piezoelectricity, photovoltaic effect as a contact electrode or as a device for photon conversion (up and down), optoelectronics, spintronics, gas detection and nonlinear optics [6]. Recently, Ag, Mg and Ca doped ZnO-Al₂O₃ heterostructure [7-9] have been reported as promising materials for the photocatalytic degradation of caffeine as a model pharmaceutical pollutant.

For a very long time, great interest has been paid to the synthesis and characterization of pure, doped and co-doped zinc oxide in different nanoscale shapes such as nanoparticles, thin films, nanobelts, nanorods, nanowires, nanotubes and nanopods [10], in order to emerge new nanosystems or highly modified and sophisticated devices which are developing rapidly and are demanding. Numerous researches have focused on the synthesis and characterization of nanostructures for the fabrication of nanoelectronic and optoelectronic devices. The physical properties can be improved by doping and co-doping ZnO. Many of studies have been performed for transition metal, nonmetal and rare-earth-doped ZnO for different applications. The existence of this large number of publications on this subject is also due to the variety of synthesis techniques of such material. To grow ZnO nanostructures, many expensive growth techniques are available, including molecular beam epitaxy (MBE) [11], different chemical vapor deposition (CVD) techniques [12,13], magnetron sputtering (MS) [14], vapor transport deposition (VTD) [15], pulsed laser deposition (PLD) [16], and thermal evaporation [17]. These numerous elaboration techniques involve very hard growth conditions, as high pressure and temperature, and use unsafe chemicals. Furthermore, simple growth techniques and low cost, such as, sol gel [18], hydrothermal growth methods [19], electrodeposition [20], and chemical bath deposition [21] can be used for the synthesis of ZnO nanostructures.

By alloying different concentrations of Mg or Be or Cd, band gap of ZnO can be tuned toward higher or lower energies. Therefore, much experimentally and theoretically studies on $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ [22] and $\text{Zn}_{1-x}\text{Be}_x\text{O}$ [23], $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ [24] alloys, has been carried out. In addition to the mentioned ZnO-based alloys, CaO which have a mineral salt structure with a band gap of 7.2 eV, can form an alloy with ZnO as that obtained by MgO, when Ca is incorporated on substitution Zn sites [25].

Recent theoretical studies by first-principles total energy calculations demonstrated that $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ alloys maintain unchanged the ZnO hexagonal crystal structure [26,27] for x between 0.25 and 0.375 at % and it is another possible candidate to obtain larger band gap modulation. Recently, more than 12% increase in the optical band gap of ZnCaO thin layers alloy with $x=0.15$ Ca concentration elaborated by the sol–gel method is reported by Misra et al. [28]. Doping with Ca in ZnO is important for optical [29], sensing [30] and biological [31] applications. However, the experimental study of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ alloy is little explored, and the solid solubility limit and physical properties modifications of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin layers are not clear at now. In this work, $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin films on p-Si substrates elaborated by sol gel method and deposited by spin coating technique have been grown. The structural, morphological and optical properties of the films will be investigated as function of the Ca compositions.

2. Experimental details

2.1. Preparation of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin films

Pure ZnO and ZnCaO thin layers were synthesized by sol–gel method and deposited by spin coating on p-Si (001) substrates. The sample preparation procedure is similar to that previously described in details in our recent published works [32]. In our case we only change the source of dopant and we have used calcium acetate hydrate $\text{C}_4\text{H}_6\text{CaO}_5$ (sigma-Aldrich, 99.9%). The molar ratio of ethanolamine $\text{C}_2\text{H}_7\text{NO}$ (sigma-Aldrich, $\geq 99.0\%$) to zinc acetate dihydrate $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (sigma-Aldrich, 99.999%) was also fixed at 1:1. The weigh content of $\text{Ca}^{2+}/\text{Zn}^{2+}$ in the ZnO sol is varied from 0% to 15%.

2.2. Characterization method

Structural characterization of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin film is explored by a Bruker D8 X-ray diffractometer (XRD) with CuK_α radiation ($\lambda_{\text{CuK}_\alpha}=1.5406\text{\AA}$). Energy dispersive X-ray spectroscopy (EDX) was performed to give the elemental analysis of the sample. The surface morphological characterization of our samples has been explored by scanning electron microscopy (SEM, Thermo Scientific FEI Q250) operating at an accelerating voltage of 20

kV. The reflectance spectra were measured using a Shimadzu SolidSpec-3700DUV. The photoluminescence (PL) measurements were carried out at 2 K using the 325 nm line excitation from a He-Cd laser and a beam power of 10 mW.

3. Results and discussions

3.1. Calcium composition

The EDX analysis of $\text{ZnCaY}\% \text{O}$ thin films on p-Si substrate is shown in Figure 1 (a-e), where Y represent the Ca weigh percentage contend used in the preparation of sol gel. The atomic percentage of the elements present in our samples are listed in table inset each curve. For verifying the composition uniformity, EDX spectra were recorded at different places of the samples and a variation of $\pm 0.15\%$ atomic percentage is detected.

The calcium percentage obtained from EDX spectra of doped samples are respectively 0.82%, 1.34%, 2.39% and 2.8%. As solid solution $\text{Zn}_{1-x}\text{Ca}_x\text{O}$, the composition x are respectively 1.6%, 2.7%, 4% and 6%. The thickness, which estimated by Nano-calc 2000 (UV-Vis Lights), of layers are approximately equal to 1.2 μm . Scanning electron microscope (SEM) was used to explore the surface morphology of all thin films which are shown in figure 2 (a-e). The morphology of all samples consists of rounded grains which are randomly distributed. However, the grain size of doped ZnO film is higher and present more and larger voids than that of pure ZnO film.

