Highly transparent, polycrystalline ZnO thin films were deposited by ultrasonic spray pyrolysis. The phase and chemical composition of the films were characterized by X-ray analysis (XRD) and X-ray photoelectron spectroscopy (XPS). According to the XRD analysis the films possess wurtzite structure with preferential (002) orientation. The morphology of the ZnO films was investigated by scanning electron microscopy (SEM). Optical transmittance higher than 80% is found in the visible region. The influence of both the substrate and postdeposition annealing temperatures on the dark conductivity and its activation energy were investigated. It has been found that the conductivity increases with increasing of the substrate and annealing temperatures while the activation energy decreases. These effects have been related to an increase of the density of oxygen vacancies. The sensing properties of the samples were tested in the presence of vapours of water, ammonia, ethanol and acetone. It has been revealed that the substrate temperature influences the gas sensitivity. The films deposited at 200°C have shown the highest sensitivity with the best results registered in the presence of ammonia vapours.

1. Introduction
ZnO thin films received much attention in the past decades due to their semiconducting and piezoelectric properties. With a direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [1,2], nanostructured ZnO films have a wide range of applications in the modern technologies. They are suitable material for electronic, optoelectronic and electromechanical devices [3], as well as for photocatalysis [4]. The physicochemical properties depend strongly on the preparation methods of the ZnO thin layers. The most commonly used physical methods include sputtering [5], pulsed laser deposition [6], molecular beam epitaxy [7] or electron beam evaporation [8]. Other techniques such as chemical vapour deposition [9], sol-gel [10] and spray pyrolysis [11] are also applied. The ultrasonic spray pyrolysis as a variant of classical spray pyrolysis has an advantage of activating the precursor solution and thus promoting the formation of nuclei [12]. The type of zinc precursor (organic or inorganic) affects strongly the morphology of ZnO layers [13-16]. Zinc acetate [13, 14], zinc chloride [13] and zinc nitrate [15] are the most commonly used precursors for deposition of ZnO films by spray pyrolysis. The zinc-ammonia complex solution is applied by Li et. al. [16] for
the preparation of ZnO powders with high surface area. Wang et. al. [12] have successfully obtained column-like, flower-like and tube-like arrays of ZnO crystals from zinc nitrate-ammonia complex solution. The zinc-ammonia complex easily undergoes decomposition even at low temperatures - below 100°C [17]. In this study a solution of zinc-ammonia complex was selected as a suitable precursor and was ultrasonically sprayed on heated glass substrates with various deposition parameters. There are two aims to their work: (i) to obtain ZnO thin nanosize films by ultrasonic spray pyrolysis and (ii) to investigate their optical, electrical and gas sensing properties.

2. Experiment
High purity ZnO powder was used as zinc source, which was dissolved in ammonia aqueous solution to obtain 0.025M zinc-ammonia complex. The acidity of the solution was adjusted with acetic acid to pH 12. Glass microscopic slides (76 x 26 mm, Waldemar Knittel Glasbearbeitungs - GmbH) were used as substrates and were ultrasonically cleaned in ethanol for three minutes then thoroughly washed with de-ionised water. The aerosol of the precursor was generated ultrasonically and was transported to the heated substrate by means of an air flow. The substrates were placed on a stainless steel holder. They were heated to temperatures in the range of 200-350°C, chosen on the basis of preliminary experiments. The temperature was monitored using fine thermocouple fixed on the substrate. The postdeposition annealing temperatures ($T_a$) were 300 and 400°C. The phase composition of the samples was studied by X-ray diffraction (XRD) with CuK$_\alpha$-radiation (Philips PW 1050). The crystallite size was estimated from the XRD spectra. A scanning electron microscope (SEM) JSM-5510 of JEOL was used for the morphology investigation of the films. The films thickness was determined with Talystep (Rank Taylor Hobson) profilograph, using needle with thickness of 0.12 μm. The optical transmittance of the samples was measured with Lambda 1050 (Perkin Elmer) spectrophotometer with a standard InGaAr photodiode.

