Nanostructured ZnO - its challenging properties and potential for device applications

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Abstract. Nanostructured ZnO possessing interesting structural and optical properties offers challenging opportunities for innovative applications. In this lecture the review of the optical and structural properties of ZnO nanostructured layers is presented. It is shown that they have a direct impact on the parameters of devices involving ZnO. An analysis of current trends in the photovoltaic (PV) field shows that improved light harvesting and efficiency of solar cells can be obtained by implementing nanostructured ZnO layers to process advanced solar cell structures. Because of amenability to doping, high chemical stability, sensitivity to different adsorbed gases, nontoxicity and low cost ZnO attracted much attention for application as gas sensors. The sensitivity of nano-grain ZnO gas elements is comparatively high because of the grain-size effect. Application of nanostructured ZnO for gas sensors and for increasing of light harvesting in solar cells is demonstrated.

1. Introduction
ZnO is a semiconductor with large optical band gap 3.0-3.4 eV and resistivity between $1 \times 10^{-3}$ and $1 \times 10^{12} \ \Omega \ \text{cm}$ depending on doping and the methods of deposition [1]. Recently, ZnO films have attracted high interest in the scientific society. They offer various advantages: i) They consist of cheap and abundant elements, ii) They can be produced by large scale coating, iii) They allow tailoring of the ultraviolet absorption, iv) They have high stabilities in a hydrogen plasma, v) They can be deposited at low growth temperatures.

ZnO is a compound occurring in the nature as the mineral zincite discovered in 1810 by Bruce in Franklin (New Jersey, USA) [1]. Regarding the historical application and development of the investigation of ZnO several periods could be pointed, as presented in table 1. In the bronze era ZnO has been produced as co-product of copper ore smelling and has been used for healing of wounds and its application in the pharmacy industry continues till now. In the middle age ZnO usage for production of brass, as a white paint in the vulcanization process, in the porcelain enamels production has started. This period can be regarded as “prehistorical”. The next period between 1900-1960 is related to the beginning of the first scientific research and dissemination of the results - the first scientific paper with results of ZnO study was published in 1912 [2], it is devoted to investigation of the electrical properties of ZnO cylindrical rods. Study mainly of the structural and electrical properties mainly of sintered polycrystalline ZnO samples has been performed [3-7]. Fabrication of ZnO thin films by evaporation has been object of study, as well [4, 5]. In 1955 the effect of internal negative photo-effect has been reported by Borissov M and Kunev S [6]. This period named “Basic research period”, can be regarded as „incubation” period which “opens the door” for the next period.
### Table 1. Periods of development of the researches devoted to ZnO

| Year | Development steps |
|------|-------------------|
| **Bronze Age** | 1. **Prehistorical Period:** Zn - Byproduct of copper ore smelting; used for healing of wound. |
| 1800 | 2. **Middle age period:** First industrial applications: Application in the production of brass (before its replacing by Zn in Cu-Zn alloy). White paint, in rubber for activation of the vulcanization process, in porcelain enamels till the middle of the 19th century. |
| 1810 | Mineral zincite discovered by Bruce in Franklin (New Jersey, USA). |
| 1900-1960 | 3. **Basic research period - incubation period:** Study of the sintered polycrystalline samples mainly. |
| 1912 | First published scientific paper: Somerville A A 1912 *Phys. Rev. I* 34 311 [2]. |
| 1930 | Study of the electrical properties and stoichiometry, Wagner C and Schottky W 1930 Z. Phys. Chem. B 11 163 [3]. |
| 1935 | Polycrystalline plates, single crystalline needles and evaporated thin films, Frithsh O 1935 *Am. Phys.* 5 375 [4]. |
| 1951 | ZnO thin films by Zn oxidation, Schalimova K V *Compt Rendus Russ. Acad. Sci.* 78 1127[5]. |
| 1954 | Negative internal photoeffect in ZnO: Borissov M, Kunev S. 1954 *Compt Rendus Bulg. Acad. Sci.* 7 21; Borissov, Kunev S. 1955 Z. Phys.Chem. 205 56[6]. |
| 1959 | Review paper: Heiland G, Mollwo E 1959 *Solis State Phys.* 8 191 [7]. |
| **1960-2005** | 4. **Development of new ZnO thin film technologies and intensive basic research for applications.** |
| 1960 | Piezoelectric properties: Hutson A R 1960 *Phys. Rev. Lett.* 4 505 [8]. |
| 1962 | Application as gas sensor: Seiama T, Kato A, Fujiishi K and Nagatani M 1962 *Anal. Chem.* 34 1502 [9]. |
| 1971 | Application for varistors: Matsuoka M 1971 *Jpn.J.Appl.Phys.* 10 736 [10]. |
| 1976 | First electronic application as thin layer for surface acoustic wave devices (SAW): Hickernell 1976 *Proc.IEEE* 64 631 [11]. |
| 1996 | Application as phosphor: Vanheusdalen K, Seager C H, Warren W L Tallant D R and Voigt J A 1996 *Appl. Phys. Lett.* 68 403 [12]. |
| 1999 | Application as TCO in thin film a-Si:H solar cells: Rech B and Wagner H *Appl. Phys. A* 69 155 [15]. |
| 1999 | In flat plate panel: Katayama M 1999 *Thin Solid Film* 341 140 [13]. |
| 1999 | ZnO nano-wire growth and application in a-Si:H solar cell: Paporte T and Lincot D 1999 *Appl. Phys. Lett.* 75 3817 [16]. Kopenkampt R, Boedecker K, Lux-Steiner M C, Poschenrieder M, Zenia F, Levy-Clement C 2000 *Appl. Phys. Lett.* 77 2575 [19]. |
| 2002 | In OLED: Hung L S and Chen C H 2002 *Mater. Sci. Eng. R* 39 143 [14]. |
| 2004 | In thin film transistor: Nomura K, Ohta H, Takagi A, Kamiya T, Hirano M, and Hosono H 2004 *Nature* 432 488 [18]. |
| **21st Century** | 5. **Nanostructured ZnO:** Demonstration and large industrial nanostructured ZnO applications period. |
“Development of ZnO thin film technologies and intensive based researches for application”. In this period (1960-2005) the potential for different applications of ZnO has been demonstrated which has passed through a scientific and technical renaissance in the last few years. Zinc oxide has been recognized as one of the most important semiconductor materials for piezoelectricity [8], gas sensing [9], electronics [10] surface acoustic wave devices [11], optoelectronics [12-14], solar cells [15-16], bio-applications [17], transparent thin film mirror [18], etc.

