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Single step deposition of different morphology ZnO gas sensing films

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Abstract

Al-doped ZnO thin films were deposited onto fixed silicon substrates by dc reactive sputtering. The inherent lateral inhomogeneity in the deposited film with areas of different morphology and sheet resistance revealed different sensing properties. This novel approach offers the possibility of controllable deposition of ZnO sensing layers for the simultaneous manufacturing of sensors with different properties in an array in a single technological step.
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Keywords: Reactive magnetron sputtering; Zinc aluminum oxide; Gas sensors

1. Introduction

Development of gas sensors to monitor combustible and/or toxic gases is one of the rapidly developing fields of sensor technology. Among others, there is a large demand for monitoring, e.g. oxygen, NH_3, water vapor and hydrocarbons. Gas sensors based on polycrystalline oxide semiconductors (e.g. SnO_2 and ZnO) play an increasing role in this filed due to their stability and favorable response (using catalysts) [1].

The key issue in ZnO sensor development is the control of the sensing layer properties in order to meet the specific requirements of gas sensing [1,2].

Hermann et al. and Song et al. [3,4] studied the properties of Al-doped ZnO (ZAO) layers sputtered onto fixed substrate and found substantial differences in the properties of the layer over the substrate.

Our work represents a novel approach for sensor application of ZAO thin films. Different layer properties were obtained reproducibly by sputtering in a single step. Sheet resistance and morphology found to be different of the sample. Therefore, they provide different responses to gas exposure.

Morphology, electron spectra, work function, sheet resistance were measured, and the corresponding sensing functionality of the films were tested.

2. Experimental

Three inches Si substrate covered with 600 nm thermal SiO_2 were coated by ZAO layers deposited by dc magnetron sputtering. The target was a rectangular Al-doped Zn alloy (99.995%) with the size of 114 mm × 440 mm with 2% (w/w) Al content. The electric supply unit was operated both in dc and adjustable pulse mode. The base pressure in the chamber was typically $p = 5 \times 10^{-6}$ mbar. Gas pressure and composition, dc bias and additional pulse parameters were monitored and fully computer controlled. All depositions were made at constant power control mode.

Magnetron sputtering generally requires continuous movement of the substrate in order to ensure the suitable layer homogeneity. In our case, however, lateral structural gradient was just achieved by sputtering onto fixed substrate (Fig. 1).

Due to the arrangement of the magnets under the target in the plasma three distinct zones were formed. These are (from the middle outwards): the center zone, the erosion zone and the border zone. The sample was positioned under the target such that different areas of the substrate were affected by different plasma zones.

Due to this arrangement a gradation in the layer formation was expected reflecting the plasma distribution.

The sputtering time was $t = 50$ s at $P = 1.4$ W/cm^2 target power in 35/15 sccm Ar/O_2 atmosphere at $p = 6 \times 10^{-3}$ mbar pressure. The substrate was set at a working distance of 6 cm from the target. The layer thickness varies from sample to sample and approximately 100 nm at its peak.

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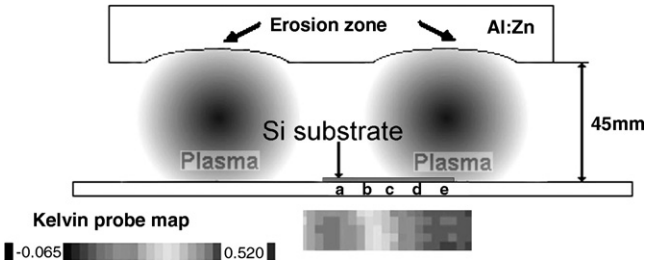

Fig. 1. Schematics of the experimental arrangement and Kelvin probe map of the sample showed at the place of the measurement.

The contact potential difference depends on the properties of the surface. Therefore, a lateral work function map (Kelvin probe mapping) taken by a scanning vibrating capacitor helps to reveal the important differences between different areas of the deposited layers.

The deposited layers were characterized by scanning electron microscopy (SEM), electron-dispersive spectra (EDS) and four probe sheet resistance measurements.

3. Results and discussion

Fig. 2 shows the sheet resistance values of the layer (measured by Veeco FPP 100 type standard four point probe tester) while going from 'a' to 'e', i.e. from the center zone towards the erosion zone. This is the region of maximum variation in the properties. The sheet resistance of the thin ZAO film gradually changed between 4 and 22 kΩ/□ with the lowest values found in the region under the target center ('a'). It is important to note that the variation of the layer thickness in the whole sample remained below 5%. This indicates that the resistance change cannot originate from layer thickness inhomogeneity.

The Kelvin probe measurement in Fig. 1 shows a good correlation between the distribution of contact potential and the resistance. The lowest contact potential was obtained at the position of minimum sheet resistance 'a'.

