Sensitivity of Co doped ZnO films to NH3 at room temperature - influence of the deposition temperature

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Abstract. The sensitivity was studied of undoped ZnO films and doped with Co (ZnO:Co) to exposure to NH3. The films were deposited by magnetron sputtering of a sintered ZnO target and co-sputtering of the ZnO target with Co chips on its surface. The influence of the substrate temperature, Ts, on the properties of the films was studied. The structural and optical properties of the undoped and Co doped ZnO films were studied by X-ray diffraction spectroscopy (XRD) and optical transmittance and reflectance. The optical band gap of the films was calculated. The variation of the sensitivity of films deposited at different Ts with the NH3 concentration is presented. The results demonstrate that the Co doped ZnO films have a higher sensitivity to ammonia and their sensitivity increases with Ts.

1. Introduction
ZnO is one of the earliest oxides which have attracted a great deal of attention for application as sensors because of its chemical sensitivity to different absorbed gases, high chemical stability, nontoxicity, low cost technology. An increase of the gas sensitivity and selectivity has been reported by doping ZnO with different elements [1-4].

We report the results of a study of the sensitivity of thin films of Co doped ZnO deposited by RF magnetron sputtering (ZnO:Co) to exposure to ammonia at room temperature. For comparison, the sensitivity of undoped ZnO films is also presented. The influence was explored of the temperature of deposition of the ZnO:Co films on their sensitivity to different ammonia concentrations.

2. Experimental
Thin films of ZnO and ZnO:Co were deposited by RF magnetron sputtering in atmosphere of Ar, as described earlier [5]. A disc of sintered ZnO was used to deposit undoped ZnO films. In the case of Co doping, chips of the doping element Co were placed symmetrically on the ZnO target in the zone of maximum erosion. The samples were deposited on glass substrates at different substrate temperatures, Ts, in the range 150 °C - 500 °C.

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X-ray diffraction spectra (XRD) of the samples structure were obtained using a Brucker D8 Advance spectrophotometer with CuKα radiation: \( \lambda_{\text{CuK}\alpha_1} = 1.540560 \, \text{Å} \) and \( \lambda_{\text{CuK}\alpha_2} = 1.544426 \, \text{Å} \) (intensity half that of \( \lambda_{\text{CuK}\alpha_1} \)). The instrumental broadening was 0.04° in 2θ geometry. Optical transmittance and reflectance spectra were obtained in the range 350-1500 nm, using a CARY UV-VIS-NIR spectrophotometer. The Co concentration was determined by two methods - Rutherford backscattering (RBS) using an ARAMIS accelerator and energy dispersive X-Ray (EDX) microanalysis in a Link AN10000 system. Both methods gave the same values for the Co concentration. The sensitivity of the ZnO films to exposure to NH\(_3\) were measured by the ratio of the resistivity measured in air to that in the presence of the target gas. The films resistivity was calculated from the I-V measurement using a Keithly 6517 electrometer. The co-planar evaporated electrodes were verified to yield ohmic behavior. The films gas sensitivity was evaluated at room temperature (26±2°C) by changing the target gas (NH\(_3\)) ammonia concentration in the air.

3. Results and discussion

The Co content in the films decreased from 5 to 4 at.% as \( T_s \) increased from 150 to 500 °C (table 1). The XRD spectra of ZnO:Co thin films obtained for 2θ scan between 25 and 75° indicated that the deposited films were polycrystalline and textured (figure 1). A reflection corresponding to the (002) plane of wurtzite ZnO is observed. It becomes more pronounced and its position shifts toward the position of the powder ZnO, namely, 34.44°. The FWHM of the (002) peak decreases with \( T_s \). The average grain size, \( D \), in the films are calculated to an accuracy of 10% applying Scherrer equation to the FWHM of the (002) peaks [6]. The data obtained from the XRD spectra are given in table 1. An improvement of the structural properties is observed for both ZnO and ZnO:Co films as the deposition temperature increases.

![Figure 1. XRD spectra of ZnO:Co thin films deposited at different \( T_s \). The corresponding spectrum of ZnO deposited at \( T_s = 500°C \) is given as well.](image)

| Notation | \( T_s \) [°C] | \( 2\theta \) [deg] | FWHM, [deg] | \( D \) [nm] | \( E_g \) [eV] | Co, at.% |
|----------|----------------|------------------|-------------|-------------|--------------|----------|
| ZnO*     | 150            | 34.30            | 0.52        | 16          | 3.33         | 0        |
| ZnO*     | 275            | 34.40            | 0.47        | 18          | 3.30         | 0        |
| ZnO*     | 500            | 34.40            | 0.33        | 25          | 3.27         | 0        |
| ZnO:Co   | 150            | 34.09            | 0.81        | 10          | 3.28         | 5        |
| ZnO:Co   | 275            | 34.27            | 0.28        | 30          | 3.31         | 4.8      |
| ZnO:Co   | 500            | 34.33            | 0.25        | 33          | 3.33         | 4        |

*The data are taken from reference [5].
The temperature is raised. The comparison of the data for both series of samples reveals that the grain sizes are larger for Co doped films deposited at $T_s = 275^\circ$C and $500^\circ$C.