The first publications on ZnO nanowires growing [16, 19, 20] together with the study of the polycrystalline ZnO films with nanosized grains [15, 21] have stimulated the development of different technologies for their fabrication and enlargement of the area of research. Nanostructured ZnO possessing interesting structural and optical properties offers challenging opportunities for innovative applications. Will it be the next period of “Demonstration and large industrial ZnO applications?”

An analysis of current trends in the PV field shows that improved light harvesting and efficiency can be obtained by implementing nanostructured ZnO layers to process advanced solar cell structures. Because of amenability to doping, high chemical stability, sensitivity to different adsorbed gases, nontoxicity and low cost, ZnO attracted much attention for application as gas sensors. In this contribution a review of the optical and structural properties of ZnO nanostructured layers fabricated by RF magnetron sputtering and electrochemical growth is presented. It is shown that they have a direct impact on the parameters of devices involving ZnO. Application of nanostructured ZnO for gas sensors and for increasing of light harvesting in solar cells is demonstrated, as well.

2. Optical, structural properties and potential for application of polycrystalline ZnO thin films in gas sensors

2.1. Nano-polycrystalline ZnO thin films deposited by RF magnetron sputtering

Polycrystalline ZnO thin films can be deposited by different physical and chemical methods: thermal evaporation in vacuum, oxidation of Zn, ZnS, ZnSe thin films, MOCVD, e-beam evaporation, DC and RF magnetron sputtering, ALD, spray pyrolysis, pulsed laser deposition, etc. [1 and ref. there]. The choice of the method of deposition should be chosen regarding the goal of their application, the properties requested for this application and, as well as, the cost of the method of their production should be limiting factor.

For some applications the ZnO films have to be doped. Doping with the III group elements (Al, Ga, In) leads to decreasing of the resistivity and good transparency of the thin films [20, 21]. Doping of ZnO polycrystalline thin films with Er, Ta, Co deposited by magnetron sputtering results in increasing of the sensitivity of the films to different gases, such as NH₃, CO₂, as well [22, 23]. The results of study of their structural properties by X-Ray Diffraction (XRD) spectroscopy [21-23] demonstrate that the deposited films are polycrystalline. Reflections corresponding to the (002), (110), (102), (110), (103), (112) and (004) planes of wurtzite ZnO are observed as shown in figure 1 a, b and c [20-23].

The value of the coefficient of absorption, α, of the samples is obtained from the spectral dependence of transmission and reflection. The value of the optical gap, Eg, is calculated using the dependences (shown in figure 1 d, e and f) of (ahv)² vs. hv by the formula [24]:

\[
\alpha (hv) = B \frac{((hv - Eg)^{1/2})}{hv}
\]

The coefficient B was assumed as a parameter for the band tail states [25, 26]. According to [10], a decrease in B implies an increase in the disorder of the structure and a consequent increase in the conduction band tail width. In our case, a decrease in B is observed with doping and with T, decreasing, which is accompanied by a deterioration of the crystalline structure of the ZnO films.

In the lower energy range where α varies exponentially with photon energy the spectral dependence of the absorption edge depends on energy, hv, by the Urbach formula [25]:

\[
\alpha (hv) = a_0 \exp \left[\left(\frac{hv}{E_0}\right)\right]
\]
where $\alpha_0$ is the Urbach absorption at the edge ($E_1$), and $E_0$ is the Urbach energy width, which is believed to be a function of the structural disorder.

Figure 1. XRD patterns (a,b,c) and the energy dependence of coefficient of absorption, $\alpha$, (d,e,f) of different series of ZnO films, deposited at different substrate temperatures $T_s$: ZnO (a and d), ZnO:Er (0.2at.%) (b and e) and ZnO:Co (4-5 at%) (c and f). The insert shows a plot of $\ln \alpha$ vs. $hv$ [22, 23].
The exponential dependence of the absorption on $h\nu$ in the Urbach region ($h\nu < E_g$) is due to the perturbation of the parabolic density of the states at the band edge – increasing structural disorder results in an increase in $E_g$ [21-27].