EDS spectra taken from locations 'a' to 'e' (Fig. 3) revealed no difference in the elemental composition. The Al content in the ZnO matrix was found to be the same in the selected regions.

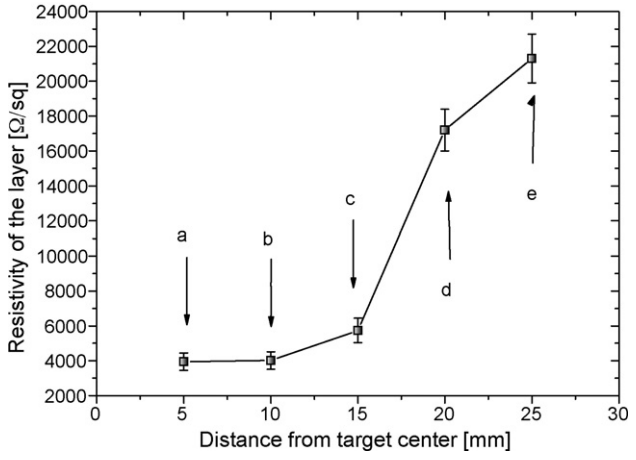

Fig. 2. Sheet resistance vs. distance from the target center ('a') in fixed substrate mode (notations 'a' to 'e' show the sampling locations chosen for analysis.)

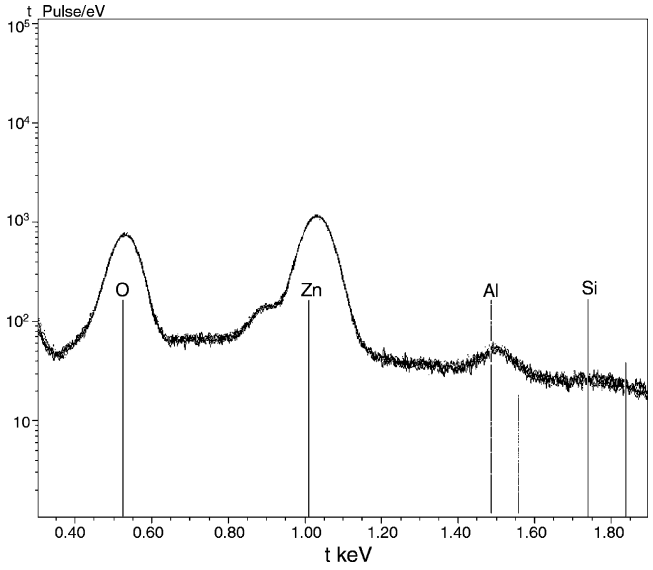

Fig. 3. EDS spectra in 5 analyzed regions of the deposited layer show uniform elemental composition.

Fig. 4 shows the cross-sectional and top-view SEM morphologies taken from 'a' and 'e' regions of the ZAO layer. The sample taken from the zone 'a' has a columnar morphology while the sample from 'e' exhibits irregular polycrystalline morphology with less recognizable grain boundaries (SEM images below).

The asymmetric arrangement of magnetrons in the sputtering system results in substantially inhomogeneous plasma properties. Due to the increased electron residence time and acceleration effect the plasma densities are much higher at the middle of the erosion zone. This causes the higher erosion rate of the target between the magnetic poles. In the intensive plasma the higher particle bombardment of the deposited layer causes significantly different layer growth and mechanism when compared to that of outside this region.

The different microstructure observed in the layers can be explained by the widely accepted view that re-sputtering caused by high-energy neutral oxygen atoms affects the aggregation of particles and accelerates the grain growth.

This qualitative physical picture provides a proper explanation of the morphology difference found between 'a' and 'e' (Fig. 4). This is also in agreement with the published results of other authors [5,6].

XRD spectra taken from 'a' to 'e' zones exhibit a drift of the [0002] ZnO–diffraction peak towards larger 2θ values. The increasing 2θ values towards 'e' zone indicate the build-up of compressive strain (Fig. 5). This corresponds to the smaller grain size, i.e. the increasing surface/volume ratio obtained in the layer affected by the intensive plasma bombardment.

The decrease of the intensity of the diffraction peak towards "e" indicates smaller amount of crystalline material in the layer. This effect can originate either from the layer thickness variation or from the increase of the proportion of amorphous phase in the material. Since the thickness variation remains less then 5%

