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Research Article

Highly Sensitive InO_x Ozone Sensing Films on Flexible Substrates

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InO_x thin films with a thickness of the order of 100 nm were grown by dc magnetron sputtering on glass, Si and flexible (PET) substrates. The electrical conductivity of InO_x thin films exhibited a change of two orders of magnitude during photoreduction with ultraviolet light and subsequent oxidation in ozone concentrations from 2370 to 15 ppb, at room temperature. Optical transparency of over 85% for all substrates was maintained. Film structural and ozone sensing properties were analyzed. Surface morphology investigations carried out by SEM for films on PET substrates showed extended surface cracking for bending angles beyond 40°. Optimization of growth conditions has led to films with extremely low detection levels for ozone down to 15 ppb at room temperature, demonstrating the wide prospective of utilizing these metal oxides as gas sensors on flexible substrates for a variety of automotive and air-conditioning applications.

1. Introduction

Metal oxides compose an interesting heterogeneous class of active materials with properties ranging from metallic and semiconducting to insulating, attracting research efforts from almost all fields of material science and physics. These materials find applications in micro/nanoelectronics, photovoltaics, light-emitting diodes, transparent thin film transistors, sensors and radio frequency identification systems (RFIDs) extending to superconductivity and magnetism.

A new thrust for the wider use of metal oxide based gas sensors is anticipated owning to the latest integration efforts on flexible substrates [1–4]. Successful application on flexible substrates may lead to simpler, faster and inexpensive fabrication techniques targeting novel roll-to-roll and printed processing applications with obvious advantages over conventional ceramic or silicon-based technologies.

Most of the recent efforts focus on the utilization of metal oxide sensing materials for the detection of volatile organic compounds (VOCs). Among these materials tin oxide (SnO_x) has been the favored and mostly studied gas sensing metal oxide over the last three decades. In all recent integration efforts the prime critical parameters for successful operation have been the heating element due to the high-temperature (>300°C) requirement for a typical operation of the SnO_x-based gas sensors [4]. However, recent reports have emerged showing sensitivity levels in the low ppb (parts per billion) range at operating temperatures from around 100°C to Room Temperature (RT), based on Indium (In) and Zinc (Zn) oxide films grown by sputtering and spray pyrolysis [5–7]. Utilization of sensing ozone levels below the 75 ppb mark, as imposed lately by International bodies [8–10], is of paramount importance for health reasons, and efforts for low cost, disposable and reliable sensing elements particularly on flexible substrates will be proved very valuable for a variety of automotive and air-conditioning applications.

In the present work we report on the growth of InO_x thin films on amorphous, 0.25 mm thick, PET (polyethylene terephthalate) flexible substrates (HiFi Co) and corresponding films grown on glass (Corning 1737 F) and Si substrates by dc magnetron sputtering at RT, and on their sensing response characteristics.

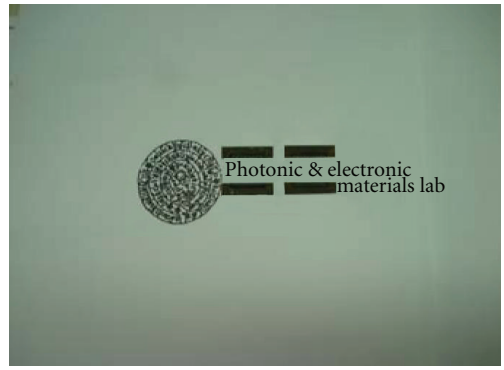
2. Experimental

Deposition of the InO_x thin films was done in a dc magnetron sputtering system (Alcatel 250) using a 99.999% pure In target. Detailed description of the deposition system may