Table 2 contains the data obtained from the analyses of XRD and optical spectra for undoped and doped ZnO samples with Al, Er, H, Ta and Co [21-27]. The (002) peak shows deviations from 34.44°, which is the value for ZnO powder. Larger deviations were observed for ZnO films deposited at lower $T_e$ and those doped with Al, Er and Ta. They indicate that the interplanar spacing changed relative to that of ZnO powder, which is probably due to factors such as lattice strain and interstitial defects due to entrancing defect and the doping as well [28]. The values of the stress, $\sigma$, derived from the XRD data were calculated using the following equation [29]:

$$\sigma = \frac{233 \cdot (c_{\text{film}} - c_{\text{bulk}})}{c_{\text{bulk}}}$$  \hspace{1cm} (3)

where $c_{\text{film}}$ and $c_{\text{bulk}}$ are lattice parameter of c axis for the films (evaluated using the Fullprof software from XRD spectra [30]) and of the bulk hexagonal ZnO ($c_{\text{bulk}} = 0.5206\,\text{Å}$) [29 and ref. there in].

Figures 2 a and 2 b display the relation between the values of Urbach energy (a) and the coefficient $B^2$ (b) in dependence on the stresses, $\sigma$, respectively, for all of the ZnO films under investigation. The changes of the structural properties of magnetron sputtered ZnO thin films (undoped and doped with

| Samples description | $T_{\text{ev}}$, °C | $2\theta$, deg | FWHM deg | $D_s$, nm | $\Delta c_{002}$, % | $\sigma$, GPa | $E_{\text{eg}}$, eV | $E_{\text{q}}$, meV | $B^2$, (cm$^2$.eV) |
|---------------------|---------------------|----------------|-----------|----------|----------------|----------------|-----------------|--------------|----------------|
| ZnO                 | 150                 | 34.30          | 0.52      | 16.0     | 0.34           | -0.81          | 3.33            | 63           | 3.90E12        |
| ZnO                 | 275                 | 34.40          | 0.47      | 17.7     | 0.08           | -0.18          | 3.30            | 59           | 4.70E12        |
| ZnO                 | 500                 | 34.40          | 0.33      | 25.2     | 0.08           | -0.18          | 3.27            | 60           | 6.30E12        |
| ZnO:Al (1 at.%)     | 150                 | 34.20          | 0.62      | 13.6     | 0.65           | -1.52          | 3.36            | 100          | 2.60E12        |
| ZnO:Al (2 at.%)     | 275                 | 34.15          | 0.61      | 13.4     | 0.80           | -1.79          | 3.41            | 120          | 7.60E11        |
| ZnO:Al (1 at.%)     | 500                 | 34.27          | 0.62      | 13.4     | 0.40           | -0.98          | 3.33            | 91           | 2.26E12        |
| ZnO:Er (0.2at.%)    | 150                 | 34.10          | 0.62      | 13.4     | 0.92           | -2.15          | 3.33            | 72           | 2.47E12        |
| ZnO:Er (0.2at%)     | 275                 | 34.30          | 0.62      | 13.4     | 0.34           | -0.81          | 3.34            | 70           | 3.29E12        |
| ZnO:Er (0.2at%)     | 500                 | 34.20          | 0.57      | 14.5     | 0.65           | -1.52          | 3.28            | 63           | 3.15E12        |
| ZnO:Er (0.4at%)     | 150                 | 34.16          | 0.59      | 14.0     | 0.80           | -1.79          | 3.34            | 65           | 3.14E12        |
| ZnO:Er (0.4at%)     | 500                 | 34.11          | 0.53      | 15.7     | 0.88           | -2.06          | 3.30            | 52           | 3.15E12        |
| ZnO:H (2 at.%)      | 150                 | 34.42          | 0.43      | 19.3     | 0             | 0              | 3.31            | 70           | 5.30E12        |
| ZnO:H (2 at.%)      | 275                 | 34.37          | 0.48      | 17.3     | 0.15           | -0.36          | 3.31            | 56           | 4.25E12        |
| ZnO:H (1 at.%)      | 400                 | 34.26          | 0.47      | 17.7     | 0.46           | -1.07          | 3.27            | 56           | 7.10E12        |
| ZnO:Ta (1 at.%)     | 150                 | 33.81          | 0.79      | 10.5     | 1.77           | -4.12          | 3.32            | 78           | 3.56E12        |
| ZnO:Ta (1 at.%)     | 275                 | 33.86          | 0.40      | 20.8     | 1.61           | -3.76          | 3.31            | 80           | 3.01E12        |
| ZnO:Ta (1 at.%)     | 500                 | 34.02          | 0.29      | 28.6     | 1.15           | -2.68          | 3.31            | 73           | 4.50E12        |
| ZnO:Ta (2 at.%)     | 150                 | 33.09          | 1.21      | 6.80     | 3.92           | -9.13          | 3.44            | 100          | 2.00E12        |
| ZnO:Ta (2 at.%)     | 275                 | 33.47          | 0.88      | 9.42     | 2.77           | -6.44          | 3.44            | 95           | 3.77E11        |
| ZnO:Ta (3 at.%)     | 500                 | 34.07          | 0.45      | 18.5     | 0.52           | -2.33          | 3.37            | 91           | 1.57E12        |
| ZnO:Co (5at.%)      | 150                 | 34.09          | 0.81      | 10.2     | 0.50           | -2.24          | 3.28            | 118          | 9.7E11         |
| ZnO:Co (4.8at.%)    | 275                 | 34.33          | 0.28      | 30.0     | 0.22           | -0.98          | 3.31            | 114          | 5.54E11        |
| ZnO:Co (4.8at.%)    | 500                 | 34.33          | 0.25      | 33.0     | 0.14           | -0.63          | 3.33            | 104          | 1.10E11        |
Al, Er, Ta and Co, and deposited in H₂ presence) are compared with changes in the values of B and Urbach energy tail, E₀, calculated from the optical properties. The values of the stress, σ, are negative - this demonstrates the presence of tensile stress in the films. It is seen that there is a correlation between the stresses and the structural disorder in the films – the increase of the stress results in an increase of the Urbach band tail width and a decrease of the coefficient B. A correlation between the values of the stress and the band tails has been observed - increasing stress is accompanied by increasing value of the band tails width. The correlation between the average grain size, D, (calculated by applying the Scherer equation to the Full Width of the Half Maximum (FWHM) of the (002) peak [31]) and the stress, shown in figure 2 c, demonstrates that the value of the stress decreases with increasing D. A similar result has been reported in [28]. The increase of the structural disorder due to the doping or to the lower deposition temperature is accompanied by decreasing of the average grain size and increasing of the stress and the strain in the ZnO films, which cause a perturbation of the parabolic density of the states at the band edges. The results can be explained having in mind that accommodation of the impurities in the lattice results in localised strains, reflected in a perturbation of the parabolic density of the states at the band edges.