3.2. Structural properties

The crystalline structure of the $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin films with different x Ca concentrations (0, 1.6, 2.7, 4 and 6 at%) was performed by XRD analysis. Figure 3 (a-e) shows the corresponding patterns. The XRD spectra of commercial ZnO powder (Sigma-Aldrich inventory: 1314-13-2) and that of pure ZnO on p-Si are also shown for comparison. Spectra are intentionally displaced in intensity for more clarity.

X-ray spectra for all samples show a superposition of layer and substrate peaks. As compared to XRD pattern of ZnO powder, all samples are polycrystalline and have hexagonal wurtzite structure with good crystallinity. No other ZnO diffraction peak is detected which prove the incorporation of Ca in ZnO matrix without altering the wurtzite structure. As shown in figure 4 pure ZnO on p-Si present a preferential orientation along the c-direction in opposite of those alloy films $\text{Zn}_{1-x}\text{Ca}_x\text{O}$. This preferential orientation is explained by the lowest (002) surface energy density in wurtzite crystal structure [33]. For alloys and compared to powder ZnO there are no significant preferential orientation, albeit the intensities of the two first peaks

(100) and (002) are practically the same. However, a deterioration of the layer mosaicity is manifested by wider and less pronounced peaks in comparison with those of powder ZnO. The average crystallite sizes of the sample have been estimated using Scherrer's equation, presented below [34]:

$$t_{ds} = \frac{k \lambda}{\beta \cos(\theta)}$$

Where k is the shape factor which is taken as 0.9, λ ($=1.5406 \text{ \AA}$) is the incident X-ray wavelength, β is the full width at half maximum (FWHM) measured in radians and θ is the diffraction peak angle. Crystallite sizes along three crystallographic planes (100), (002) and (101) are calculated and presented in table 1 for all samples.

Practically no significant change in the crystallite size ($\sim 22 \text{ nm}$) is observed for the layers on p-Si substrates but smaller than the commercial powder ($\sim 42 \text{ nm}$). Grain size can be affected by different parameters such as precursor concentration [35], nature of solvent [36], thickness [37], temperature [38] etc. In our previous work [18] and using the same chemical product and synthesis process, crystalline size ($\sim 22 \text{ nm}$) of ZnO layer deposited on glass, ZnO, Sapphire (001) and p-Si (001) and (111) substrates were close to those obtained for $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ in this work. The similitude of crystallites size obtained along the three crystallographic plane show the independence of the broadening Bragg diffraction peaks with Miller indices of the corresponding crystallographic planes. This indicated a spherical symmetry in the crystallite shape as seen by SEM (figure 2).

But peak diffraction broadening can be caused by crystallite size and also by lattice strain. It is a description of the lattice parameters distribution arising from crystal deformations. Different methods like the Rietveld refinement, pseudo-Voigt function, and Warren – Averbach analysis can be used to determinate the crystallite size and lattice strain [39]. We have chosen to use the Williamson and Hall (WH) plot to distinguish each part contribution of crystallite size and strain in FWHM of X ray diffraction peak. WH analysis is an easy procedure which deconvolves size and strain effect by considering the FWHM peak as a function of 2θ [28,40] which is represented by:

$$\beta \cos \theta = \frac{\lambda}{t_{WH}} + 4\varepsilon \sin \theta$$

Where t_{WH} is the crystallite size and ε is the strain. The plot of $(\beta \cos \theta)$ versus $(\sin \theta)$ should be a straight line. Hence, the data can be fitted using a straight line, where the strain in the sample is obtained from the slope and the intercept on the y-axis gives the inverse of average

crystallite size in the materials. The WH plot for our sample are presented in figure 5 and the obtained values of strain and crystallite size are summarized in table 1 and represented in figure 6 as function of x Ca concentration.

Crystalline size determined by the two methods are close to those obtained in references [41-46] but higher than that reported by A. Srivastava et al. (3 - 15 nm) [45]. The positive and negative signs of ε indicate respectively tensile and compressive strains. Positive strain values are obtained for 0% and 1.6% $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ which is higher even when the amount of Ca concentration is low. For Ca compositions higher than 2.7%, the absolute values of strain are greater than those for $x = 0\%$ and $x = 1.6\%$. Calculated crystalline size by Debye Scherrer formula and by WH plot are very close ($\varepsilon \cong 0$) for higher Ca composition ($x=4$ and 6%). But for other samples the strain is not negligible, so the crystallite size deduced by the two methods are different showing that the increase of the FWHM diffraction peak is due to the simultaneous effect of strain and crystallite size.

The dislocation density (δ) along the three crystallographic plane is calculated using the formula $\delta = \frac{1}{t_{\text{DS}}^2}$ [46,47], which represents the amount of defects in the films along each

planes and is summarized in Table 1. Calculated dislocation density for thin film vary between 14.79×10^{14} and 22.67×10^{14} lines/m² which is about four times larger than that estimated in ZnO powder which is due to the substrate influence on the layer.