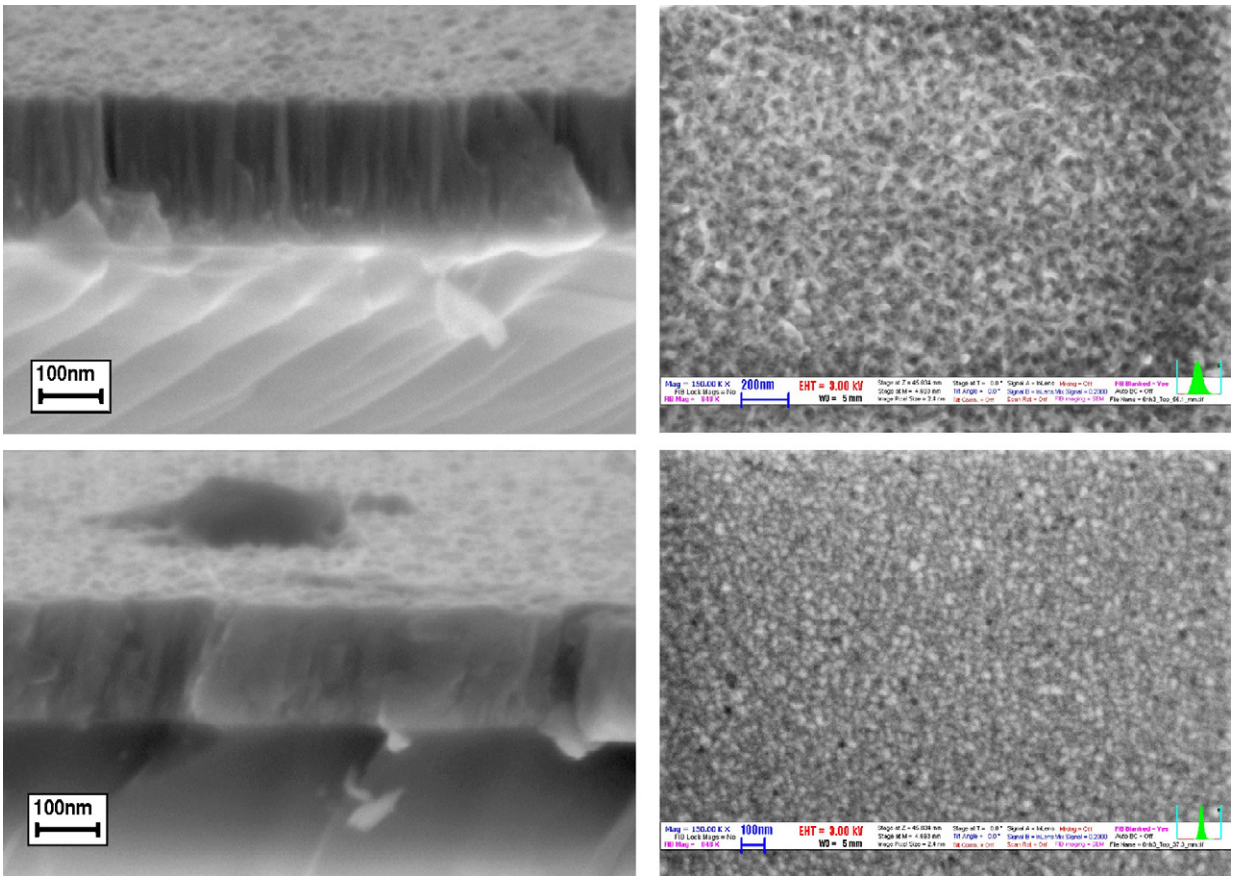

Fig. 4. Cross-sectional (left) and top-view (right) SEM micrographs (upper pictures are taken at 'a', lower ones are at 'e').

the first explanation can be ruled out and the decay of the X-ray signal can be related to the higher amount of amorphous material.

This is in agreement with the conclusions drawn from the SEM morphology examinations. Region 'e' has smaller average grain size with higher relative amount of grain boundaries.

The selected regions of the ZAO layer were exposed to four concentrations of NH_3 in synthetic air up to 4000 ppm. The sample was heated up to 150 °C and the NH_3 gas was introduced for 5 min. Fig. 6 shows a typical sheet resistance versus time response.

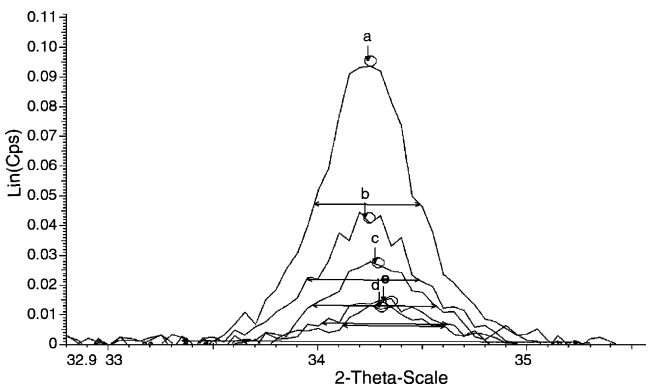

Fig. 5. XRD spectra taken from 'a' to 'e' places of the sample.