2.2 Application of ZnO nano-polycrystalline films in gas sensors
ZnO is one of the first oxide materials, which have attracted the attention for their potential application as gas sensors due to their chemical sensitivity to different gases, high chemical stability, non-toxicity...
and low cost [23, 32-36]. The material properties are determined mostly by its structure and surface morphology, which strongly depend on the preparation method. In the last few years, ZnO has been an object of intensive investigation, particularly in its low dimensional structures – thin layers with nanometer crystallites, nano-wires, nano-rods or nano-tubes, nano-balls and others [36 -38].

The sensitivity of the ZnO films to NH$_3$ was determined by two approaches - as the ratio of the resistivity measured before and after exposure to NH$_3$ and by the frequency shifts of the quartz crystal microbalance (QCM) after gas exposure. The variation in the sensitivity (the ratio of the resistivity) of undoped and H doped ZnO films with NH$_3$ concentration is shown in figure 3 [23]. Initial trend of saturation at higher NH$_3$ concentrations (>18 000 ppm) is also observed. It is seen that the sensitivity of the ZnO:H films is higher than that of the ZnO films. The ZnO:H film deposited at $T_s = 400^\circ$C exhibited a higher sensitivity than that deposited at 150$^\circ$C, for NH$_3$ concentrations < 18,000 ppm.

It is well accepted that the sensitivity of semiconductor gas sensors is attributed to the chemisorption of oxygen and OH$^-$ on the oxide surface and the subsequent reaction between adsorbed species and the tested gas, which causes the resistance change [39]. It is known that atmospheric oxygen molecules and water vapor are adsorbed on the surface of the ZnO in the forms of O$^-$ and OH$^-$, thereby reducing the electrical conductivity. When a ZnO sensor is exposed to a reductive atmosphere, the test gas like NH$_3$ reacts with the surface species, the trapped electrons are returned to the conduction band of the ZnO, causing an increase in the conductivity of the sensor. The different effective surface area of the films could be one of the reasons for their different sensitivity. However, the effective surface area estimated from the grain size (calculated from XRD spectra) is almost the same for all set of samples studies here. Thus, the results presented here require another explanation. The adsorbed hydrogen and OH$^-$ species in the ZnO:H films during the deposition could explain the higher response of samples ZnO:H as compared to that of the pure ZnO films and the ZnO:H sample deposited at higher $T_s$. One of the possible reactions on the substrate during the process of sputtering in an Ar+H$_2$ atmosphere is:

$$\text{ZnO} + \text{H}_2\text{gas} \leftrightarrow 2\text{Zn} + \text{H}_2\text{O}_{\text{gas}}$$  \hspace{1cm} (4)

Figure 3. (a) A sensitivity of ZnO:H and ZnO films toward NH$_3$ at room temperature. The insert is the sensitivity at lower NH$_3$ concentration. (b) Transient response of a ZnO:H film ($T_s$=400$^\circ$C) for a 250 ppm NH$_3$ concentration [23].

The thermodynamic analyses [39] show, that this reaction will be shifted to the right with increasing of the temperature. According to the equation (4) the deposition at 150$^\circ$C would results in higher concentration of H and at 400$^\circ$C – in higher water vapor presence in ZnO:H films. Possibly the presence of OH$^-$ would accelerate the surface reaction between the reducing gas with NH$_3$OH as a product, additionally to the NH$_3$ reaction with adsorbed oxygen species. Thus, the samples with higher OH$^-$ concentrations (deposited at $T_s = 400^\circ$C in Ar+H$_2$) would be more sensitive to a lower NH$_3$ concentration.
The ability of the undoped ZnO thin films and those doped with Er, Ta and Co to sorb ammonia vapor is demonstrated by the QCM method [40]. For this purpose, the resonance frequency shift response was measured. The sorption process was investigated over an aqueous solution of ammonia with 100 ppm concentration. The change in the frequency, $\Delta f$, of the QCM, as a function of its mass loading is detected. Surface morphology and cross section images of ZnO film used for this purpose (deposited by RF magnetron sputtering in Ar atmosphere) are shown in figure 4. The column structure of the film is clearly seen with size of the nanocrystallites of about 100 nm. Figure 5 shows the frequency change, $\Delta f$, as function of the exposure time over a 100 ppm ammonia solution for different samples. The highest rate of the change in frequency, $S_p$, is registered in the first two minutes, for all investigated samples. After that, the rate slowly decreases and the frequency approaches to a constant value. The rate of change for the first two minutes is calculated in order to estimate the sensitivity of each kind of ZnO layer. The $S_p$ value and the total sorbed mass, $\Delta m$, was evaluated using the relationship between $\Delta f$ and $\Delta m$ for AT- cut of quartz crystal given by the Sauerbrey equation [41]:

$$\Delta f = - (2.26 \times 10^{-6} f^2 \Delta m)/A,$$

where $f$ (MHz) is the frequency of the QMB before exposure to ammonia, $\Delta m$ (g) is the mass of the sorbed gas on the surface of the ZnO films and $A$ ($\text{cm}^2$) is the surface area of the electrodes.