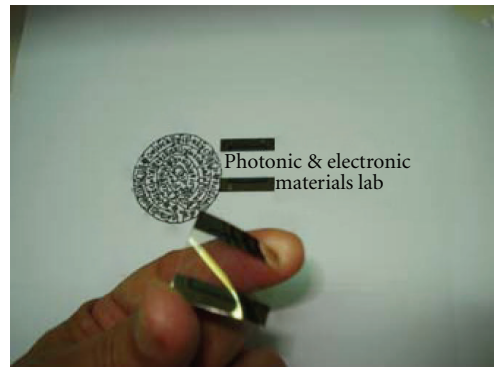
be found in refs [5, 11]. Films were grown with thicknesses in the range of 50 to 200 nm, at constant total pressure of 8×10^{-3} mbar, in a 100% oxygen plasma atmosphere at RT. Surface morphology was studied with Scanning Electron Microscopy (SEM). Electrical and sensing characterization (photoreduction/oxidation process) was performed in a home-designed system [12] at FORTH. During photoreduction the samples were directly irradiated in vacuum by a low power (4.5 mW/cm^2) UV light (254 nm) mercury pencil lamp at a distance of approximately 3 cm for 20 minutes till achieving a steady state. Our choice of a photoreduction process under vacuum rather than in ambient air was deliberate as we wanted to demonstrate sensitivity responses at ozone detection limits well below the concentration of Ozone in ambient air. It is well documented that the content of air in Ozone varies among other with altitude, season, temperature and humidity and takes values from 30 to 90 ppb [8–10]. These levels increase in the presence of UV and so detection of concentrations below these levels is impossible. Thus, by applying the photoreduction process at ambient air conditions one would be unable to fully photoreduce the film since at the same time on the film surface an oxidation process would be present due to (a) residual ozone in air, (b) ozone produced by the UV absorbed by the oxygen in air and (c) re-adsorption of atomic oxygen leaving the film surface after UV irradiation. The only experimentally correct procedure to fully reduce the film without competing oxidation processes and separate the photoreduction from subsequent oxidation with controlled oxidizing gas concentrations was to do the experiment under vacuum thus pumping away all residual and process produced gases during photoreduction, that is, having a gas free surface on which ultra low and accurately controlled gas mixtures could be introduced demonstrating the intrinsic sensing properties of the tested films. Subsequently, the chamber was back-filled with a controlled amount of Ozone flow (concentrations from 2370 to 15 ppb in synthetic air) as produced by an Ozone generator (Thermo 49i). The treatment lasted until a steady state of film maximum resistivity was reached, a process that span from 20 to 40 minutes after which no further changes in resistivity could be observed. The process of photoreduction and oxidation was repeated several times to establish repeatability. Sensing response was recorded in terms of the fractional resistance change [13] utilizing an electric field of 1 or 10 V cm^{-1} and monitoring the corresponding current with a pico-electrometer. Current-voltage (I-V) measurements were taken before each cycling to ensure the ohmic nature of the conducts.

3. Results and Discussion

The superior properties of InO_x over other metal oxides such as SnO_2 and ZnO in as far as ozone detection is concerned, have been elaborated in the past [14, 15]. These were attributed to the distinct surface structure of InO_x with the polar nature of a pure oxygen terminated subplane exhibiting a low binding energy for a number of oxygen atoms. This, in combination with the surface oxygen deficiency on these films, leads to enhanced ozone sensitivity levels of the order of a few parts-per-billion (ppb) with fast response and recovery times.



(a)



(b)

Figure 1: (a) Transparent InO_x films on glass (left) and PET (right) substrate. (b) Flexibility of the film on PET.

Figures 1(a) and 1(b) demonstrates the high level of the InO_x film transparency both on the glass and 0.25 mm thick PET substrate. Optical transparency of more than 85%, detected by UV-VIS spectroscopy (not shown here) was maintained for either substrate while the optical band-gap (Eg) was 3.75 eV.

Film surface morphology analysis by SEM has shown smooth surfaces with a characteristic granular polycrystalline structure [5] for flat and bended films to angles up to 40°, beyond which extended cracks were developed as shown in Figure 2. A detailed investigation of the mechanical properties of these films as a function of bending angle and the study of the elastic to inelastic transition limits is currently under way. In the present, we report on the film sensing responses which were fond to be independent of the applied substrate.

Figure 3 exhibits six circles of photoreduction-oxidation process for the InO_x films in three stages. During photoreduction (stage A), films reach 60% of their steady state conductivity within the first minute and a maximum value of 10^2 Ohm^{-1} cm^{-1} after five minutes of the UV light exposure in vacuum. The conductance rise when the film is illuminated with UV light is due both to the generation of free carriers within the film, and to photo-desorption of

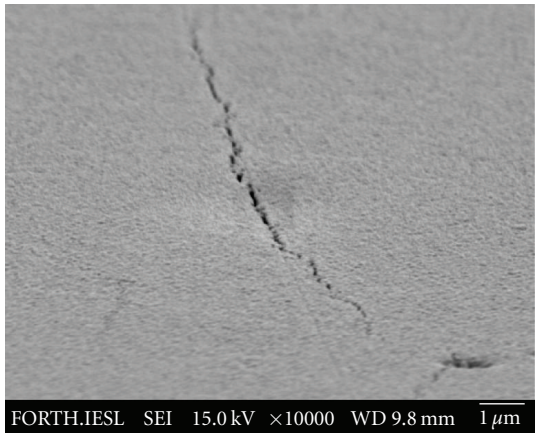


Figure 2: SEM image of the InO_x film on PET substrate under a bending angle of 40°.

