In-Situ Photoluminescence from III-V Semiconductor Electrodes

E. Harvey[1], C. Heffernan[1], E. Morley[1], D.N. Buckley[1] and C. O'Raifeartaigh[2]

Materials & Surface Science Institute
University of Limerick, Ireland
[1]Dept. of Physics, University of Limerick
[2]Waterford Institute of Technology

The III-V semiconductor-liquid interface is of interest in a variety of disciplines ranging from energy conversion to surface passivation of devices. The report of visible photoluminescence (PL) from electrochemically formed porous GaAs and InP has also renewed interest in the localized dissolution of III-V semiconductors by electrochemical methods. The optical sensitivity of these materials affords us a method of probing the *in-situ* luminescent properties when such semiconductors are used as electrodes in photo-electrochemical cells. While there have been several reports of *in-situ* PL studies of GaAs (1) and GaP/electrolyte (2) systems, InP and GaN have been examined to a lesser extent (3). In this paper we report the characteristics of the *in-situ* photoluminescence intensity (PLI) of GaN and InP as a function of electrode potential and solution pH.

Experiments were carried out on n-GaN electrodes consisting of epitaxial GaN deposited on a sapphire substrate by MOCVD. For PL experiments, electrodes were illuminated by a He-Cd laser in indifferent electrolytes. The pH of the solution was varied between 0 and 14 and estimates of the flatband potential were made from the corresponding Mott-Schottky plots. The flatband potential was found to shift by approximately –0.057 V/pH unit. Cyclic voltammetric measurements were also carried out at each pH value. The PLI at 365 nm was monitored as the electrode potential was varied. Fig. 1 shows the variation of PLI with electrode potential in an electrolyte of pH 7. The PLI can be seen to remain approximately constant up to a potential of –1.0 V after which it increases up to a limiting value at more negative potentials. On the reverse scan the PLI at any given potential is reduced relative to the forward scan. Similar PLI-potential characteristics were measured at the other pH values and such variation of the PLI with electrode potential indicates that GaN surfaces are not pinned in the indifferent electrolytes used. In each case the maximum PLI was found to be of the order of 2-5 times the PLI measured at open circuit. The maximum PLI was found to occur at potentials more negative than the flatband potential, perhaps as a consequence of the formation of an accumulation layer which leads to a rise in the recombination rate.

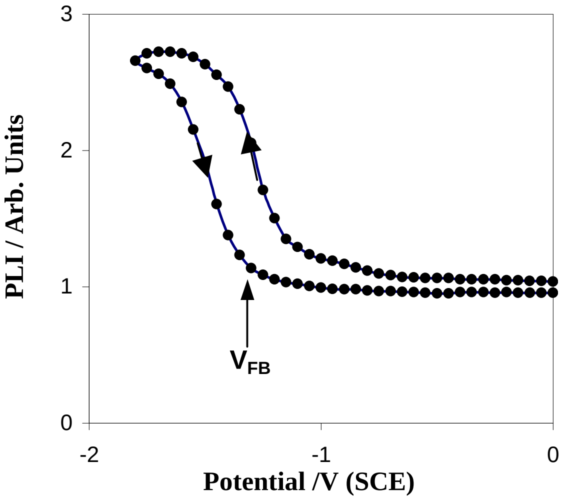

Fig. 1 PLI from n-GaN as a function of electrode potential, in an electrolyte of pH 7.

Similar measurements were carried out on n-InP electrodes. The flatband potential was found to vary linearly with pH in this case by an amount of -0.048 V/pH unit. The PLI (using a He-Ne laser) was monitored at 928 nm as the electrode potential was changed. Hysteresis was again observed in the PLI-potential curves when the potential was cycled. At more positive potentials the PLI was independent of potential. Data was normalized relative to this baseline value. Fig.2 shows the normalized PLI-potential curves measured from InP electrodes in solutions with pH values in the range of 0 to 14 (potential varied cathodically). Clearly the onset of the increase in PLI occurs at increasingly negative potentials as the pH is increased. The observed value of PLI at the flatband potential exceeds the baseline value by a similar factor (approximately 6.7) at all values of pH. Thus, we observe a linear pH-dependence (approximately -0.048 V/pH unit) of the potential at which the PLI is significantly increased over the baseline value. It is also noted that the increase in PLI with increasing potential follows a more gradual curve at higher pH values.

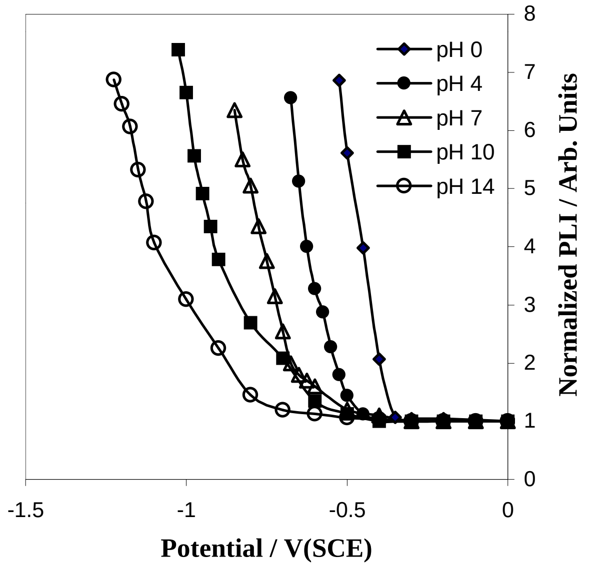

Fig. 2 PLI measured from n-InP electrodes as a function of electrode potential.

REFERENCES

(1) T.A. Abshere and G.L. Richmond, *J. Phys. Chem. B*, **104**, 1602 (2000)
(2) Y. Nakato, K. Morita and H. Tsubomura, *J. Phys. Chem.*, **90**, 2718 (1986)
(3) A. Etcheberry, J. Gautron and J.L. Sculfort, *Appl. Phys. Lett.*, **46**, 744 (1985)