The total sorbed mass on the samples is calculated for the whole period until saturation is achieved. The data are presented in table 3. The lowest rate of sorption and the smallest total sorbed mass (4.5 Hz/min and 4.86 ng, respectively) are registered for ZnO. In the case of ZnO films doped with Ta, and Co, values of 8.5 Hz/min and 8.76 ng and 5.65 Hz/min and 12.78 ng for the sorption rate and mass, respectively, are obtained. It has to be noted that the largest rate of change of the frequency – 13.2 Hz/min is measured in the case of sorption on the ZnO:Er layers, which corresponds to a total sorbed mass of 32.20 Higher sensitivity was observed for Er doped ZnO films, compared to the undoped and ZnO:Co and ZnO:Ta films. The differences in the grain size in the films could be one of the reasons for the different behaviour of the QCM sensors. The higher sorbed mass is detected for the sample with smaller grain size which possesses larger effective surface area leading to higher concentration of the adsorption centres.

3. Properties and potential for application of electrochemically grown nanostructured ZnO
ZnO nano-rods, nanowires, nano-dots represent important class of nanostructures which has attracted the attention of the scientific society due to their very interesting and unique properties with potential for various device applications. In particular the nano-materials with suitable size of their nanostructures could improve the light harvesting by solar cells and thus their efficiency. Different methods of deposition of nanostructured (NS) ZnO layers have been applied, such as chemical vapour deposition, metal-organic CVD, aqueous solution growth, electro-chemical deposition (EChD), etc.
Table 3. Values of the optical band gap, $E_g$, the average grain size, $D$, the rate of sorption, $S_p$, and the sorbed mass, $\Delta m$, over 100 ppm NH$_3$ for different kinds of samples. The values of $D$ are calculated using values of $2\theta$ (given in the brackets) and the corresponding FWHM [40].

| Samples      | $E_g$, eV | $D$, Å, (2θ) | $S_p$, Hz/min | $\Delta m$, ng |
|--------------|----------|--------------|--------------|--------------|
| ZnO:Er       | 3.30     | 95 (002)     | 13.2         | 32.20        |
| ZnO:Co       | 3.35     | 105 (002)    | 5.65         | 12.78        |
| ZnO:Ta       | 3.46     | 131 (015)    | 8.5          | 8.76         |
| ZnO          | 3.30     | 177 (002)    | 4.50         | 4.86         |

Figure 5. Time-frequency shift characteristics of quartz crystal microbalance with: (a) ZnO, (b) ZnO:Er, (c) ZnO:Ta, (d) ZnO:Co films; (e) presents the frequency shifts for the all samples for 120 sec. over a 100 ppm NH$_3$ solution over a 100 ppm NH$_3$ solution [40].

3.1. Correlation between the surface roughness of NS ZnO and haze ratio in optical reflection

The method of EChD has some advantages - it is a low temperature method the ZnO nanostructures can be deposited on very large area and it is applicable in industrial conditions. ZnO nanostructured

Figure 6. SEM plane views of SnO$_2$:F film (a) and ZnO layers; samples: 2 - (b), 6 - (c), 7 - (d) and 9 - (e) [43]. The markers correspond to 500 nm.
films were deposited by an electrochemical process from acid aqueous solution of ZnCl₂ (5 \times 10^{-3} \text{ M}) and KCl (0.1 \text{ M}) with pH 4.0 at temperature of 60\textdegree C in flowing air and suspension containing ZnO powder as precursors using a three-electrode electrochemical cell and saturated calomel electrodes (SCE) as reference electrode described earlier in [42,43]. It is supposed that ZnO powder suspension could serve as a source of seeding particles. For comparison a layer without adding of the ZnO suspension was prepared as well (sample 2). Duration of the ZnO deposition was 60 min. The prepared ZnO films were 0.55 – 1.57 μm thick. Different regimes were explored – sample 2 – without drops, (dr.), sample 3– 1x dr., sample 4– 2x dr., sample 5– 2x dr. + H₂O₂, samples 6 and 6’– 3x dr., samples 7 and 7’– 3x dr. + annealing at 300\textdegree C, sample 8– 3x dr. + H₂O₂ and sample 9– 3x dr. + Ni seeding layer. In the case of sample 9 thin Ni seeding layer (1 - 2 nm thick) was chemically deposited on the surface of the glass/SnO₂:F substrate before ZnO EChD growth. The surface morphology was studied by SEM (figure 6) and AFM (figure 7) and the thickness of the film was determined by AFM. The crystalline structure was studied by X-Ray Diffraction spectrometry (XRD) (figure 8). The XRD patterns demonstrate that the deposited ZnO films are polycrystalline with reflection corresponding to the (100), (002), (101), (102) and (103) planes of wurtzite structure with c-axis perpendicular to the substrate. The most intensive is the XRD peak of the (002) plane. From the FWHM of the (002) peak, Δ2θ, the average size of the grains, \( D \), is estimated. The value of the optical band, \( E_g \), is calculated using transmittance and reflectance spectra [43]. The calculated values are presented in table 4.