The lattice parameters 'a' and 'c' for $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ alloy deposited on p-Si substrates are calculated and listed in table 2 by using following equation [18]:

$$d_{hkl} = \left(\frac{4h^2 + h.k + k^2}{3a^2} + \frac{\ell^2}{c^2} \right)^{-1/2}$$

Where lattice parameter are planar spacing. The experimental errors on d_{hkl} is the inter estimated to be 0.003Å. The a-, c- lattice constant determined by XRD, the ratio c/a and the cell volume are plotted as functions of Ca composition in figure 7 (a) and (b) respectively. Lattice variation curves slightly deviate from Vegard's law as reported by Bai et al. [48] obtained by theoretical approach using density-functional theory, so it is consistent with known results for wurtzite structure [27]. The calculated lattice constants are close to that given by JCPDS card 36-1451 and those of commercial ZnO powder. For alloys, lattice parameters and cell volume increase as the Ca composition increases while the ratio (c/a) decrease slightly from 1.6017, which differ very little from those of commercial powder and JCPDS data (c/a~1.602), to 1.600 for all alloys deposited on p-Si substrate. These

observations are similar to those obtained by Bai et al. [48]. The increase of crystal lattice confirms the substitution of Zn cation by Ca cation as the ionic radius of Ca^{2+} (0.99 Å) is larger than that of Zn^{2+} (0.74 Å) [49].

3.3. Optical properties:

3.3.1 Optical reflectance

The determination of the energy band gap (E_g) of the crystalline material at room temperature is mainly given by the analysis of optical absorption. Reflectance Spectroscopy measurements on $\text{Zn}_{1-x}\text{Ca}_x\text{O}/\text{p-Si}$ were conducted in the ultraviolet-visible region (UV-Vis region) from 300 nm to 600 nm. It is a suitable method for the absorption edges estimation because silicon band gap is lower than that of zinc oxide. Our samples being thick (thickness $\geq 1 \mu\text{m}$), this prevents accidental loss by partial transmission when measuring the percent reflectance. Figure 8 shows the comparison of the reflectance as a function of wavelength for the different samples. Reflectance percentage increases for all sample from about 375 nm (3.3 eV) and reach a maximum from about 430 nm (2.88 eV). The presence of some non-equidistant Fabry–Perot interference oscillations in the reflectance spectrum of ZnO/Si sample proves the presence of an abrupt interface between the substrate and the layer but the thickness is non-uniform (however it indicates a good optical quality of the sample).

The optical absorption can be obtained by the Kubelka-Munk function

$$F(R) = \frac{\alpha}{k} = \frac{(1-R)^2}{2R}, \text{ where } R = R_{\text{sample}}/R_{\text{substrate}} \text{ is the reflectance UV-vis spectra, } \alpha \text{ is the}$$

absorption coefficient and k is the scattering coefficient [50]. As sample thicknesses are greater than the light wavelengths measured (0.6-0.3 μm), the scattering coefficient K is practically independent of frequency [51].

To derive the band gap energies (E_g) for our sample, $[F(R)h\nu]^2$ versus photon energy $h\nu$ (h is Planck's constant and ν is the photon's frequency) is plotted as shown in figure 9. The band gap of thin layer is the intersection value of the linear curve portion with the energy axis [51].

The optical band gap estimated from reflectance spectra of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin films increase from 3.144 eV to 3.262 eV, as seen in table 3 which provides supportive evidence that Ca is incorporated on substitution Zn sites in ZnO .

An enhancement of 3.75% of band gap is obtained for $x=6\%$. It's higher than 3.35% reported by Cao et al. [66] due to 5.3% Ca doping ZnO thin films deposited by PLD and less than 4.28% and 4.14% for respectively 1.47% and 5% Ca doping ZnO film reported by Misra et al. [28] and Srivastava et al. [45]. However, Cao et al. [46] and Misra et al. [28] reported

respectively a band gap of pure ZnO 3.27 eV and 3.391 eV higher than the one obtained in the present work 3.144 eV and then 3.16 eV reported in reference [45,47]. In fact, the layer thickness of the present work and the annealing temperature are close to that used in the reference [30], hence this could explain the similarity in band gap energy values between these two works. Effects of substrate temperature and thickness on energy band gap of ZnO grown on glass by atomic layer deposition have been reported by J. Iqbal et al. [52]. They show a variation of ZnO band gap from 3.06 eV to 3.10 eV as substrate temperature and thickness increase.

3.3.2 Photoluminescence

Low temperature (2K) photoluminescence spectra of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ alloy as function of the Ca composition are shown in figure 10. We distinguish in figure 10 (a) two emission region: near-band-edge (NBE) UV emission and deep-level (DL) visible emission. The broad visible emission band, in the range 2-2.8 eV for all alloys is expected to be due to different lattice defects like zinc vacancies (V_{Zn}), zinc interstitials (Zn_i), oxygen vacancies (V_{O}) and oxygen interstitials (O_i) [53]. The intensity of PL spectra is low, about 3 orders of magnitude compared to the standard ZnO. Indeed, the quality of thin films obtained by our procedure is not as good as that obtained by other more sophisticated deposition methods. The intensity of the visible emission band for the alloys is greater than that of pure ZnO. However this increase is random with the composition x of Ca. This can be explained by the variation of the impurities and the structural defects for each x composition [54]. Compared to visible emission band, the NBE although it is structured, its intensity is lower except for the alloy $x = 4\%$ that they have the same order of magnitude.