The optical transmission spectra of the ZnO:Co samples in the ultraviolet-visible region are shown in figure 2. For comparison, the corresponding spectrum of undoped ZnO film deposited at $T_s = 500^\circ$C is given as well. The spectra of ZnO:Co films show characteristic absorption bands about 567, 613 and 662 nm, resulting from d-d electron transitions of the tetrahedrally coordinated Co$^{2+}$ ions due to $^4A_2(F) \rightarrow ^2A_1(G)$, $^4A_2(F) \rightarrow ^4T_1(P)$ and $^4A_2(F) \rightarrow ^2E(G)$, respectively. It is shown in [7] that the valence state of Co atoms in the ZnO lattice is Co$^{2+}$ and that Co$^{2+}$ ions substitute for Zn$^{2+}$.

The absorption coefficient, $\alpha$, is calculated from the transmission and reflection spectra [5]. Its spectral dependence is presented in figure 3. The formula for direct allowed transitions is used to obtain the optical band gap, $E_g$, and the values are calculated to an accuracy of 5% (table 1). The optical band gap is in the range 3.27-3.33 eV. These values are typical for ZnO and Co doped ZnO films [5, 8]. The value of $E_g$ for undoped ZnO films decreased with $T_s$ due mainly to a decrease of the Burstein-Moss effect, as reported earlier [9]. The optical band gap of ZnO:Co films increases with $T_s$, probably due to a decrease of the Co concentration, as the RBS and EDX analyses show.

![Figure 2. Transmittance spectra of ZnO:Co thin films deposited at different $T_s$. The bands of Co$^{2+}$ d-d-electron transitions are marked by arrows.](image)

![Figure 3. A plot of $(\alpha \times h\nu)^2$ against $h\nu$ for ZnO (deposited at $T_s = 500^\circ$C) and ZnO:Co (deposited at different $T_s$) films.](image)

A decrease of the optical gap of ZnO-CoO alloys as the CoO concentration is increased has been reported by other authors as well [7, 8]. The Co doped films exhibit significant band tailing in the lower energy region, which is not present in the spectral dependence of $\alpha$ for undoped ZnO films (figure 3 and [9]). This could be attributed to point defects, such as Zn vacancies, substitution of Zn$^{2+}$ by Co$^{3+}$ (Co$_{\text{Zn}}$), or interstitial Co$^{3+}$, as assumed in [10].

The variation of the sensitivity of ZnO:Co deposited at different $T_s$ and of ZnO deposited at $T_s = 500^\circ$C, with the NH$_3$ concentration up to 18750 ppm is shown in figure 4. The undoped ZnO films deposited at lower $T_s$ (150 $^\circ$C and 275 $^\circ$C) have very low sensitivity to the NH$_3$ concentration used; their sensitivity is not presented here. The sensitivity to NH$_3$ of ZnO:Co films increases with $T_s$. The ZnO:Co film demonstrates sensitivity that is two orders of magnitude higher than that of the undoped ZnO film deposited at the same $T_s = 500^\circ$C. Additionally, it must be noted that our previous study performed by a quartz crystal microbalance demonstrated that the rate of sorption and the total NH$_3$ sorbed mass (for equal time of exposure) in ZnO:Co are higher than that in an undoped ZnO film [4]. A typical transient response curve of a ZnO:Co thin film to ammonia is shown in figure 5. The response time is larger than the recovery time.

Usually the gas sensitivity increases as the grain size in the films decreases [11]. However, this is not the case here (table 1 and figure 4). The higher sensitivity of Co doped ZnO films reported in this work could be due to the presence of higher concentration of point defects at the surface of the grains,
such as interstitial Co$^{3+}$ and Co$_{Zn}$, where higher concentration of O$_2^-$ and OH$^-$ could be adsorbed. It is widely accepted that NH$_3$ reacts with the surface species and the trapped electrons are returned to the conduction band causing an increase in the conductivity of the ZnO:Co films and, respectively, the sensitivity of the sensor [3].

4. Conclusion

A study is performed on the influence of the substrate temperature of ZnO and ZnO:Co thin films deposited by RF magnetron sputtering on their structural and optical properties, and sensitivity to ammonia. The optical band gap decreases with $T_s$ for the undoped ZnO films and increases in the case of Co doped ZnO films. The optical transmission spectra reveal the presence of Co$^{2+}$ in the ZnO:Co films. The sensitivity to NH$_3$ of ZnO:Co films increases with $T_s$. The ZnO:Co film exhibit sensitivity about two orders of magnitude as high as that of the undoped ZnO film deposited at the same $T_s = 500$ °C. It is shown that ZnO thin films doped with Co may find applications as room temperature sensors.

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