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Intrinsic Doping and Ageing of Sputter Deposited In_2O_3 thin films

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The Transparent Conductive Materials (TCM) class groups several materials that play crucial roles in all the applications based on light management and electrical conduction. Among them, Transparent Conductive Oxides (TCO) cover a large market share thanks to their versatility, optical and electrical properties, relatively low cost, compatibility with industrial processes etc. Most TCOs are realized via metallic doping of wide band gap binary oxides, but this can result in limitations such as light absorption, dopant clustering, solid solubility of dopants, generally higher processing costs. In this frame, our work was aimed at the investigation of strategies to induce intrinsic doping in sputter deposited In2O3 thin films, so avoiding extrinsic metal doping. According to established literature reports, In2O3 can present remarkable n-type conductivity thanks to point defects such as oxygen vacancies (VO), indium interstitials or antisites, being VO the most effective ones. The advantages of intrinsic doping are lower thermal budget (TCOs achieve their best performances after treatments at T>200°C), no degradation of optical transparency (no metal contaminants within the material), generally shorter processing times and lower costs. In our experimental work, we employed UV irradiation (also known as photoreduction) or Ar+ Ion Implantation to induce VO formation in 100 nm thick In2O3 films grown via RF Magnetron Sputtering at room temperature, either with or without ex-situ thermal annealing at 200°C. We carried out extensive characterization on the electrical, optical and structural properties of our samples, to study conductivity, transparency, structure and possible modifications upon treatments. Our findings show that both the photoreduced and the Ar+ irradiated samples had their sheet resistance improved by a factor of ~103, down to ~200 Ω/sq, while preserving the typical oxide transparency of ~90% over the visible and near-infrared spectrum. Furthermore, we found that the ion implantation process induces strong crystallization of In2O3 unannealed films, as observed via Scherrer analysis of XRD diffractograms. One major issue with intrinsically doped In2O3 is that the so obtained conductivity vanishes over time, because of VO saturation and replenishing upon air exposure. So we monitored the ageing of electrical properties over several days, and observed a rapid quenching of the conductivity. To counteract the conductivity degradation we encapsulated the intrinsically doped samples within a thin sputter deposited SiO2 layer, right after the doping treatment. Thanks to that, we were able to isolate the ageing due to air exposure from the spontaneous one, and so we could observe the differences between ion- and UV-irradiated samples. Nevertheless, the SiO2 capping proved to be very effective against the ageing of electrical properties, as the conductivity of encapsulated samples was well preserved over two weeks of observation time.