Figure 10 (b) displays the near-band-edge emission in the range 2.9 - 3.6 eV for all alloys. The peaks at around 3.36 eV dominates and is attributed to the exciton transition bound to neutral donors (D^0X) [44]. For pure ZnO sample, a small peak at 3.303 eV seem to corresponds to the expected position for the first longitudinal optical (1LO) phonon replicas of D^0X with an exact energy separation of 69 meV which is close to 72 meV reported by Meyer et al. [55]. PL spectra of alloys samples present three close peaks in the range 3.300 - 3.333 eV, the intensity of the peak at greater energy increases with the concentration x of Ca. In the literature, several attributions of the emission band at 3.33 eV origins, often named “Y” band, are reported. It can be related to donor-bound exciton (D^0X) [56], acceptor-bound exciton (A^0X) [57], two electron satellites (TES) [58,59], electron-acceptor transitions (e, A) [60] and transitions related to point [61,62] and/or structural defects [63,64].

As the peak at low energy 3.303 eV (among the three peaks) appear in all PL spectra, so we attribute it to D^0X-1LO . However the two other peaks around 3.316 eV and 3.331 eV is related to radiative recombination of excitons bound to structural-defect such as dislocations and stacking faults induced by the Ca incorporation in ZnO lattice [55,63,65]. Which can explain the change of their relative intensities with the composition x .

A donor-acceptor-pair (DAP) transition appears at around 3.24 eV for all alloys [55]. For pure ZnO, a broad band is located around 3.04 eV which can be originating from zinc vacancies as reported by Jeong et al. [66]. But this band is wider for alloy thin film and for $x \geq 4\%$, we can see a peak around 3.15 eV very close to the emission of Ca^{2+} (3.152 eV). This emission is assigned for ZnO layer on silicon [67] and calcium doped zinc oxide nanoparticles [55] to the electron transition from conduction band to the valence band. It seems to us that the latter attribution is the most likely view the values of the band gap obtained by reflectance spectra. The free exciton emission with the A-valence band (FX_A) is also seen at 3.376 eV [55].

For the alloy $x = 6\%$, a clear and broad band around 3.508 eV confirms the increase of the band gap for this sample. However, it should be noted that the exciton recombination band at low temperature does not change its position with calcium composition for $x \leq 4\%$, which indicates no significant change in band gap opposed to results obtained by reflectance spectra.

4. Conclusion

$Zn_{1-x}Ca_xO$ alloy thin films with different compositions were synthesized by sol gel method and deposited on p-type silicon substrate (001) by spin-coating. A 6% Ca composition is reached without phase segregation which is confirmed by X-ray diffraction. In fact, all samples have a wurtzite structure and the effect of the composition x on morphological, structural and optical properties have been detailed studies. The band gap estimated by UV-visible reflectance measurement is varied from 3.144 eV to 3.262 eV when the Ca composition x increase to 6% and reached 3.508 eV in low-temperature PL spectra. The analysis of low temperature PL spectra shows a weak luminescence but the band edge exciton and the green band around 2.45 eV are well observed. However the appearance of Y line in PL around 3.33 eV for alloys samples suggest an increase of structural defects with the incorporation of Ca. The $Zn_{1-x}Ca_xO$ alloyed thin films can be a possible candidates for the applications in optoelectronic devices.

ACKNOWLEDGMENTS

The authors would like to thank the USCR "Environmental Scanning Electron microscopy FEI Q250 Thermo Fisher", University of Monastir for helpful technical assistance with equipment facilities. We also thank Pr. Tarek Benameur for fruitful discussion.

There are no conflicts to declare.

Credit author statement

Affif Fouzri: Conception, acquisition, analysis and interpretation of data, writing- original draft preparation, final approval of the version to be published. **Nouf Ahmed Althumairi:** Acquisition, analysis and interpretation of data, writing- original draft preparation. **Vincent Sallet:** Critically revising the article for important intellectual content, final approval of the version to be published. **Alain Lusson:** Acquisition of data, critically revising the article for important intellectual content, final approval of the version to be published.