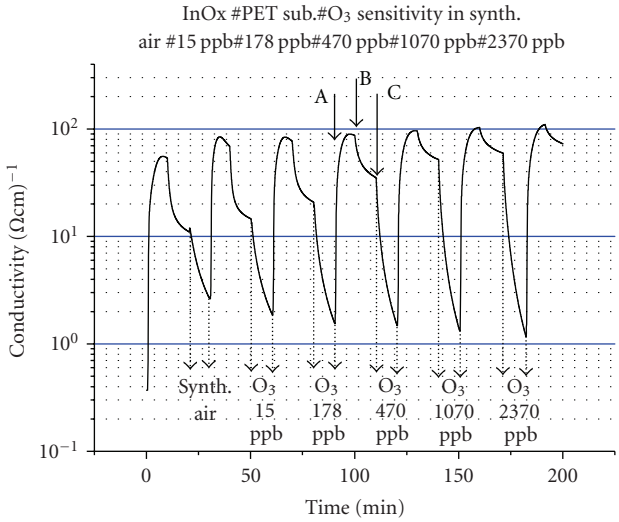


Figure 3: Photoreduction-oxidation process of the InO_x films.

surface species with a subsequent thinning of the electron depletion layer near the film surface. Consequently, the applied UV lamp was switched-off (stage B) and a reduction in conductivity of the order of 30% was recorded, probably due to an inherent oxidation process associated by absorption of residual oxygen in the chamber. During the following stage (C) the films were exposed to accurately controlled ozone concentrations in synthetic air (used as reference) ranging from 2370 to 15 ppb.

Figure 4 shows a normalized comparison of the exponential decays during the oxidation process at the above ozone concentrations. Although previous results utilizing SnO_2 [6] and aerosol spray pyrolysis of ZnO [7] have shown corresponding sensitivity levels for ozone of the order of 15 ppb too, to our knowledge, this is the first time that such extremely low sensing levels are reported for metal oxide thin films at room temperature (RT) on flexible substrates. The differences in the exponential decay is a measure, on the one hand, of the efficiency of these films to screen the various

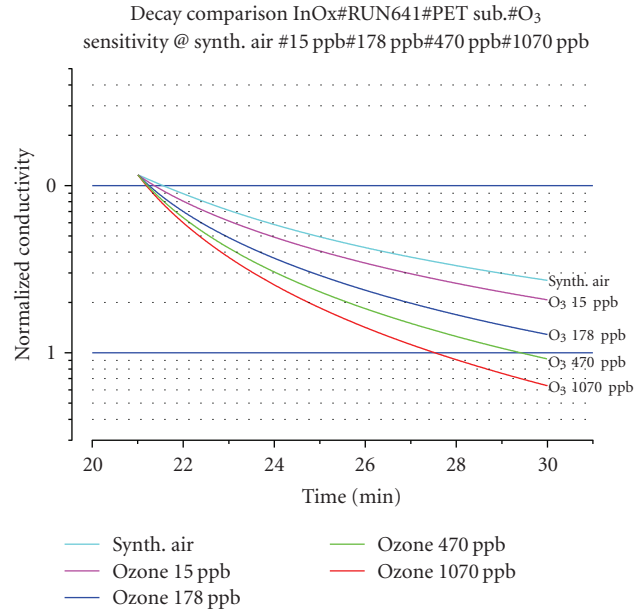


Figure 4: Normalized exponential decays from 1070 to 15 ppb ozone exposures.

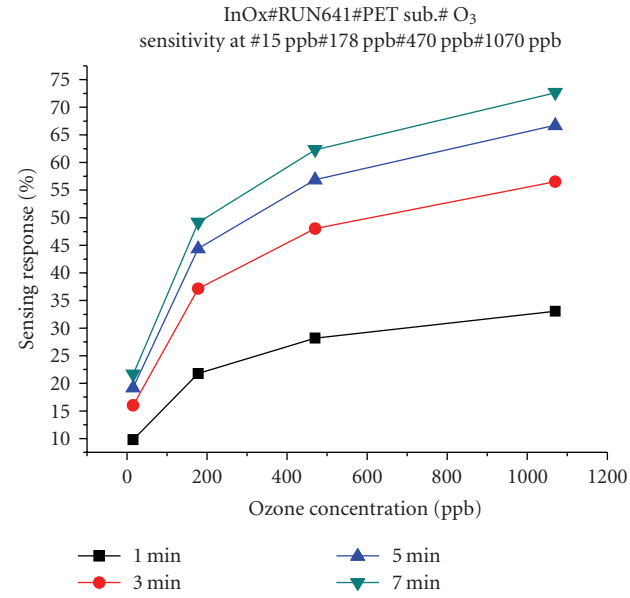


Figure 5: Sensing responses at ozone concentrations from 1070 to 15 ppb.

ozone concentrations down to the extremely low level of 15 ppb and on the other, to resolve these responses from the synthetic air, used as reference signal, within the first minute of analysis.

