Electrical conductivity and gas-sensing properties of doped and undoped single-crystalline In_2O_3 thin films: bulk vs. Surface

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Indium oxide is a well-known material for conductometric gas sensors, showing a change in conductivity when exposed to oxidizing gases such as ozone [1]. Particularly attractive is the possibility to reverse the conductivity changes by UV-induced photoreduction of the surface [2], enabling gas sensor operation at room temperature. For polycrystalline layers it has been shown that a thin surface-near layer has the major contribution to the gas sensitivity [1]. A detailed understanding of the underlying mechanisms, however, is difficult due to the complex electric transport phenomena in the typically used polycrystalline material with contributions from the bulk of the grains, the surface, and the grain boundaries. We aim to get a better understanding of the gas-sensing mechanism using MBE-grown single-crystalline In_2O_3 thin films with only two conductivity contributions: bulk and surface. By thickness reduction, oxygen-annealing or Mg-doping [3], the bulk contribution to the overall conductivity was systematically decreased. The In_2O_3 films possess a surface electron accumulation layer (SEAL) that governs the surface conductivity and can be removed by oxygen plasma treatment of the surface [3]. Conductance measurements in air revealed that sub-optical-band gap UV-illumination gradually increased the film conductance (Fig. 1, left). The slow conductance saturation suggests desorption of surface oxygen adatoms by photoreduction. Comparing the absolute and relative changes in conductance ΔG and $\Delta G/G_0$ (Fig. 1, left) of an as grown and an oxygen-annealed film, we found similar ΔG for both films and therefore the higher sensitivity $\Delta G/G_0$ for the oxygen-annealed film. More insulating Mg-doped films show similar ΔG and further increasing $\Delta G/G_0$ up to medium Mg-doping concentrations (Fig. 1, right). Conversely, removing the SEAL reduces ΔG as well as $\Delta G/G_0$ drastically (Fig. 1, right). These observations indicate the gas response to be exclusively related to the SEAL. As an important practical consequence the sensitivity can be maximized by eliminating the (parasitic) bulk conductivity through deep acceptor doping. Measurements in ozone will test this approach for the real application.

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[2] Ch. Y. Wang et al. (2011): Photon stimulated sensor based on indium oxide nanoparticles I: Wide-concentration-range ozone monitoring in air. Sens. Actuators B 152, 235.

[3] O. Bierwagen (2015): Indium oxide—a transparent, wide-band gap semiconductor for (opto)electronic applications, Semicond. Sci. Technol. 30, 024001.

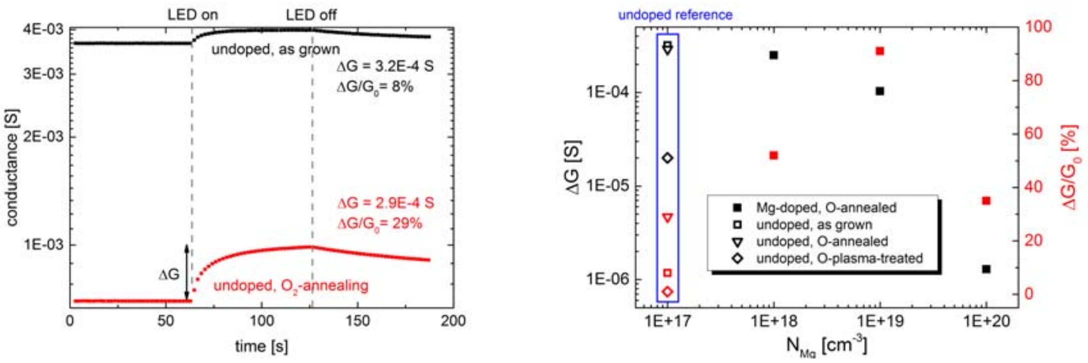

Fig 1: Gas-response measurements an as grown an one O_2-annealed undoped film (left) and summary of absolute and relative changes in conductance of undoped films which have undergone different post-growth treatments and Mg-doped films (right).