References

- [1] S. Calnan, A. N. Tiwari, High mobility transparent conducting oxides for thin film solar cells, *Thin solid films* **518** (2010) 1839-1849.
- [2] C. Sushma, S. Girish Kumar, Advancements in the zinc oxide nanomaterials for efficient photocatalysis, *Chemical Papers* **71** (2017) 2023-2042.
- [3] D. C. Look, Recent advances in ZnO materials and devices, *Materials Science and Engineering B: Solid-State Materials for Advanced Technology* **80** (2001) 383-387.
- [4] J. Rosowska, J. Kaszewski , B. Witkowski , Ł. Wachnicki , I. Kuryliszyn-Kudelska , M. Godlewski, The effect of iron content on properties of ZnO nanoparticles prepared by microwave hydrothermal method, *Optical Materials* **109** (2020) 110089.
- [5] S. Singhal, J. Kaur, T. Namgyal, R. Sharma, Cu-doped ZnO nanoparticles: Synthesis, structural and electrical properties, *Physics B*, **407** (2012) 1223-1226.
- [6] S. Abed, M. S. Aida, K. Bouchouit, A. Arbaoui, K. Iliopoulos, B. Sahraoui, Non-linear optical and electrical properties of ZnO doped Ni Thin Films obtained using spray ultrasonic technique, *Optical Materials* **33** (2011) 968–972.
- [7] A. Elhalil, R. Elmoubarki, M. Sadiq, M. Abdennouri, Y. Kadmi, L. Favier, S. Qourzal, N. Barka, Enhanced photocatalytic degradation of caffeine as a model pharmaceutical pollutant by Ag-ZnO-Al₂O₃ nanocomposite, *Desalination and Water Treatment* **94** (2017) 254–262.
- [8] A. Elhalil, R. Elmoubarki, M. Farnane, A. Machrouhi, M. Sadiq, F.Z. Mahjoubi, S. Qourzal, N. Barka, Photocatalytic degradation of caffeine as a model pharmaceutical pollutant on Mg doped ZnO-Al₂O₃ heterostructure, *Environmental Nanotechnology, Monitoring & Management*, **10** (2018) 63-72.
- [9] A. Elhalil, R. Elmoubarki, M. Farnane, A. Machrouhi, F.Z. Mahjoubi, M. Sadiq, S. Qourzal, N. Barka, Synthesis, characterization and efficient photocatalytic activity of novel Ca/ZnO-Al₂O₃ nanomaterial, *Materials Today Communications*, **16** (2018) 194-203.
- [10] Z. L. Wang, Nanostructures of zinc oxide, *MaterialsToday* **7** (2004) 26-33.
- [11] Y. W. Heo, V. Varadarajan, M. Kaufman, K. Kim, D. P. Norton, F. Ren, P. H. Fleming, Site-specific growth of Zno nanorods using catalysis-driven molecular-beam epitaxy, *Appl. Phys. Lett.* **81** (2002) 3046-3048.
- [12] X. Liu, X. Wu, H. Cao, R. P. H Chang, Growth mechanism and properties of ZnO nanorods synthesized by plasma-enhanced chemical vapor deposition, *J. Appl. Phys.* **95** (2004) 3141-3147.

- [13] J. M. Ntep, S. S. Hassani, A. Lusson, A. Tromson-Carli, D. Ballutaud, G. Didier, R. Triboulet, ZnO growth by chemical vapour transport, *J. Cryst. Growth* **207** (1999) 30-34.
- [14] S. Kim, M. C. Jeong, B. Y. Oh, W. Lee, J. M. Myoung, Fabrication of Zn/ZnO nanocables through thermal oxidation of Zn nanowires grown by RF magnetron sputtering, *J. Cryst. Growth* **290** (2006) 485-489.
- [15] L. Liao, D. H. Liu, J. C. Li, C. Liu, Q. Fu, M. S. Ye, Synthesis and Raman analysis of 1D-ZnO nanostructure via vapor phase growth, *Appl. Surf. Sci.* **240** (2005) 175-179.
- [16] B. Q. Cao, M. Lorenz, A. Rahm, H. Wenckstern, C. Czekalla, J. Lenzner, G. Benndorf, M. Grundmann, Phosphorus acceptor doped ZnO nanowires prepared by pulsed-laser deposition, *Nanotechnology* **18** (2007) 455707.
- [17] G. Shen, Y. Bando, C. J. Lee, Synthesis and Evolution of Novel Hollow ZnO Urchins by a Simple Thermal Evaporation Process, *J. Phys. Chem. B* **109** (2005) 10578-10583.
- [18] W. Chebil, A. Fouzri, A. Fargi, B. Azeza, Z. Zaaboub, V. Sallet, Characterization of ZnO thin films grown on different p-Si substrate elaborated by sol-gel spin-coating method, *Mater. Res. Bull.* **70** (2015) 719-727.
- [19] M. Guo, P. Diao, X. Wang, J. S. Han, H. Ma, X. H. Zhao, X. H. Zhao, A novel route to synthesize cubic $\text{ZrW}_{2-x}\text{Mo}_x\text{O}_8$ ($x = 0-1.3$) solid solutions and their negative thermal expansion properties, *J. Solid State Chem.* **178** (2005) 3166-3171.
- [20] S. P. Anthony, J. I. Lee, J. K. Kim, Tuning optical band gap of vertically aligned ZnO nanowire arrays grown by homoepitaxial electrodeposition, *Appl. Phys. Lett.* **90** (2007) 103107-1-3.
- [21] W. Chebil, A. Gokarna, A. Fouzri, N. Hamdaoui, K. Nomenyo, G. Lerondel, Study of the growth time effect on the structural, morphological and electrical characteristics of ZnO/p-Si heterojunction diodes grown by Sol-gel assisted chemical bath deposition method, *J. Alloys Compd.* **771** (2019) 448-455.
- [22] A. Fouzri, M. A. Boukadhaba, A. Touré, N. Sakly, A. Bchetnia, V. Sallet, Structural, morphological and optical properties of Cd doped ZnO film grown on a- and r-plane sapphire substrate by MOCVD, *Applied Surface Science* **311** (2014) 648-658.
- [23] M. Chen, Y. Zhu, A. Chen, Z. Shen, Z. Tangb, Optical investigations of Be doped ZnO films grown by molecular beam epitaxy, *Materials Research Bulletin* **78** (2016) 16-19.
- [24] S. C. Su, C. C. Ling, Y. M. Lu, T. Mei, L. Z. Zhao, B. Niu, The optical properties of high quality ZnO/ZnMgO quantum wells on Si (111) substrates, *Solid State Commun.* **152** (2012) 311-313.