Indeed, Figure 5 depicts the recorded differences in the 7, 5, 3 and 1 minute of the oxidation decay process, demonstrating the capacitance to resolve extremely low ozone concentrations (15 ppb) while providing reliable readouts (10% sensing response) within the first minute of the exposure time.

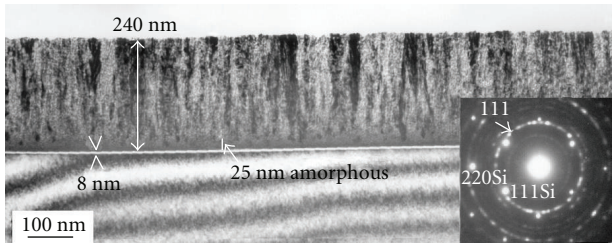


Figure 6: XTEM micrograph of the film structure on Si [001] orientation wafer. The thickness of the film is 240 nm with an initial 25 nm amorphous layer followed by a crystalline columnar structure. Between the substrate and the In2O3-x film a very thin amorphous layer about 8 nm is observed.

It is widely accepted that surface effects and specific surface characteristics are related to processes such as catalytic activity or surface adsorption and are key for superior chemical sensor response. Films grown with the above conditions have gone through an extensive structural investigation. They have shown to exhibit a characteristic polycrystalline structure with a 20 nm mean width of columnar grains, as studied by combined cross-section TEM (XTEM) and Plane View TEM (PVTEM) supported by independent AFM. Detailed analysis on these films and an account of their structural characteristics have already been published recently elsewhere [16]. They revealed that the columnar morphology was an inherent property of the mode of growth independent of the chosen substrate. The films were amorphous in the early stage of growth (Figure 6) becoming crystalline after a critical thickness subject to the incubation time needed in order an amorphous material to generate nucleation centres at a given temperature.

Observations have also shown a correlation of critical surface parameters such as grain size, texturing, porosity and grain shape with the film sensing characteristics. AFM study of the film surfaces confirmed granular polycrystalline morphology. It was found that both the average lateral grain size and the surface roughness mainly increased with increasing the film thickness, a parameter that is directly controlled by the deposition temperature, and the growth total pressure.

It is generally accepted that film sensitivity correlates with surface parameters using the conduction model of metal oxide gas sensors approximation given by Barsan and Weimar [17]. The basic mechanism of gas detection is the interaction of the gaseous species with the surface of the semiconducting sensitive metal oxide layer. As a consequence of this surface interaction charge transfer takes place between the absorbed species and the semiconducting sensitive material [18]. According to this model, for small grains and narrow necks, when the mean free path of free charge carriers become comparable with the dimension of the grains, the surface influence on the mobility dominates over bulk phenomena. In the presence of the ionic species on the surface, after UV photoreduction, the electronic concentration in the surface states increases. The surface states concentration is correlated with the roughness and grain size via surface-to-volume ratio. Thus, the basic mechanism of gas detection is the interaction of the gaseous species with the surface of the semiconducting sensitive metal oxide layer. However, since sensitivity is measured in terms of film conductivity which is directly effected by the size of the grain and thus the volume and type of scattering mechanisms that the free electrons are experiencing, it has been shown that films with grain size of the above order and grown under the reported growth conditions fulfill the above model criteria providing a convincing explanation for the reported enhanced gas sensitivities and thus the ultra low detection limits obtained.

The above film response characteristics combined with the room temperature growth and operation requirements, open-up the road for low-cost, highly sensitive gas sensing elements on flexible substrates challenging corresponding efforts based on carbon nano-tubes [19] while serving recent integration advances on flexible tag microlab gas sensor systems [3, 20].

4. Conclusions

InO_x thin films have been grown by DC magnetron sputtering on glass and PET substrates. High optical transparency for both substrates was maintained. Surface morphology investigations carried out by SEM for films on PET substrates showed extended surface cracking for bending angles beyond 40°. 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 (15 ppb), at room temperature, demonstrating the wide prospective of utilizing these metal oxides as gas sensors on flexible substrates for a variety of applications.

Acknowledgments

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