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Ultra-low gas sensing utilizing metal oxide thin films

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A B S T R A C T

The structure, functionality and sensing response of metal oxide films is discussed with emphasis on ZnO and InO_x prepared by Aerosol Spray Pyrolysis in ambient atmosphere and DC Magnetron Sputtering techniques under vacuum. Optical, structural and electrical characterization techniques applied for the in-depth analysis of the film properties are described. Sensing response towards ozone is presented utilizing a conventional conductivity technique as well as surface acoustic wave (SAW) structures and devices. It is shown that sensing responses of extremely low ozone concentrations in the range of a few parts per billion (ppb), at room temperature (RT), may be obtained by appropriate control of the film nanostructure. It is also shown that InO_x employed as sensitive layer on top of surface acoustic wave structures can lead to strong frequency shifts for low concentrations of NO_2, H_2 and O_3 gases.

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1. Introduction

Gas sensors have been extensively used to detect and monitor a wide variety of volatile and other radical gases. In particular, gas sensors have a huge variety of applications such as in environmental quality control, public safety, medical applications, automotive applications and for air conditioning systems in aircrafts, spacecrafts, vehicles, and houses [1–6]. According to a recent industrial market report, in the USA the demand for sensors increased with an average annual growth rate 1(AAGR) of 4.6% from a market value of $6.1 billion in 2004 to $7.6 billion in 2009 [7].

Semiconducting metal oxides (MOs) such as SnO_2, TiO_2, InO_x and ZnO are used for gas sensing applications due to the sensitivity of their electrical conductivity to the ambient gas composition, which arises from charge transfer interactions with reactive gases such as O_2, NO_x, CO, hydrocarbons (HC), volatile organic compounds (VOC) and ozone (O_3) [8]. Ozone is a strong multipurpose oxidizing gas which plays a fundamental role in the formation of photo-chemical smog in urban polluted areas [9]. It may also be met in a wide field of industrial and agriculture applications. Ozone, in concentrations over the 40 ppb threshold, is known to be harmful to the human body according to existing USA Federal Drug Agency and EU standards [10]. Thus a big thrust, for the development of gas sensors, driven by the need to improve the detection of radical gases, including ozone, and trace element detection limits for security and environmental reasons, has emerged. The sensitivity and response time of MO- based ozone sensor films strongly depend on the porosity of the material used. In addition, the grain size of the polycrystalline MO film has also a noticeable effect on its gas sensing properties. However, the gas sensing mechanism of polycrystalline MOs films is only partially understood and the effect of grain size on the gas sensitivity requires further clarification [11].

In the present work the emphasis is on the recent trends to develop ozone sensors fabricated mainly by InOx and ZnO polycrystalline films utilizing two of the most intensively studied techniques, i.e. Aerosol Spray Pyrolysis (ASP) [12,13] and DC magnetron sputtering [14–17]. The influence of the grain size and the surface morphology from films obtained by the above different deposition techniques, achieving sensing responses of the order of a few parts per billion for ozone at room temperature, are reported. A study of the sensitivity of MO films to other harmful gases (NO_2, H_2 and volatile organic vapours [18]) will also be reported.

Structural and ozone-sensing analyses carried out, particularly on InO_x thin films (with a thickness of the order of 100 nm) grown by dc magnetron sputtering onto glass, Si and flexible (PET) substrates, are of interest [19] The reason for involving flexible substrates is that their successful application may lead to simpler,

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faster and inexpensive fabrication techniques targeting novel roll-to-roll and printed processing applications with obvious advantages over conventional ceramic or silicon-based technologies. Recent results utilizing conductivity change techniques [19] have shown that optimized films with columnar growth structure and nano size grains of the order of 20 nm used as gas sensing elements exhibited extremely low detection levels for ozone down to 6ppb at room temperature. Such results underline the wide potential of applying these metal oxides as gas sensors on flexible substrates for a variety of applications.

Surface Acoustic Wave (SAW) devices show high sensitivity towards electrical perturbations caused by the gas interaction at their active surface and have been studied since 1979 [20]. A detailed account of the operating principles of SAW devices is beyond the scope of this work and readers are directed to other existing reviews [21–23]. In brief, using a layered SAW device as the sensor, a higher level of acoustic energy trapping at the surface is realized, making it possible to greatly enhance the structures' sensitivity to such interactions. In the work described in this article it is shown that the use of InO_x as the sensitive layer on top of surface acoustic wave structures largely increases the sensitivity levels of such devices to O_3, NO_2 and H_2, making it a promising base material for gas sensing. In the results presented below, the sensor's performance for different NO_2, H_2 and O_3 pulse concentrations is analyzed in terms of response time, recovery time and response magnitude as a function of operational temperature. Very strong positive frequency shifts (91 kHz) for 8.5 ppm of NO_2 and negative (319 kHz) for 1% of H_2, along with 31.5 kHz at 10 ppb and 78.5 kHz at 25 ppb of O_3 in synthetic air are presented, demonstrating the high sensitivity of the combined layered SAW structures with the applied InO_x selective layer.