- [25] Y. Z. Zhu, G. D. Chen, H. G. Ye, Electronic structure and phase stability of MgO, ZnO, CdO, and related ternary alloys, *Phys Rev B*. **77** (2008) 245209.
- [26] S. Nazir, N. Ikram, B. Amin, M. Tanveer, A. Shaukat, Y. Saeed, Structural, electronic and optical calculations of $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ alloys: A first principles study, *J Phys Chem Solids* **70** (2009) 874-880.
- [27] X. F. Fan, H. D. Sun, Z. X. Shen, J. L. Kuo, Y. M. Lu, A first-principle analysis on the phase stabilities, chemical bonds and band gaps of wurtzite structure $\text{A}_x\text{Zn}_{1-x}\text{O}$ alloys (A= Ca, Cd, Mg), *J Phys: Condens Matter*. **20** (2008) 235221.
- [28] K. P. Misra, R. K. Shukla, A. Srivastava, Blueshift in optical band gap in nanocrystalline films deposited by sol-gel method, *Appl Phys Lett*. **95** (2009) 031901.
- [29] B. Karthikeyan, T. Pandiyarajan, K. Mangaiyarkarasi, Special morphologies of Mg, Ca, and Y-doped $\text{ZnO}/\text{La}_2\text{O}_3$ composite for photocatalysis, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **82** (2011) 97-101.
- [30] W. Water, Y. S. Yang, The influence of calcium doped ZnO films on Love wave sensor characteristics, *Sens. Actuators A* **127** (2006) 360-365.
- [31] A. S. H. Hamud, C. Karthikeyan, S. Sasikumar, V. S. Kumar, S. Kumareson, G. Ravi, Impact of alkaline metal ions Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural, optical, thermal and antibacterial properties of ZnO nanoparticles prepared by the co-precipitation method, *J. Mater. Chem. B* **1** (2013) 5950-5962.
- [32] W. Chebil, M. A. Boukadhaha, I. Madhi, A. Fouzri, A. Lussan, C. Vilar, V. Sallet, Structural, optical and NO_2 gas sensing properties of ZnMgO thin films prepared by the sol gel method, *Physica B* **505** (2017) 9-16.
- [33] Y. Zhang, H. Zheng, J. Su, B. Lin, Z. Fu, Comparison Study of the Luminescent Properties of the White-Light Long Afterglow Phosphors: $\text{Ca}_x\text{MgSi}_2\text{O}_5+x:\text{Dy}^{3+}$ ($x = 1, 2, 3$). *J. Lumin.* **129** (2007) 531-535.
- [34] N. Akin, S. Sebnem Cetin, M. Cakmak, T. Memmedli, S. Ozcelik, Effect of film thickness on properties of aluminum doped zinc oxide thin films deposition on polymer substrate, *J Mater Sci: Mater Electron* **24** (2013) 5091-5096.
- [35] S. O'Brien, L. H. K. Koh, M. Çopuroğlu, G. M. Crean, D. P. Norton, C. Jagadish, I. Buyanova, G.-C. Yi, Zinc Oxide and Related Materials, Boston, MA, USA, 26–30 November 2007, Materials Research Society Symposium Proceedings 1035E (2008) L05–09.
- [36] A. R. Bari, M. D. Shinde, V. Deo, L. A. Patil, Effect of solvents on the particle morphology of nanostructured ZnO, *Indian J Pure Ap Phy* **47** (2009) 24-27.

- [37] M. F. A. Alias, R. M. Aljarrah, H. KH. Al-Lamy, K. AW. Adem, Investigation the Effect of Thickness on the Structural and Optical Properties of Nano ZnO Films Prepared by d.c Magnetron Sputtering, *International Journal of Application or Innovation in Engineering & Management (IJAIEEM)* **2** (2013) 198-203.
- [38] T. Ivanova, A. Harizanova, T. Koutzarova, B. Vertruyen, Study of ZnO sol–gel films: Effect of annealing, *Materials Letters* **64** (2010) 1147-1149.
- [39] A. Kanti Deb, P. Chatterjee, Estimation of lattice strain in alumina–zirconia nanocomposites by X-ray diffraction peak profile analysis, *Journal of Theoretical and Applied Physics* **13** (2019) 221–229.
- [40] K. Omri, A. Bettaibi, K. Khirouni, L. El Mir, The optoelectronic properties and role of Cu concentration on the structural and electrical properties of Cu doped ZnO nanoparticles, *Physica B: Condensed Matter* **537** (2018) 167-175.
- [41] H. Mahdhi, K. Djessas, Z. Ben Ayadi, Synthesis and characteristics of Ca-doped ZnO thin films by rf magnetron sputtering at low temperature, *Materials Letters* **214** (2018) 10-14.
- [42] L. El Mir, Luminescence properties of calcium doped zinc oxide nanoparticles, *Journal of Luminescence* **186** (2017) 98-102.
- [43] T. Das, B. K. Das, S. Parashar, K. Parashar, Temperature and Frequency Dependence Electrical Properties of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$, *Nanoceramic. Bull. Mater. Sci.* **40** (2017) 247-251.
- [44] H. Mahdhi, J. L. Gauffier, K. Djessas, Z. Ben Ayadi, Structural, optical and electrical properties of transparent conductive ZnO:Ca films prepared by rf magnetron sputtering from aerogel nanopowders, *Optik* **137** (2017) 156-166.
- [45] A. Srivastava, N. Kumar, K. K. P. Misra, S. Khare, Blue-light luminescence enhancement and increased band gap from calcium-doped zinc oxide nanoparticle films, *Materials Science in Semiconductor Processing* **26** (2014) 259-266.
- [46] L. Cao, J. Jiang, L. Zhu, Realization of band-gap engineering of ZnO thin films via Ca alloying, *Materials Letters* **100** (2013) 201-203.
- [47] A. Srivastava, N. Kumar, K. Prakash Misra, S. Khare, Enhancement of band gap of ZnO nanocrystalline films at a faster rate using Sr dopant, *Electron. Mater. Lett.* **10** (2014) 703-711.
- [48] L. N. Bai, J. S. Lian, W. T. Zheng, Q. Jiang, First-principles study of optical properties in Ca-doped ZnO alloys, *Cent. Eur. J. Phys.* **10** (2012) 1144-1149.
- [49] X. Linhua, S. Xiao, C. Zhang, G. Zheng, J. Su, Z. L. Wang, Optical and structural properties of Sr-doped ZnO thin films, *J. Mater. Chem. Phys.* **148** (2014) 720-726.