The ZnO layer grown without adding of ZnO suspension (sample 2) consists of grains with size of about 56 nm (very inhomogeneous grains size, \( D \)) and has an average surface roughness of ~82 nm (figure 7b). It is seen from figures 6 and 7 that the grain size in the layers increases with adding of different quantity of the suspension which is in agreement with the obtained from the XRD data (table 4). Annealing of the film at 300\textdegree C in air for 1 hour results in changes in the morphology – the
Table 4. Structural and optical characteristics of the electrochemically deposited ZnO films: the optical band gap, $E_g$; the position of the (002) peak in the XRD spectra, $2\theta$; the FWHM of (002) peak, $\Delta 2\theta$; the values of the stress, $\sigma$; the average grains size, $D$; the thickness, $d$; the average roughness, $R$; the haze ratio. For comparison the corresponding data for the SnO$_2$:F films are given, too [43].

| Sample     | $E_g$, eV | $2\theta$, deg. | FWHM, deg. | $\sigma$, GPa | $D$, nm | $d$, nm | $R$, nm | Haze, (%) @400 nm | Haze, (%) @550 nm | Haze, (%) @1000 nm |
|------------|-----------|-----------------|------------|---------------|--------|--------|---------|-----------------|-------------------|---------------------|
| 1: SnO$_2$:F | 3.75      | 34.39           | 0.14       | -0.25         | 59     | 910    | 29      | 30              | 13                | 3                   |
| 2: w/10 drops | 3.39      | 34.39           | 0.15       | -0.24         | 56     | 550    | 315     | 82              | 65                | 23                  |
| 3: 1 x drops | 3.37      | 34.41           | 0.16       | -0.12         | 52     | 580    | 89      | 85              | 82                | 35                  |
| 3*: 1x drops | 3.38      | 34.38           | 0.14       | -0.32         | 59     | 620    | 89      | 86              | 74                | 24                  |
| 4: 2x drops | 3.38      | 34.37           | 0.10       | -0.38         | 83     | 700    | 147     | 88              | 86                | 34                  |
| 5: 2xdr+H$_2$O$_2$ | 3.46    | 34.39           | 0.12       | -0.25         | 69     | 1570   | 82      | 90              | 73                | 29                  |
| 6: 3x drops | 3.42      | 34.39           | 0.11       | -0.25         | 76     | 750    | 299     | 93              | 82                | 50                  |
| 6*: 3x drops | 3.41      | 34.34           | 0.13       | -0.58         | 64     | 1000   | 225     | 91              | 82                | 50                  |
| 7: 3xdr. | 3.26      | 34.48           | 0.13       | -0.36         | 64     | 1060   | 153     | 86              | 78                | 46                  |
| 7*: 3xdr+ann. | 3.27    | 34.50           | 0.13       | -0.47         | 64     | 850    | 78      | 91              | 77                | 31                  |
| 8: 3xdr+H$_2$O$_2$ | 3.47    | 34.38           | 0.12       | -0.32         | 69     | 900    | 75      | 89              | 65                | 22                  |
| 9: 3x dr.+Ni | 3.51      | 34.38           | 0.12       | -0.32         | 69     | 810    | 33      | 38              | 25                | 13                  |

Individual grains grow into conglomerates (figure 7 d) and the surface roughness of this sample decreases.

The spectral dependence of the haze ratio of the ZnO samples in the range of 400 - 1000 nm is presented in figure 9 a. The values of the haze ratio of the electrodeposited ZnO layers are much higher than those of the SnO$_2$:F coating. Higher values of haze ratio are observed for the samples deposited with higher quantity of the added ZnO suspension. It has to be noted that the layers with higher values of the average roughness determined by AFM (table 4) demonstrate haze ratio in reflection. Figures 9 b show the variation of the haze ratio with the roughness of the deposited films at two wavelengths of 550 nm. It is seen very clearly (from figure 9 b and table 4), that the value of the haze ratio increases with increasing the surface roughness with maximal values of about 93%. 86% and 50% at 400 nm, 550 nm and 1000 nm, respectively. The results demonstrate that higher values of haze ratio in reflection in the spectral range of 400 - 1100 nm have ZnO layers with larger average grain size and higher average surface roughness. ZnO layers with similar properties could be applied as light trapping structures in thin film solar cells.

3.2. Application of ZnO nanostructured array layers in solar cells
3.2.1 Application as ARC on SHJ solar cells

Electrochemically deposited ZnO nanostructured layer with nanometre sized features have been

![Figure 10](image-url)
Figure 11. Spectra of specular reflectance (a, b, c) and diffused reflection (d, e, f) of samples 1-C6 (a, d), 1-C4 (b, e) and 1-C2 (e, f) without and with deposited ZnO NS array film [45].