Dark current and steady state photocurrent (under white light illumination) dc measurements were carried out by means of a Keithley 6487 Picomammeter using sputtered gold co-planar contacts on the top surface of the layers; the contacts produce a gap cell with an active area of ~ (1×10) mm$^2$. Current-voltage ($I$-$V$) characteristics, measured at applied electric fields in the range 1 - 10$^2$ V cm$^{-1}$, showed Ohmic-like behaviour of the contacts. Temperature dependences of the dark current were measured at a heating rate of 0.1 °C sec$^{-1}$. Prior to each measurement, the samples were heated in dark up to 423 K in order to achieve charged carrier equilibrium and to desorb water molecules captured on the film surface. No changes in the dark current and the slope of its temperature dependence have been observed when the measurement was repeated. A preliminary test of the films gas sensitivity has been performed by measuring the dc dark current or photocurrent at room temperature before (in a vacuum cryostat evacuated to ~ 1 Pa), $I_d$, and after exposure $I_{d,p}$ to ammonia, water, ethanol, acetone and isopropanol vapours in air as the carrier gas. Vapour content in the air entering the cryostat was determined by the vapour drawn into the cryostat from a soaked piece of cloth fixed to the valve entrance. Normally, the evacuation of the cryostat for 3 - 5 minutes was enough to completely return the samples in the initial state (i.e. to recover the initial $I_d$ values).

3. Results and discussions

| Deposition Time | Substrate Temperature |
|-----------------|----------------------|
|                 | 200°C | 250°C | 300°C |
| 30 min          | 100   | 110   | 170   |
| 60 min          | 90    | 145   | 240   |
| 90 min          | 50    | 75    | 340   |
The film's thickness was in the range of 50-340 ± 10 nm. As seen in Table 1 it is affected by the film deposition time and substrate temperature \((T_{\text{sub}})\). The observed decrease in thickness with deposition time at lower \(T_{\text{sub}}\) can be explained with dissolving of the amorphous phase. It is known that amorphous substances are markedly more soluble than their crystalline counterparts due to the free energy difference between amorphous and crystalline forms. The film's transition from amorphous phase to crystalline state starts at \(T_{\text{sub}}\) 250°C and by 300°C the decomposition reactions are completed and ZnO is well crystallized. That is why at higher \(T_{\text{sub}}\) the increase of deposition time leads also to thickness increase.

The phase composition was estimated by XRD measurements (Figure 1). They revealed formation of wurtzite hexagonal ZnO phase. The films are preferentially oriented in direction (002). The intensity of the (002) peak decreases with the enhancement of the deposition \((T_{\text{sub}})\) and annealing temperatures \((T_{\text{a}})\), which is in good agreement with the literature [18,19].

Figure 2 shows SEM images of two samples obtained at different substrate temperatures. They are dense with smooth surface morphology, without cracks. Secondary agglomerate particles are seen on the film surface; their size increases with the increase of substrate temperature. The formation of particles on the surface is also reported by Znaidi L. et.al. for ZnO sol gel films, obtained from diluted solution [20].

The transmittance spectra of the films are presented in Figure 3; the best samples possess transparency of over 80%. Figure 3 (a) shows a transmittance decrease with the enhancement of substrate temperature. This result correlates with the data of the thin film thickness, which grows with the temperature. The annealing of the samples leads to more transparent layers, which is in accordance with the literature [21]. This effect is explained with the full decomposition of the zinc precursor and the lack of organic residues. A characteristic minimum is seen which is centered in the range 365-370 nm (3.4-3.35 eV) i.e. at the optical band gap energy of ZnO (3.37 eV). No dependence of the minimum position on the preparation parameters has been found. Such feature has been observed by other authors in both room temperatures transmittance [22] and absorption [23] spectra of ZnO films and has been related to exciton absorption [23].

