Anodization of Indium Phosphide in Sulfide Electrolytes: Film Formation and Oscillatory Behavior

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Surface passivation treatments of III-V semiconductors is sometimes required to alleviate problems associated with surface states. In particular anodic treatments in sulphur-containing electrolytes appear to result in passivated surfaces which are more stable.[1,2] However, cracking of the anodically grown surface film on a p-InP electrode in a sulphur-containing electrolyte has also been reported.[3] Photoenhanced oxidation of GaN has been found to result in an increase in photoluminescence intensity[4]; however cracking of the oxide film formed has also been reported for the case of GaN.[4] Thus, the nature of anodic films on compound semiconductors is important, both from a fundamental and a technological point of view. In this paper we review results on the growth of anodic films, elucidate the nature of cracking of these films and discuss some interesting oscillatory behavior observed during the anodization of InP.

The surface properties of InP electrodes were examined following anodization in an $(NH_4)_2S$ electrolyte. An observed current peak in the cyclic voltammogram was attributed to selective etching and film formation and AFM images revealed surface pitting. Importantly for the understanding of passivation processes in sulphide solutions, two different types of surface film were observed to form, depending on the applied potential. At lower potentials a compact film forms while at higher potentials a transition from compact to porous film formation occurs.

Above 1.7 V, formation of a thick porous film has been observed which has been determined by EDX, XPS and electron diffraction measurements to be composed of In_2S_3. Examination of this film by electron microscopy shows that it has a columnar morphology. The surface of the film has a cracked appearance as shown in Fig. 1 and it has been demonstrated unambiguously by time-lapse optical microscopy that this cracking is not present when the electrode is removed from the cell but is an artifact of film drying. The measured film thickness has been found to increase linearly with the charge density passed and comparison between experimental measurements and theoretical estimates for the thickness indicates that a constant porosity of over 70% is maintained throughout the film. Film cracking is attributed to shrinkage during drying of this highly porous, electrolyte-soaked film and does not necessarily imply stress in the wet as-grown film.

Spontaneous oscillations in current have been observed during anodization of InP in aqueous $(NH_4)_2S$ under three significantly different sets of conditions: potential sweep, constant potential and constant current. Their frequency increases with increasing anodic bias and values in the range of 0.1 Hz to 1.25 Hz have been recorded. Typical results obtained during potential sweep experiments are shown in Fig. 2. At various scan rates, the average current density was found to be proportional to the frequency of the oscillations so that the charge per cycle remained constant with a value of approximately 0.3 C cm^{-2}. Despite the differences in experimental conditions, current oscillations observed under constant potential conditions also showed a proportionality between average current density and frequency and a similar value of approximately 0.3 C cm^{-2} for the charge per cycle.

The current in the oscillatory region corresponds to the continuous growth of a thick porous film on the electrode. As a consequence of the porous, electrolyte-soaked nature of this film, an easy access pathway exists for diffusion of ions between the substrate and the bulk electrolyte and so film growth is not inhibited. The mechanism of current oscillations will be discussed. It is suggested that it involves large changes in electrolyte composition within the porous film, possibly including perhaps solid film formation at the interface of the InP and the porous surface film.

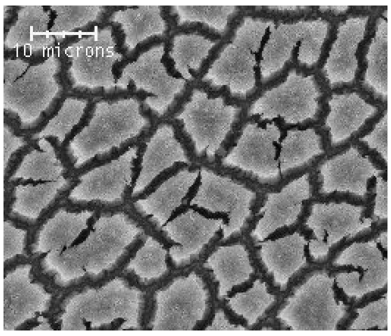

Fig. 1 SEM micrograph of the surface film formed on InP after a cyclic potential sweep between 0.0 V and 2.0 V in 3 mol dm^{-3} $(NH_4)_2S$ at a scan rate of 10 mV s^{-1}.

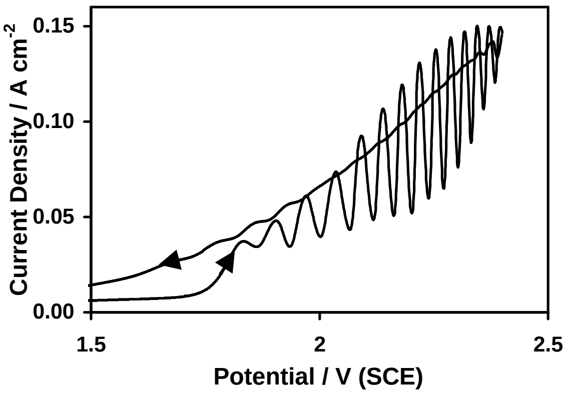

Fig. 2 Cyclic voltammogram between 0.0 V and 2.4 V in 3 mol dm^{-3} aqueous $(NH_4)_2S$ at a scanrate of 10 mV s^{-1}. To highlight the oscillatory behavior, only the region between 1.5 V and 2.4 V is shown.

References

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