ULTRA SENSITIVE OZONE SENSING ZnO FILMS

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1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor of wurtzite structure with a direct energy wide-bandgap of about 3.37 eV at room temperature. [1]. Until now ZnO-based elements have attracted much attention as gas sensors because of their chemical sensitivity to volatile and other radical gases, their high chemical stability, non-toxicity, low cost and simplicity in fabrication [2]. In the present work we report on the structural characteristics and the room temperature sensing response of ZnO films fabricated in a home-made Aerosol Spray Pyrolysis (ASP) system, to ultra low ozone concentrations ranging from 2400 to 16 ppb.

2. Experimental details

The ZnO films were fabricated in a home-made aerosol spray pyrolysis system. Various parameters such as nozzle to substrate distance, solution vaporize rate, pressure of carrier gas (nitrogen), deposition temperature, deposition time and precursor concentration [$Zn(NO_3)_2$, 0.1 M] were optimized in order to get good quality films. The films were analysed by X-ray Diffraction (XRD), Scan Electron Microscopy (SEM) and Cross-Section Transmission Electron Microscopy (XTEM). The responses to varying ozone concentrations, as supplied by a commercial ozone generator/analyser (Thermo 49i), were monitored by applying a coplanar conductometric set-up.

3. Results and Discussion

All results reported hereby are based on films fabricated at 350 ^oC.

Typical XRD pattern shown the (100), (002), (101) and (102) characteristic peaks indicative of a single face crystalline nature of ZnO in the Wurtzite type structure. The dominant (002) peak at $2\theta=34.44^0$ underlined the very high level of orientation along the c-axis perpendicular to the substrate.

In an aerosol spray pyrolysis process there are two sources that may contribute to a deposition rate variation. The first is related to the precursor solution atomization and the second to the droplet transport and decomposition on the surface.

However the XTEM analysis revealed the nature of the growth process adopted by the present experimental set-up which points out that the observed irregularities are characteristic of the ultrasonic nature of the atomization process and the thermodynamic environment as the droplets strike the substrate. It should be underlined that the present ASP films were shown to have comparable grain sizes to those of sputtered films [4] showing very high sensing responses. At the same time and besides the very fine grain size composition these ASP films have shown a very high porosity of the order of 100 nm promoting them as candidates for highly absorbing gas sensing elements. (Fig.1).

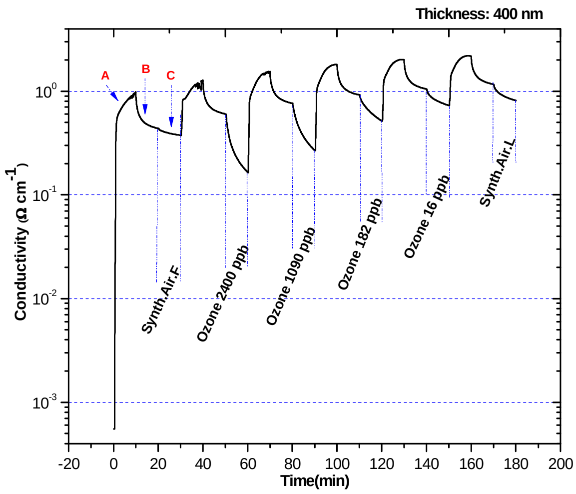

Fig.1 The film response after exposure to ozone concentrations from 2400 to 16 ppb. A corresponds to the photoreduction stage, B "lamp-off" stage, C oxidation stage.

Indeed, by growing these films on glass substrates with geometrically ordered Ohmic conducts and exposing to a photoreducing / oxidation process, their sensing response to ultra low ozone concentrations was tested. Sensor response (S) is defined as the ratio of (Ro-Rg)/Rg (where Ro denotes the resistance under ozone exposure and Rg the resistance in the applied synthetic air /gas). (Fig. 2)

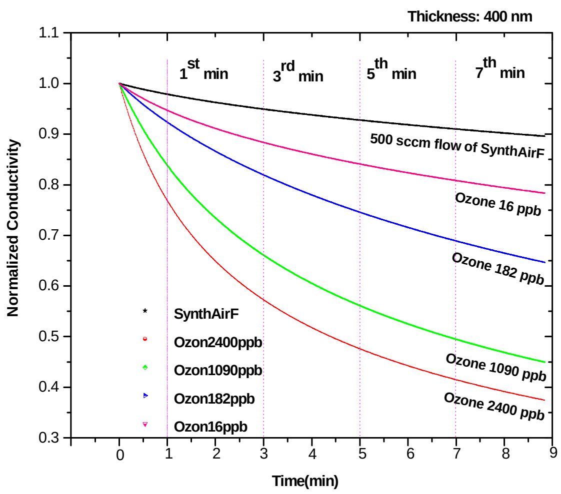

Fig.2. Normalized rate of response to the different ozone concentrations. Differences in the exponential decay during the oxidation process under various ozone concentrations.

Furthermore the film responses at various concentrations with respect to the synthetic air, plotted as a function of time has shown a satisfactory resolution 3.5% from Synthetic Air at ultra low (16 ppb) ozone concentrations right after the first minute of analysis. (Fig.3)

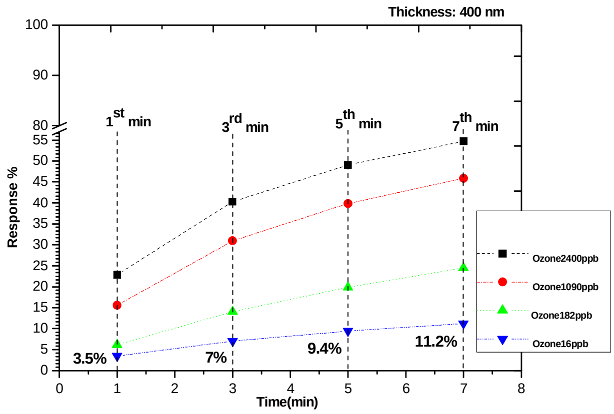

Fig.3. Film responses to ozone concentrations in the range of 2400 to 16 ppb as a function of time.

4. Conclusions

Highly porous ZnO films with characteristic c-axis columnar growth structure deposited on glass substrates in a home-made aerosol spray pyrolysis system at 350 ^{0}C have been fabricated. Films have shown to produce clear response signals to ozone concentrations as low as 16 ppb with a response time of 1 min., which is the lowest, ever reported in the open literature.

5. References

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