Table 5. The deposition conditions of the ZnO NS array films and comparison of the parameter of the SHJ without and with ZnO NS growth [45].

| Solar cells parameters                  | 1-C2    | 1-C4    | 1-C6    |
|----------------------------------------|---------|---------|---------|
| Isc (mA), with ZnO NS                  | 30.637  | 30.689  | 30.237  |
| Isc (mA), without ZnO NS               | 30.514  | 29.839  | 28.979  |
| ΔIsc (mA)                              | 0.123   | 0.850   | 1.258   |
| ΔIsc (%), relative increasing          | 0.4     | 2.85    | 4.3     |
| Voc (mV), with ZnO NS                  | 695     | 694     | 689     |
| Voc (mV), without ZnO NS               | 697     | 697     | 691     |
| FF, (%), with ZnO NS                   | 72.74   | 72.90   | 71.61   |
| FF, (%), without ZnO NS                | 74.00   | 73.50   | 73.02   |
| ΔFF                                    | 1.26    | 0.60    | 1.41    |
| η, (%), with ZnO NS                    | 15.492  | 15.535  | 14.917  |
| η, (%), without ZnO NS                 | 15.733  | 15.278  | 14.521  |
| Δη, (%)                                | -0.241  | 0.257   | 0.396   |
| Δη, (%), relative changes               | -1.5    | 1.68    | 2.7     |
| t, (min)                               | 1.5     | 1.5     | 1.5     |
| Iel. chem. (mA)                        | 3       | 6       | 6       |
| Uel. chem. (mV)                        | 1000    | 1000    | 950     |

applied as antireflective coating (ARC) on the front surface of heterojunction Si solar cells (SHJ) – Ag grid/ITO/p-a-Si:H/(i)a-Si:H/(n)/c-Si/(i)/a-Si:H/(n+)/a-Si:H/Al [44,45]. The ZnO NS were deposited
for 1.5 min with applying of different electrochemical potential: in the case of solar cell 1-C6 – at 950 mV, of 1-C4 and 1-C2 - at 1000 mV. The ZnO nanostructures have been deposited between the fingers of the Ag grid electrodes on SHJ solar cells with sheet resistance of ITO of 80Ω/□ and different thickness of ITO (80 nm in the case of 1-C6 and 1-C4 and 150 nm for 1-C2, respectively). In the case of samples 1-C6 and 1-C4 the nano-rods sized about 100-200 nm are distributed in different surface area with different density. The SEM of the sample 1-C2 reviles the presence of largest nano-ZnO features about 800 nm with relatively large distance between them. Differences in the ZnO nanostructures distribution on the surface of different solar cells can be explained by the difference in the surface properties, thickness and resistivity of the ITO layers and by the different conditions applied during electrochemical deposition on solar cells.

The spectra of specular reflectance and diffused reflection of the three samples of the series, before and after the deposition of ZnO nanostructured array films, presented in figure 11 show that the values of reflectance decrease which is more pronounced in the sample 1-C6. The value of diffused reflection decreases in the samples 1-C6 and 1-C4 and increases in the case of sample 1-C2. The differences in the surface morphology and microstructure of the textured ZnO films determine the difference in the optical reflection properties, as reported in [46].

The study demonstrates that the ZnO nanostructured array films grown on the front side of the SHJ

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Figure 12. AFM (a) and SEM (b) images of ZnO NRs array on stainless steel (SS) substrate [47].

Figure 13. Spectra of diffused reflection, total reflection and haze in reflection of ZnO NRs array deposited on different structured SS substrates [47, 48].
solar cells act as ARC leading to decreasing of the reflectance, improvement of the short circuit current (by about 4.3%) and efficiency (by about 2.7%) of the thin film SHJ solar cells (table 5). An improvement in the short circuit current and efficiency of the SHJ solar cells is achieved in the samples where the values of reflectance and diffuse reflection decrease after ZnO NS array films deposition on the front side. The higher increase in $J_{sc}$ and efficiency, $\eta$, is observed in the samples where larger decreasing of the values of reflectance and diffuse reflection are obtained as a result of deposition of ZnO NS array films leading to improvement of the light harvesting [44].

### Table 6. Parameters of thin film a-Si:H solar cells with different scattering substrates [47]

| Substrate structure | $V_{oc}$, mV | $J_{sc}$, mA/cm² | FF | Eff. |
|---------------------|--------------|------------------|-----|------|
| SS/BR/NR            | 803          | 13.4             | 0.47| 5.11%|
| SS/BR/NR/BR        | 850          | 13.8             | 0.62| 7.28%|
| SS/Replica of Asahi-U texture/BR | 851 | 12.4             | 0.62| 6.56%|

#### 3.2.2. ZnO nano-rod arrays as back reflector in thin film solar cells

The ZnO nano-rods (NRs) prepared by an electrochemical process are implemented in the a-Si:H thin films n+-i-p⁺ solar cells on flexible stainless steel (SS) foil, aiming at increasing the $J_{sc}$ without deterioration the open circuit voltage, $V_{oc}$, and the fill factor, $FF$ [47]. Figures 12 a and b show the AFM and SEM images of ZnO NRs array on SS substrate. The surface morphology consists of nano-rods with diameter size of single NR between 200 and 500 nm and high of about 200-300 nm. The thin film solar cell structure deposited on such kind of flexible substrate is SS/back reflector (BR)/n-type a-Si:H/i-a-Si:H/p-μc-Si:H/ITO/Ag grid. The BR consists of a stack of Ag and AZO, with thicknesses of respectively 300 nm and 80 nm. In addition to the components of the basic BR (figure 13 a) there is the scattering medium consisting of either ZnO NRs coated by a stack of Ag (300 nm) and AZO (80nm) (figure 13 b) or a nano-imprinted replica of Asahi-U texture (figure 13 c).