Typical temperature dependence of the dark current, \(I_{\text{d}}\), is shown in Figure 4 (a) in semi-log coordinates. The observed linearity, which was seen for all sample, indicates that:

\[
I_{\text{d}} \sim \exp(-E_{\text{g}}kT)
\]
which corresponds to a thermally activated process. In eq. (1) \( E_d \) is the dark current activation energy which is sum of the Fermi level position, \( E_F \), and the height of intergrain potential barriers, \( E_b \) (\( E_d = E_F + E_b \)), \( k \) is the Boltzmann constant and \( T \) is the measuring temperature. The values of the activation energy \( E_d \) for a series of samples obtained at different substrate and annealing temperatures are summarized in figure 4 (b). It is seen that the activation energy decreases from 0.8-0.9 eV down to \( \sim 0.3 \) eV with increasing \( T_{\text{sub}} \). Assuming electron transport in the conduction band of these undoped films, the observed substantial \( E_d \) change with increasing \( T_{\text{sub}} \) can be explained with a Fermi level shift to the conduction band bottom and lowering of \( E_b \). Hence one can assume a donor concentration enhancement with the temperature but the donor nature is unclear.

A comparison of the temperature dependences of the photocurrent (\( I_p \)) and dark current of two samples is shown in figure 5. It is seen that the samples exhibit high photoconductivity (\( I_p/I_d = 10^3-10^4 \) at room temperature) which is interesting for photodetector applications. The photocurrent activation energy may be used to determine \( E_b \) (\( I_p = I_{p0} \exp(-E_b/kT) \sim \mu_D \tau \), where \( \mu_D \) is the photoexcited carrier lifetime. It has been ascertained that it is 0.16-0.20 eV for the films deposited at \( T_{\text{sub}}=200^\circ \)C and decreases to \( \sim 0.1 \) eV for the films prepared at \( T_{\text{sub}}=300^\circ \)C. This observation supports the above assumption for \( E_b \) lowering with increasing \( T_{\text{sub}} \).

The detected sensitivity of the films, estimated by the change of the dark current and photocurrent caused by the adsorption of gas molecules, is summarized in table 2. A dark current increase was registered after exposure to the tested vapours which indicates that the absorbed gas molecules...
Figure 4. (a) $I_d$ vs $1/T$ plot for a ZnO specimen; (b) dark current activation energy vs $T_{sub}$ for films, treated at two different temperatures denoted in the figure.

Figure 5. Temperature dependence of the dark current and photocurrent of two ZnO films.

may decrease the height of the intergrain potential barriers. On the contrary, upon analyte exposure the photocurrent decreases, which is probably due to $\tau$ decrease but the changes are relatively small. The films response time, i.e. the time for achieving the maximum dark current (photocurrent) alteration, was quite short, between 5 and 30 sec. As seen from the table the $I^d$ changes are strong for the samples obtained at the lowest substrate temperature (200°C) and the ratio $I^d/I^o = 3 \times 10^5$ under exposure to ammonia vapour is significantly higher than $I^d/I^o = 5 \times 10^4$ obtained for the water vapour. The sensitivity of these films to the other tested vapors (ethanol, acetone) is much lower, which indicates a good selectivity of the films. With increasing substrate temperature the film dark conductivity increases by 3-4 orders of magnitude. This observation supports the above assumption for a donor concentration increase. The conductivity increase reduces the intergrain potential barriers and this probably cause the strong gas sensitivity decreases.

Table 2. Sensitivity of ZnO films to water, ethanol, acetone and ammonia vapours in carrier gas air
4. Conclusions
Highly oriented (002) ZnO thin films are obtained by ultrasonic spray pyrolysis. In the visible range the films show over 80% transmittance. It is found that the film dark conductivity increases and its activation energy decreases with increasing substrate and annealing temperatures. Based on these observations an increase of the donor density with the temperature increase is assumed. The substrate deposition temperature also influences the gas sensitivity of the films. Within this study the films deposited at 200°C show sensitivity to the tested vapours; it is highest to ammonia vapours.

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