In two previous publications (1, 2) it has been shown that thermal oxidation of liquid indium metal droplets gives rise to hollow, hemispherical In$_2$O$_3$ structures which exhibit maximum quantum efficiencies of $\approx$90% at 310 nm. Oxide films of the same mean thickness, grown in essentially the same way except that they were exposed to the oxygen plasma during oxidation gave maximum quantum efficiencies of $\approx$40%; these films being referred to as plasma oxidized In$_2$O$_3$. On the other hand, uniform, flat films of In$_2$O$_3$ grown by reactive sputter deposition from an indium metal target in a 100% O$_2$ plasma, exhibited maximum quantum efficiencies of $\approx$18% at 290 nm. The source of the vast improvement of the rough thermally grown films over the flat sputter-deposited films was shown to be comprised of two contributions, one based on geometry and the other related to an improvement in the solid-state properties of the former over the latter. While the plasma oxidized films have the same geometry as the thermally grown films, they were exposed to the oxygen plasma for $\approx$2 min during oxide growth, hence they would be expected to suffer impact damage as well as having a thin sputtered In$_2$O$_3$ film coating the hemispherical oxide structures. This was cited as the reason for a poorer photoresponse of the plasma grown films compared to those thermally grown. Based on this result it was estimated that geometry and improved solid-state properties were each responsible for $\approx$50% of the improvement of the rough thermally grown films over the flat reactively sputtered oxide films.

Based on this result, it was expected that the plasma-grown films, see for example Ref. (1). These latter films exhibited no improvement in photoresponse after H$_2$ loading as shown by Fig. 3a and b. However the doping density of the plasma-grown films underwent substantial change with hydrogen loading leading to a 10$^2$-10$^3$ increase in the product K$_N$ (compare Fig. 4 and 5). On the other hand, the doping density of the reactively sputtered In$_2$O$_3$ films increased by a factor of 10 upon hydrogen loading (see Fig. 6).

Continuous potential cycling of the hydrogen loaded plasma grown films between -1.0 and 1.0V (SCE) for 12h had no deleterious effect on the improved photoanodic behavior nor could the hydrogen be anodically stripped out. The uptake of hydrogen is therefore irreversible, in contrast to the situation with sputtered TiO$_2$ films where the hydrogen could be driven out at high anodic potentials (3). Attempts to incorporate hydrogen into the oxide during lattice growth by depositing indium in an argon-hydrogen mixture followed by plasma or thermal oxidation resulted in bluish colored, metallic, incompletely oxidized films.

The quantum improvement in photoresponse of the plasma grown films accompanying H$_2$ loading is clearly not due, even in part, to a modification or change in the optical or dielectric properties of the oxide since neither the reactively sputtered nor thermally grown films showed any photoanodic improvement upon H$_2$ loading. This is further supported by the bandgap plots of Fig. 3 which show the same bandgaps before and after H$_2$ uptake. The source of the improvement must therefore be a reduction in defect or recombination centers present in the plasma grown films while absent in the thermally grown oxide. Interestingly, while the photoanodic behavior of the plasma oxidized films undergo a dramatic improvement upon hydrogen uptake, both the reactively sputtered and thermally grown films do not. That the thermally grown films do not improve is probably because they possess already the optimal properties of the oxide since neither the reactively sputtered nor thermally grown films are electrochemically hydrogenated.
Fig. 2. Quantum efficiency plots for the electrodes of Fig. 1, those for the reactively sputtered and plasma oxidized film are from Ref. (2).

maximum solid-state properties that cannot be improved upon. However, the reactively sputtered films show no improvement at all, this in spite of the fact that they will most likely possess the highest concentration of lattice defects, this being supported by the nonlinear Mott-Schottky plots and the higher doping densities (compare Fig. 4 and 6). Comparison of the doping densities of these two films after the electrochemical uptake of hydrogen reveals less hydrogen was taken up by the sputtered films. The structure type to which In$_2$O$_3$ belongs is the C-rare earth oxide. Oxides in this class crystallize in a fluorspar type lattice (CaF$_2$) characterized by vacancies in the anion sublattice. This suggests that In$_2$O$_3$ should be able to take up hydrogen readily. There are several possible reasons why the plasma-grown films are taking up more hydrogen than the reactively sputtered films. First, being hollow collapsed hemispherical structures [see Ref. (2)], these films have higher surface areas than the sputtered films. Second, as the XRD spectra of Fig. 7 show, there are strong orientation differences between the two differently grown oxides. This is to be expected since the growth mechanisms are so radically different, with the flat reactively sputtered films being grown one atomic layer at a time while the plasma (and thermally) grown films grow radially by metal migration through the oxide crust. Besides strong orientation effects, slight differences in film density, In/O ratio and the defect structure, type and concentration of defects will exist. Since incorporation of tin from the underlying ITO layer into the reactively sputtered In$_2$O$_3$ will occur but is not expected in the plasma-grown films, this will also result in defect differences between the two types of film. That the hydrogen is having no beneficial effect on the photoanodic properties of the sputtered films is probably due to the hydrogen having much less impact in a much more defective structure due to grain boundaries, point defects brought about by impact damage and impurity diffusion from the underlying ITO substrate.

Several conclusions can be drawn from these studies of electrochemical hydrogen loading of In$_2$O$_3$ formed by react-
A Model for the Anodic Dissolution of the Zinc Electrode in the Prepassive Region

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The general features of slow potentiodynamic sweeps for the zinc electrode in alkaline electrolyte have been established in previous experiments (1, 2). A typical current-potential curve (1M KOH, 25°C) can be divided into four regions: an initial dissolution region, a first linear region, a second linear region, and a passive region (Fig. 1). In this work we refer to the two linear regions as prepassive. In 1N hydroxide near room temperature, the prepassive region encompasses a potential range between about -1.3 to -1.0V vs. Hg/HgO (corresponding to -1.2 to -0.9 vs. SHE); these limits vary with hydroxide concentration, temperature, and hydrodynamic conditions.

Previously, we proposed a three-step mechanism for the anodic dissolution of zinc in the initial dissolution region (3), which was similar to a model developed by Bockris et al. (5). From simulations based on the model we quantified the effects of mass transport on the initial reaction rate in rotating disk electrode experiments (4). Our initial dissolution model is only valid in a limited potential range near the rest potential. At higher potentials simple extrapolation of that model predicts currents that are higher than the observed current densities; therefore, in the prepassive region other processes, such as film formation, must be involved in the overall process. Based on experimental evidence generated in this investigation and in previous studies, we deduced a reaction scheme that accounts for the general features of the simulated current-potential behavior.

Experimental

Rotating disk experiments were carried out on a Pine Instrument ASR rotator with the Model APDT36 disk assembly and RDE 3 potentiostat. Zinc disks 0.5 cm diameter and 99.99% pure were used. The charge passed was

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