Nanto et al. [7] found the resistance of the ZnO sensor to be stable at 350 °C in continuous operation under air ambient for 3 months. In contradiction with these results our experience showed degradation of ZAO resistors at 300 °C operational temperature. However, at 150 °C our samples showed good stability even when they were exposed to repeated heat cycles.

The relative sensitivity of the response ($\Delta R/R$) [%] was calculated from the ratio of resistance values before and after the introduction of the ammonia–air mixture.

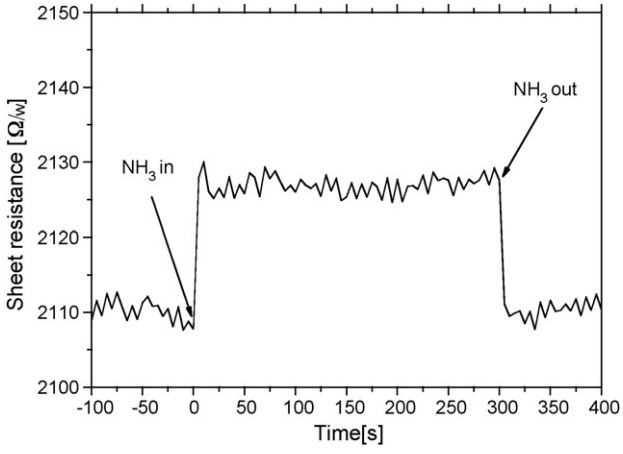

Fig. 6. Typical response of the ZAO resistor to the NH_3 exposure (at 150 °C, 3000 ppm).

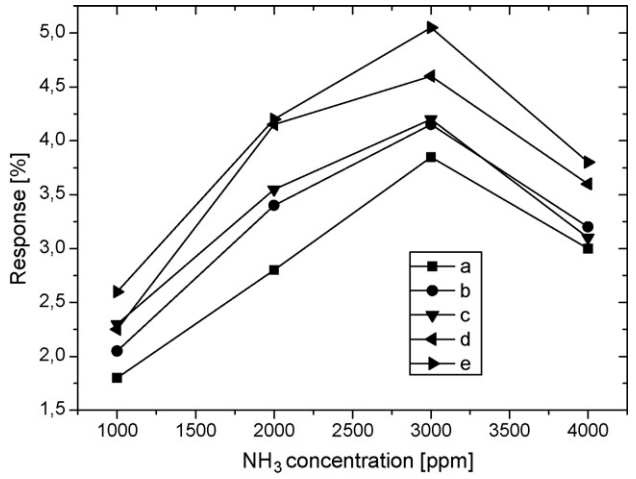

Fig. 7. Sensor response to different NH_3 concentrations affected by the layer morphology.

As it can be seen in Fig. 7, the areas with columnar morphology show lower sensitivity. This indicates that the morphology and the amount of grain boundaries play a key role in determining the sensing properties. It can also be noted that the relative sensitivity has a characteristic maximum at 3000 ppm. This phenomenon was also observed by Nanto et al. [7]. The possible explanation of decreasing sensitivity above 3000 ppm is that the decomposition of ammonia gas produces hydrogen and this affects the ammonia sensitivity.

4. Conclusion

Al-doped ZnO layers with gradually changing properties were successfully deposited by reactive dc sputtering onto fixed substrate. Analysis of the layers showed substantial difference in the sheet resistance due to the change in the polycrystalline morphology. Samples taken from different regions were characterized for NH_3 gas sensing properties.

Most electronic noses use sensor arrays that react to volatile compounds on contact. The adsorption of volatile compounds on the sensor surface causes a response specific to its concentration. Since different areas of our deposited layer exhibit different sensitivity to NH_3 contamination, discrete sensors for different concentration ranges can be formed using these areas of the layer.

The described method for the formation of ZAO layers with gradually changing sensitivity offers the possibility of sensor array preparation for electronic nose purposes in a single process step.

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Biographies

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Zoltán Lábadi received his PhD in Budapest University of Technology and Economics in 2001. He is currently a research fellow at the Research Institute for Technical Physics and Materials Science. His current interest is thin film solar cell materials and characterization.

István Bársony graduated in electrical engineering from the Technical University of Ilmenau, Germany in 1971. He holds a C.Sc from the Hungarian Academy of Sciences (1978) and a PhD from the Technical University of Budapest (1996) and a D.Sc from the HAS (2001). During his professional career he was working on research assignments in Hungary mainly in silicon technology, in Japan (1983–1986) on imaging application of the Static Induction Transistor, in the Netherlands (1988–1993) at the MESA Research Institute of the University of Twente on Rapid Thermal Multi-Processing. Since 1993 he has been with the Research Institute for Technical Physics and Materials Science of the Hungarian Academy of Sciences, MFA Budapest, from 2004. He is the director of MFA. He has led several international projects a/o on solar cell and microsystems research. He holds 12 patents, published over 80 scientific papers and is a professor of nanotechnology at the University of Veszprém.