- [50] J. Z. Kong, A. D. Li, H. F. Zhai, Y. P. Gong, H. Li, D. Wu, Preparation, characterization of the Ta-doped ZnO nanoparticles and their photocatalytic activity under visible-light illumination, *J. Solid State Chem.* **182** (2009) 2061-2067.
- [51] H. Zhang, G. Liu, Y. Cao, J. Chen, K. Shen, A. Kumar, M. Xu, Q. Li, Q. Xu, The magnetic and adsorption properties of $\text{ZnO}_{1-x}\text{S}_x$ nanoparticles, *Phys. Chem. Chem. Phys.* **19** (2017) 26918-26925.
- [52] J. Iqbal, A. Jilani, P. M. Z. Hassan, S. Rafique, R. Jafer, A. A. Alghamdi, ALD grown nanostructured ZnO thin films: effect of substrate temperature on thickness and energy band gap, *J. King Saud Univ. Sci.* **28** (2016) 347-354.
- [53] Verdad C. Agulto, Melvin John F. Empizo, Keisuke Kawano, Yuki Minami, Kohei Yamanoi, Nobuhiko Sarukura, Allan Christopher C. Yago, Roland V. Sarmago, Two-step fabrication of ZnO-PVP composites with tunable visible emissions, *Optical Materials*, **76** (2018) 317-322.
- [54] Xu Li, Xinghua Zhu, Kangxin Jin, Dingyu yang, Study on structural and optical properties of Mn-doped ZnO thin films by sol-gel method, *Optical Materials*, **100** (2020) 109657.
- [55] B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworzak, U. Haboeck, A. V. Rodina, Bound exciton and donor–acceptor pair recombinations in ZnO, *Phys. Status Solidi (b)* **241** (2004) 231-260.
- [56] K. Johnston, M. O. Henry, D. McCabe, E. McGlynn, M. Dietrich, E. Alves, M. Xia, Identification of donor-related impurities in ZnO using photoluminescence and radiotracer techniques, *Phys. Rev. B* **73** (2006) 165212.
- [57] H. Kato, M. Sano, K. Miyamoto, T. Yao, Homoepitaxial Growth of High-Quality Zn-Polar ZnO Films by Plasma-Assisted Molecular Beam Epitaxy, *Jpn. J. Appl. Phys.* **42** (2003) L1002-L1005.
- [58] T. Hirai, Y. Harada, S. Hashimoto, N. Ohno, T. Itoh, Luminescence of bound excitons in ZnO:Zn phosphor powders, *J. Lumin.* **113** (2005) 115-120.
- [59] S. F. Chichibu, T. Onuma, M. Kubota, A. Uedono, T. Sota, A. Tsukazaki, A. Ohtomo, M. Kawasaki, Improvements in quantum efficiency of excitonic emissions in ZnO epilayers by the elimination of point defects, *J. Appl. Phys.* **99** (2006) 93505.
- [60] B. Wang, M. J. Callahan, L. O. Bouthillette, C. Xu, M. J. Suscavage, Hydrothermal growth and characterization of nitrogen-doped ZnO crystals, *J. Cryst. Growth* **287** (2006) 381-385.

- [61] H. Shibata, M. Watanabe, M. Sakai, K. Oka, P. Fons, K. Iwata, A. Yamada, K. Matsubara, K. Sakurai, H. Tampo, K. Nakahara, S. Niki, Characterization of ZnO crystals by photoluminescence spectroscopy, *Phys. Status Solidi C- Current Topics in Solid State Physics* **1** (2004) 872-875
- [62] H. Tampo, H. Shibata, P. Fons, A. Yamada, K. Matsubara, K. Iwata, K. Tamura, H. Takasu, S. Niki, The effects of thermal treatments on the electrical properties of phosphorus doped ZnO layers grown by MBE. *J. Cryst. Growth* **278** (2005) 268-272.
- [63] H. Alves, D. Pfisterer, A. Zeuner, T. Riemann, J. Christen, D. M. Hofmann, B. K. Meyer, Optical investigations on excitons bound to impurities and dislocations in ZnO, *Opt. Mater.* **23** (2003) 33-37.
- [64] M. R. Wagner, G. Callsen, J. S. Reparaz, J. H. Schulze, R. Kirste, M. Cobet, I. A. Ostapenko, S. Rodt, C. Nenstiel, M. Kaiser, A. Hoffmann, A. V. Rodina, M. R. Phillips, S. Lautenschläger, S. Eisermann, B. K. Meyer, Bound excitons in ZnO: Structural defect complexes versus shallow impurity centers, *Phys. Rev. B* **84** (2011) 035313.
- [65] A. Gokarna, R. Aad, J. Zhou, K. Nomenyo, A. Lusson, P. Miska, G. Lerondel, On the origin of the enhancement of defect related visible emission in annealed ZnO micropods, *J. Appl. Phys.* **126** (2019) 145104.
- [66] S. H. Jeong, B. S. Kim, B. T. Lee, Photoluminescence dependence of ZnO films grown on Si(100) by radio-frequency magnetron sputtering on the growth ambient, *Appl. Phys. Lett.* **82** (2003) 2625-2627.
- [67] Q. P. Wang, D. H. Zhang, Z. Y. Xue, X. T. Hao, Violet luminescence emitted from ZnO films deposited on Si substrate by rf magnetron sputtering, *Applied Surface Science* **201** (2002) 123-128.

