# Anodic Behavior of InP: Film Growth, Porous Layer Formation and Current Oscillations

D.N. Buckley[†‡], C. O'Dwyer[†‡], E. Harvey[†]*, T. Melly[†‡],
M. Serantoni[‡], D. Sutton[‡], and S.B. Newcomb[‡]

[†]*Department of Physics, University of Limerick, Ireland*
[‡]*Materials & Surface Science Institute, University of Limerick, Ireland*
**present address Hewlett-Packard, Leixlip, Co. Kildare, Ireland*

The nature of anodic films on compound semiconductors, their structure and composition, and the relationship to growth conditions are important, both from a fundamental and a technological point of view. For example, surface passivation treatments of III-V semiconductors is sometimes required to alleviate problems associated with surface states, such as catastrophic optical damage in lasers[1] and low current gain in heterojunction bipolar transistors (HBTs).[2] In particular anodic treatments in sulphur-containing electrolytes appear to result in relatively stable, passivated surfaces.[3,4] Photoenhanced oxidation of GaN has been found to result in an increase in photoluminescence intensity, thus indicating the passivating nature of the surface oxide formed in this case.[5] Metal-oxide-semiconductor (MOS) structures using photo-electrochemically formed oxide layers on GaN have been fabricated.[6] However, cracking of the anodically grown surface films on InP and GaN has also been reported.[7-10] In this paper we review results[8-14] on the growth of anodic films, the cracking of these films, the formation of porous layers and interesting oscillatory behavior observed during the anodization of InP.

The anodization process has been investigated using cyclic voltammetry, current-time measurements at constant potential and potential-time measurements at constant current. The anodized electrodes have been examined in detail by optical microscopy, electron microscopy, atomic force microscopy and ellipsometry. The anodic behavior of InP in 1 mol dm$^{-3}$ KOH was investigated and compared with its behavior at higher concentrations of KOH. In 1 mol dm$^{-3}$ KOH a thin surface film is formed at potentials in the range 0.6 V to 1.3 V. The thickness of this film was determined by spectroscopic ellipsometry as a function of the upper potential and the measured film thickness corresponds to the charge passed up to a potential of 1.0 V. Anodization to potentials above 1.5 V in 1 mol dm$^{-3}$ KOH results in the growth of thick, porous $In_2O_3$ films. These films are observed to crack due to shrinkage on drying in ambient air. Comparisons between the charge density and film thickness measurements indicate a porosity of approximately 77% for such films. Similar thick, porous films with a porosity of over 70% are formed in $(NH_4)_2S$ electrolytes at higher potentials and have been identified as $In_2S_3$. These films also crack due to shrinkage during drying.

Anodization in KOH concentrations of 2 mol dm$^{-3}$ or greater, leads to selective etching of InP and formation of a thick porous InP layer near the surface of the electrode. Interestingly, a non-porous region, ~30 nm in thickness, remains at the surface of the electrode with the porous layer immediately underneath it. The pores within the porous layer appear to propagate from holes through the near-surface layer. Transmission electron microscopy studies of the porous layers formed under both potentiodynamic and potentiostatic conditions show that both the thickness of the porous layer and the mean pore diameter decrease with increasing KOH concentration. The degree of porosity, estimated to be 65%, was found to remain relatively constant for all the porous layers studied.

Current oscillations were observed under potential sweep conditions when an n-InP electrode was anodized in a KOH electrolyte. Similar oscillatory behavior was observed during anodization in an $(NH_4)_2S$ electrolyte. In both cases oscillations were observed above 1.7 V (SCE). The charge per cycle was found to increase linearly with potential for the InP/KOH system but was observed to be independent of potential for the InP/$(NH_4)_2S$ system. The period of the oscillations in the InP/KOH was found to increase with applied potential. In this case the oscillations were asymmetrical and the rising and falling segments had a different dependence on potential. Transmission electron microscopy studies showed that in both cases in the oscillatory region, the electrode was covered by a thick porous film. Possible mechanisms will be discussed.

## References

1. D.A. Shaw and P.R. Thornton, *Solid State Electronics*, **13**, 919 (1970)
2. C.J. Sandroff, R.N. Nottenberg, J.C. Bischoff and R. Bhat, *Appl. Phys. Lett.*, **51** 33 (1987)
3. J. Yota and V.A. Burrows, *J. Vac. Sci. Technol. A*, **11**, 1083 (1993)
4. Z.S. Li, X.Y. Hou, W.Z. Cai, W. Wang, X.M. Ding and X. Wang, *J. Appl. Phys.*, **78**, 2764 (1995)
5. L.H. Peng, C.H. Liao, Y.C. Hsu, C.S. Jong, C.N. Huang, J.K. Ho, C.C. Chiu and C.Y. Chen, *Appl. Phys. Lett.*, **76**, 511 (2000)
6. T. Rotter, R. Ferretti, D. Mistele, F. Fedler, H. Klausing, J. Stemmer, O.K. Semchinova, J. Aderhold and J. Graul, *J. Crystal Growth*, **230**, 602 (2001)
7. L.J. Gao, J.A.Bardwell, Z.H. Lu, M.J. Graham and P.R. Norton, *J. Electrochem. Soc.*, **142**, L14 (1995)
8. E. Harvey, D.N. Buckley, D. Sutton, S.B. Newcomb and S.N.G Chu, *J. Electrochem. Soc.* **149,** B398 (2002)
9. E. Harvey, D.N. Buckley and S.N.G Chu, **133,** 785, *Monatshefte fur Chemie* **133,** 785 (2002)
10. E. Harvey and D.N. Buckley, in *Proceedings of the 32nd State-of-the-Art Program on Compound Semiconductors*, PV 2000-1, p. 265, (ECS Pennington, NJ, 2000)
11. E. Harvey, D.N. Buckley, and S.N.G. Chu, *Electrochem. Solid State Lett*, *5*, G22 (2002)
12. C. O'Dwyer, T. Melly, E. Harvey, D.N. Buckley, V.J. Cunnane, M. Serantoni, D. Sutton, and S.B. Newcomb in *Proceedings of the 37th State-of-the-Art Program on Compound Semiconductors*, **PV 2002-14**, p. 233 (ECS Pennington, NJ, 2000)
13. C. O'Dwyer, D.N. Buckley, V.J. Cunnane, D. Sutton, M. Serantoni and S.B. Newcomb, in *Proceedings of the 37thSOTAPOCS*, **PV 2002-14**, p. 259 (ECS, 2002).
14. C. O'Dwyer, T. Melly, E. Harvey, D.N. Buckley, V.J. Cunnane, D. Sutton, and S.B. Newcomb in *Proceedings of the 37th State-of-the-Art Program on Compound Semiconductors*, **PV 2002-14**, p. 275 (ECS, Pennington, NJ, 2002).