The spectra of reflectance, diffused reflectance and haze in reflectance of three different back reflectors on SS substrate are shown in figure 13. The highest value of haze ratio in reflectance demonstrates the BR with ZnO NRs covered by two layers structure consisting of Ag (300 nm thick) and ZnO:Al (80 nm thick). The parameters of the solar cells obtained from I-V characteristics demonstrate that when the ZnO NRs are coated with Ag and AZO (cell № 2), the solar cell shows 0.4 mA/cm² higher $J_{sc}$ than the reference cell of № 1 and 1.4 mA/cm² higher $J_{sc}$ than the cell of № 3 deposited on substrate with the nano-imprinted replica of Asahi-U texture, and highest value of efficiency without deterioration of the $V_{oc}$ and $FF$ (table 6). The optical enhancement of the solar cell by ZnO NRs is explicitly demonstrated in the external quantum efficiency (EQE) spectra in the wavelength range from 400 nm to 800 nm (figure 14) [47,48].

#### 3.2.3. Application of NS ZnO layer in gas sensors

The gas sensitivity of the electrochemically-deposited ZnO nanostructured (NS) thin films on QCM was studied by exposure to NO₂. The resulting structure was kept in air until saturation in the frequency value was reached. The temperature in the test chamber was kept constant (25 °C ± 0.5 °C).
by a thermostat. The concentration of the NO\textsubscript{2} gas flowing into the thermal stabilized measurement chamber was 500 ppm. The resonance frequency was measured by a frequency counter and recorded on a PC. The experimental setup for measuring the sensing properties of the ZnO-QCM system was described in detail in [49]. The frequency accuracy was \( \sim 0.1 \) Hz. The oscillators consisted of thermo-stable polished AT-cut quartz plates with a diameter of 8 mm with gold electrodes with a thickness of 600 nm and a surface area of 0.1256 cm\textsuperscript{2} in an HC-49 type package. A 16-MHz base resonance frequency was thus obtained [50].

Figure 15 shows a SEM micrograph of a NS ZnO thin film deposited at constant charge density for 60 min. The structure of this thin film consists of planar hexagonal ZnO nano-whiskers (NW) with a thickness of about 100 − 300 nm and different lengths (0.5 − 1μm), stacked with the narrow side to the substrate surface. The thickness of the ZnO film is 0.5 μm. The SEM micrograph reveals the porous surface morphology of the deposited layer.

The ability of the ZnO thin films to sorb NO\textsubscript{2} was evaluated by the QCM method. For this purpose, the resonance frequency shift was measured. The sorption process was investigated in a gas flow of NO\textsubscript{2} with a concentration of 500 ppm by following the change in the frequency, \( \Delta f \), of the QCM as a function of the mass loading. Figure 16 shows this change as a function of the exposure time. The highest rate of frequency change, \( S_p = 11.5 \) Hz/min, was registered in the first two minutes. After that, the rate decreased more slowly, with the frequency reaching a constant value within about five minutes after exposure to NO\textsubscript{2}. When the gas flow was switched off, the frequency returned to its initial value within two minutes due to desorption of the gas, the fastest change occurring in the first minute. The rate of change was calculated for the first five minutes after exposure to the NO\textsubscript{2} in order to estimate the sensitivity of the electrodeposited ZnO layer. The average value of the frequency-change rate, \( S_p \), and of the total sorbed mass, \( \Delta m \), were evaluated on the basis of the time-frequency characteristics measured using the relationship between \( \Delta f \) and \( \Delta m \) for AT-cut quartz plates as given by the Sauerbrey equation (equation (5)) [41]. In our experiments, the frequency shift measured, \( \Delta f \), was 38 Hz, and the sorbed mass, \( \Delta m \), was calculated to be 8.39 ng. The \( S_p \) value of 7.6 Hz/min was calculated as the ratio of the frequency shift to the time of saturation (five minutes). The electrochemically-deposited ZnO layer with grown nano-whiskers had a highly developed surface interacting with the NO\textsubscript{2} molecules. When the concentration of the gas in the chamber is raised, the NO\textsubscript{2} molecules are adsorbed in the ZnO layer; as a result, the resonator’s mass increases and its frequency decreases. When the gas flow in the chamber is stopped, the NO\textsubscript{2} molecules start desorbing and the frequency of the quartz resonator returns to its initial value.

The results obtained demonstrated a potential application of the electrochemically-deposited nanostructured ZnO layers as room-temperature gas sensors of NO\textsubscript{2}.

Figure 15. SEM image of a ZnO layer deposited electrochemically for 60 minutes on a quartz resonator [50].

Figure 16. Frequency-time characteristic of a quartz crystal microbalance with an electrodeposited nanostructured ZnO layer under and after exposure to a 500-ppm NO\textsubscript{2} flow [50].
4. Conclusion
The described results in this review article show that ZnO nano-polycrystalline and nanostructures arrays layers offer very interesting and promising properties due to the nanoscale structures and larger developed effective surface area. The results obtained demonstrated a potential application of the magnetron sputtered undoped and doped ZnO thin films and electrochemically-deposited nanostructured ZnO layers as room-temperature gas sensors of NH$_3$ and NO$_2$.

The proposed novel solar cell architectures that make use of nanomaterials have demonstrated increasing light harvesting and improvement of the parameters of the solar cells as a result of the effects due to the nano-scaled structures. Future advances in and the rate at which large scale application of the new challenging effects using ZnO in development of new devices can be achieve, will depend entirely on the amount of resources the society chooses to invest and the scientific researches’ efforts in the field of the nanotechnology. All this will determinate the next period as period of Demonstration and large industrial applications of nanostructured ZnO.

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