Tables

Sample	t _{DS} (nm)			t _{WH} (nm)	ϵ	Dislocation Density $\delta \times 10^{14}$ lines/m ²		
	(100)	(002)	(101)			(100)	(002)	(101)
x=0%	26	23	23	29	1.10×10^{-3}	14.79	18.90	18.90
x=1.6%	26	21	21	30	1.35×10^{-3}	14.79	22.67	22.67
x=2.7%	21	22	24	11	-5.83×10^{-3}	22.67	20.66	17.36
x=4%	22	22	22	22	-5.50×10^{-5}	20.66	20.66	20.66
x=6%	22	24	22	21	-4.10×10^{-4}	20.66	17.36	20.66
ZnO powder	42	42	46	26	-2.16×10^{-3}	5.66	5.66	4.72

Table1: Crystallite sizes calculated by DS formula and WH plot, strain and dislocation density of Zn_{1-x}Ca_xO thin layer on p-Si substrate with different Ca concentrations, and those of commercial ZnO powder.

Sample	Lattice parameters		c/a	V (Å ³)
	a (Å)	c (Å)		
x=0%	3.241	5.191	1.6017	47.236
x=1.6%	3.243	5.194	1.6016	47.319
x=2.7%	3.251	5.205	1.6010	47.655
x=4%	3.266	5.227	1.6005	48.304
x=6%	3.270	5.232	1.6000	48.450
Commercial powder ZnO	3.256	5.216	1.6019	47.889
ZnO powder JCPDS (N° 36-1451)	3.2498	5.2066	1.6021	47.620

Table 2: Lattice parameters, c/a ratio and V the cell volume of Zn_{1-x}Ca_xO thin layer on p-Si substrate with different Ca concentrations and those of commercial powder. For comparison lattice parameters of the JCPDS XRD database, file number 36-1451 is also listed.

Sample	E_g (eV), from reflectance. spectra
x=0%	3.144
x=1.6%	3.171
x=2.7%	3.189
x=4%	3.230
x=6%	3.262

Table 3: Band gap values of $Zn_{1-x}Ca_xO$ thin layer on p-Si substrate with different Ca concentrations obtained from UV-Vis reflectance spectroscopy.

Figures

Figure 1: EDX analysis carried out on ZnCaY%O thin films on p-Si substrate (a) Y=0%, (b) Y=4%, (c) Y=6%, (d) Y=10% and (e) Y=15%. Where Y represent the Ca weigh percentage contend used in the preparation of sol gel.

(a)

(b)

(c)

(d)

(e)

Figure 2: SEM images of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin layer on p-Si substrate (a) $x = 0\%$, (b) $x = 1.6\%$, (c) $x = 2.7\%$, (d) $x = 4\%$ and (e) $x = 6\%$.

Figure 3: X-ray diffraction spectra of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin films on p-Si substrate (a) $x=0\%$, (b) $x=1.6\%$, (c) $x=2.7\%$, (d) $x=4\%$ and (e) $x=6\%$. XRD patterns of commercial ZnO powder and un-doped sample are also drawn for comparison.

Figure 4: X-ray diffraction spectra ($30^\circ \leq 2\theta \leq 40^\circ$) for $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ layers on p-Si substrate for the different x Ca concentration. XRD patterns of commercial ZnO powder is also drawn for comparison.

Figure 5: Williamson–Hall plots for $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ films on p-Si substrate, where (a), (b), (c), (d) and (e) correspond respectively to $x=0\%$, 1.6% , 2.7% , 4% and 6% . (f) WH plot for commercial ZnO powder.

Figure 6: Variation of WH crystallite size and strain with x Ca concentration of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ alloys.

Figure 7: Variation of (a) lattice parameters and (b) the cell volume and ratio c/a with x Ca concentration of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ alloys.

Figure 8: Reflectance spectra of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin films on p-Si substrate for the different x Ca concentration.

Figure 9: Kubelka-Munk transformed reflectance spectra for $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin films on p-Si substrate, where (a), (b), (c), (d) and (e) correspond respectively to $x=0\%$, 1.6% , 2.7% , 4% and 6% .

Figure 10: Photoluminescence spectra of $\text{Zn}_{1-x}\text{Ca}_x\text{O}$ thin films on p-Si substrate for the different x calcium concentration at low temperature (2K).