2. Experimental results and discussion

2.1. ZnO thin films grown by DC magnetron sputtering

ZnO thin films with thickness up to 1 μm were deposited onto Corning glass and silicon substrates in an Alcatel DC magnetron system using a 99.999% pure metallic zinc target of 150 mm diameter. The base pressure of the ultra high vacuum (UHV) chamber was below 5×10^{-7}mbar while, during the deposition, the pressure was 8×10^{-3}mbar. For conductivity studies all films were deposited onto Corning glass substrates, which had thermally-evaporated NiCr ohmic contacts applied in a UHV chamber evacuated, prior to deposition, to below 10^{-6} mbar. The sputtering atmosphere consisted of 100% oxygen plasma.

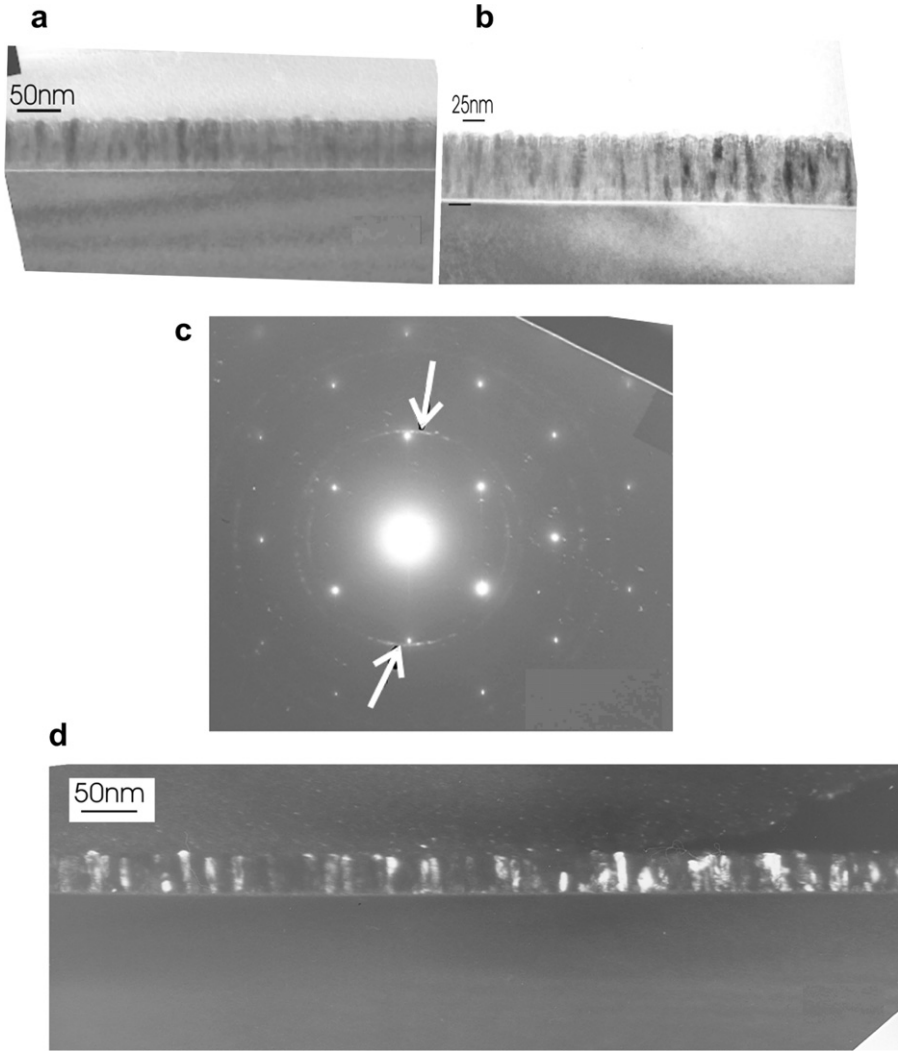

Fig. 1. (a) TEM images exhibit morphology of a typical 50 nm thick ZnO film (b) images at higher magnification. (c) Diffraction arcs reveal strong preferred orientation. (d) Dark field (DF) micrographs micrograph exhibiting ZnO columnar mode structure.

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