Characteristics of InP in KOH and $(NH_4)_2S$ Solutions under Anodic Conditions

E. Harvey, C. O'Dwyer, T. Melly and D.N. Buckley

Department of Physics and Materials & Surface Science Institute
University of Limerick
Ireland

The report of visible photoluminescence from porous GaAs (1) has renewed interest in the localized dissolution of III-V semiconductors by anodization methods. Furthermore the surface properties of InP and GaAs have shown improvements in their surface qualities after anodization in sulfur containing solutions (2,3). Little work has been concentrated on the mechanisms that lead to pore formation or film growth. In this paper we relate the current-voltage behavior to the physical features observed when n-InP is anodized in a KOH or $(NH_4)_2S$ electrolyte.

A series of cyclic voltammetric measurements was carried out on n-InP in the dark, in a KOH electrolyte. The initial potential was 0 V versus the saturated calomel electrode (SCE) and each electrode was scanned up to an upper potential, E_U, and back. Current voltage curves for forward scans, with scan rates of 1 mV s^{-1} - 10 mV s^{-1} are shown in Fig. 1(a-e). A current peak can be observed on each of these anodic scans and following this peak the current drops to a very low value. For a scan rate of 1 mV s^{-1} (Fig.1(a)), the current is observed to increase sharply at potentials above 1.2 V(SCE), termed the breakdown potential, E_B. Subsequently, the current on the reverse scan is high. Experiments show that at higher scan rates, breakdown occurs at progressively higher values of E_B. However it is also observed that when $E_U < E_B$, the currents on the reverse scan are also very low.

In comparison, similar measurements were made in an $(NH_4)_2S$ solution. A peak is observed on the forward scan and is followed by a plateau region, as shown in Fig. 2. Atomic force microscopy studies of the films formed indicate that film growth continues within the plateau region. When the upper potential in the cyclic voltammogram corresponds to the end of the plateau region, then, the current is reduced over most of the potential range on the reverse scan(4). However, this current is not nearly as low as in the KOH electrolyte. As shown in Fig. 2, we again observe a rapid increase in current at a higher potential E_B,.

The characteristics of the I-V curves suggest that, below E_B, the nature of the film formed in both solutions is blocking in nature, but the extent of the passivation is much greater in the KOH solution. Estimates for the various films formed in KOH indicate that the electric field is approximately constant at E_B. This is consistent with a compact, passivating film. This contrasts with the less compact films formed in $(NH_4)_2S$ for which micrographs show a columnar type structure. The higher current on the reverse scan may be attributed to the more porous nature of the film.

A final noteworthy feature in the cyclic voltammograms is the observations of oscillations of the current in the higher potential regime of both systems. These fluctuations will be discussed further.

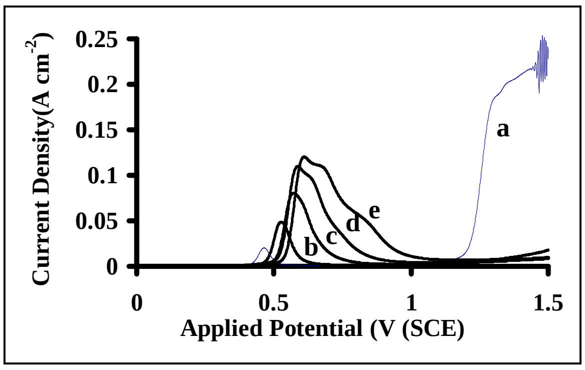

Fig. 1 Cyclic voltammogramms of InP in KOH up to 1.5 V(SCE). Sweep rates of (a) 1 mV s^{-1} (b) 2.5 mV s^{-1} (c) 5 mV s^{-1} (d) 7.5 mV s^{-1} (e) 10 mV s^{-1}.

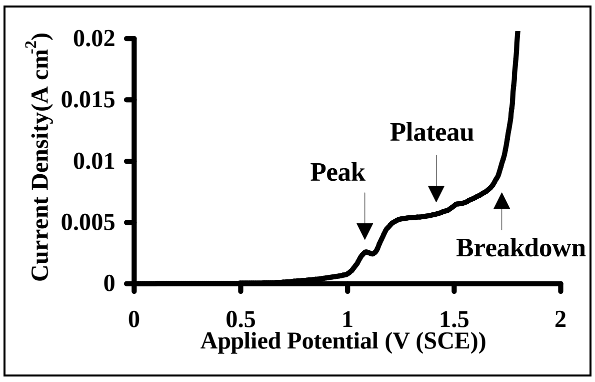

Fig. 2 Cyclic voltammogram of InP in $(NH_4)_2S$ up to 1.8 V(SCE). Sweep rate of 10 mV s^{-1}.

REFERENCES

(1) P. Schmuki, D.J. Lockwood, H.J. Labbe, J.W. Fraser, Appl. Phys. Lett., **69,** 1620 (1996)

(2) I.K. Han, D.H. Woo, H.J. Kim, E.K. Kim, J.I. Lee, S.H. Kim, K.N. Kang, J. Appl. Phys., **80**, 4052 (1996)

(3) X.Y. Hou, W.Z. Cai, Z.Q. He, P.H. Hao, Z.S. Li, X.M. Ding,X. Wang, Appl. Phys. Lett. **60**, 2252 (1992)

(4) E. Harvey, D.N. Buckley, in *Proceedings of the 32nd State-of-the-Art Program on Compound Semiconductors*, R.F. Kopf, A.G. Baca and S.N.G. Chu, Editors, PV 2000-1, p. 265, The Electrochemical Society, Proceedings Series, Pennington, NJ (2000).